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### Citation

KRUŽELÁK, Jan, Andrea KVASNIČÁKOVÁ, Rastislav DOSOUDIL, Ivan HUDEC, and Jarmila VILČÁKOVÁ. Influence of curing system composition and aging on the performance of rubber magnets based on NBR and EPDM. *Polymer-Plastics Technology and Materials* [online]. vol. 62, iss. 2, Taylor and Francis, 2022, p. 177 - 187 [cit. 2023-08-11]. ISSN 2574-0881. Available at <https://www.tandfonline.com/doi/full/10.1080/25740881.2022.2100792>

### DOI

<https://doi.org/10.1080/25740881.2022.2100792>

### Permanent link

<https://publikace.k.utb.cz/handle/10563/1011078>

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# Influence of curing system composition and aging on the performance of rubber magnets based on NBR and EPDM

<sup>a</sup>Department of Plastics, Rubber and Fibres, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Bratislava, Slovakia;

<sup>b</sup>Department of Electromagnetic Theory, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava, Bratislava, Slovakia;

<sup>c</sup>Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, Zlín, Czech Republic

Ján Kruželák @jan.kruzepak@stuba.sk @Department of Plastics, Rubber and Fibres, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Bratislava, Slovakia

## ABSTRACT

Rubber magnetic composites were fabricated by incorporation of strontium ferrite in constant loading level in ethylene propylene diene monomer rubber and acrylonitrile butadiene rubber. Different curing additives based on peroxide, sulfur and combined sulfur/peroxide systems were introduced for cross-linking of rubber matrices. Both sulfur and peroxide curing systems lead to the formation of cross-links with different length and structure, which subsequently results in different properties of rubber products. Moreover, due to various bonding energies of the formed cross-links, rubber articles exhibit different propensity to degradation factors as to thermo-oxidative aging. Therefore, the work was aimed at the investigation of curing system composition and aging on cross-link density and properties of rubber magnetic composites. The achieved results point out to close correlation between cross-link density and physical-mechanical characteristics with exception of tensile strength, which showed increasing tendency with increasing amount of peroxide in combined vulcanization systems. It can be stated that no significant changes in physical-mechanical and magnetic properties were recorded during aging.

**KEYWORDS** Rubber magnets; magnetic filler; cross-link density; sulfur; peroxide; co-agent

## 1. Introduction

It is already well known that incorporation of magnetic powdery fillers into different rubber matrices leads to the fabrication of smart materials known as rubber magnetic composites.<sup>[1-3]</sup> Magnetic characteristics of fillers and elastic properties of rubber matrices are mutually combined into one structural unit, which reveals new possibilities of their technological applications. Rubber magnetic composites have already been used in industrial applications, as magnetic imaging, recording media, sensors of electromagnetic fields, but also in radar and microwave technology, biotechnology, etc.<sup>[4,5]</sup>

Barium and strontium ferrites with stoichiometry  $\text{SrFe}_{12}\text{O}_{19}$  or  $\text{BaFe}_{12}\text{O}_{19}$  belong to the technologically important types of magnetic materials with high remanent magnetization and coercivity. Attributes such as low price, excellent chemical stability, simple manufacturing along with suitable magnetic characteristics enable wide applications of ferrites in form of permanent magnets.<sup>[6,7]</sup> Moreover, they are not sensitive to demagnetization, and they retain the permanent magnetism in normal conditions.

Optimization of rubber material properties is achieved during vulcanization or curing. To vulcanize and cross-link of rubber matrices, sulfur curing systems are predominantly used. Sulfur curing systems form sulfidic crosslinks with various lengths (mono-, di- and polysulfidic cross-links) between elastomer chain segments. In generally, materials cross-linked with sulfur curing systems exhibit good physical-mechanical and dynamic properties. Although, they are less resistant to elevated temperatures and to environmental degradation factors .<sup>[8-10]</sup>

By application of organic peroxides as curing agents, rubber chains are cross-linked with carbon-carbon bonds. Carbon-carbon cross-links exhibit high bonding energy, and thus the main features of peroxide cured materials are high thermal stability and good resistance to thermo-oxidative aging.<sup>[9, 11-13]</sup> On the other hand, tensile characteristics, dynamic, and elastic properties are usually lower when compared to sulfur cured vulcanizates. For that reason, low molecular weight organic compounds with activated double bonds are often added to rubber compounds cured with organic peroxides. These compounds, known as co-agents, have been reported to increase the crosslinking efficiency of the peroxide vulcanization process and cross-link density of vulcanizates, too .<sup>[9,12, 14-18]</sup> This subsequently results in enhancement of physical-mechanical properties.

Both sulfidic and carbon-carbon bonds are formed between rubber chains when combining curing systems and that pave the way for possibility to influence the properties of final materials in targeted manner.

It has been described in many scientific works that the incorporation of magnetic powdery fillers into various rubbers results in significant enhancement of their magnetic properties, though negative impact on tensile characteristics has often been reported. <sup>[19-21]</sup> The reason could be attributed to mutual incompatibility between the fillers and the rubber matrices and poor adhesion on the interface filler-rubber. In the current study, the content of magnetic filler was kept constant in all composites and the work was aimed at the change in composition of vulcanization systems to influence the characteristics of the composites. The rubber magnets were subsequently exposed to the conditions of thermo-oxidative aging to assess the effect of heat and oxygen on the performance of rubber magnets, as both factors play crucial role in thermo-oxidative aging of polymers.

## **2. Experimental**

### *2.1. Materials*

Acrylonitrile butadiene rubber NBR (SKN 3345, content of acrylonitrile 31-35%, Sibur International, Russia) and ethylene propylene diene monomer rubber EPDM (TER 4049, content of 5-ethylidene-2-norbornene (ENB) monomer 4.5%, content of propylene 40%, Versalis S.p. A., Italy) served as rubber matrices. Strontium ferrite SrFe<sub>12</sub>O<sub>19</sub>, with commercial trademark FD 8/24 was supplied from Magnety, Světlá Hora, Czech Republic. Dicumyl peroxide DCP (Merck Schuchardt OHG, Germany) as peroxide curing agent was used in combination with co-agent - acrylic acid zinc salt ZDA (zinc diacrylate, Sigma-Aldrich, USA). Sulfur curing system consisted of stearic acid (Setuza, Ústí nad Labem, Czech Republic) and zinc oxide (Slovlak, Košeca, Slovakia) as activators, N-cyclohexyl-2-benzothiazole sulfenamide CBS (Duslo, Šála, Slovakia) as accelerator and sulfur (Siarkopol, Tarnobrzeg, Poland) as curing agent.

**Table 1.** Composition of composites in phr and their designation.

	S0 – P2	S0.5 – P1.5	S1 – P1	S1.5 – P0.5	S2 – P0
Rubber	100	100	100	100	100
ZnO	3	3	3	3	3
Stearic acid	2	2	2	2	2
Ferrite	50	50	50	50	50
CBS	0	1.5	3	4.5	6
ZDA	6	4.5	3	1.5	0
Sulfur	0	0.5	1	1.5	2
DCP	2	1.5	1	0.5	0

*CBS - N-cydohexyl-2-benzothiazole sulfenamide, ZDA - acrylic acid zinc salt, DCP - dicumyl peroxide*

## 2.2. Methods

### 2.2.1. Preparation and curing of rubber compounds

The ingredients of rubber formulations were compounded in a laboratory kneader Brabender (Brabender GmbH & Co. KG, Duisburg, Germany) in two-step mixing process. The speed of the rotor was set up to 55 rpm and temperature of kneading chamber was 90°C. In the first step which took 9 min, the rubber and the filler were compounded. The additives of curing system were added in the second step and the compounding procedure took 4 min at 90°C. The compounded rubber formulations were finally cooled down and sheeted by using two-roll calender.

There were prepared five types of rubber composites with magnetic filler and different composition of vulcanization system. In the first composite, only peroxide curing system was applied while the last composite was fabricated only with sulfur curing system. In other three composite types, the mutual ratio of both curing systems was uniformly changed. The content of strontium ferrite as well as the total amount of curing additives were kept on constant level. The composition of rubber compounds and their designations are summarized in **Table 1**. Phr stands for parts per hundred parts of rubber.

The curing process of rubber compounds was performed at 160°C and pressure of 15 MPa in a hydraulic press Fontijne (Fontijne, Vlaardingen, Holland) following their optimum cure time. The optimum cure times  $t_{c90}$  for rubber compounds based on NBR are mentioned in **Table 2** and for rubber compounds based on EPDM in **Table 3**. After curing, thin sheets with dimensions 15 x 15 cm and thickness 2 mm were obtained.

### 2.2.2. Determination of cross-link density

To determine the cross-link density, sample of composites were immersed in xylene (composites based on EPDM) or in acetone (composites based on NBR). Solvent diffused into the rubber matrices and disrupted physical interactions within the rubbers. The weight of samples was measured every hour until equilibrium swelling state was reached. This means that the whole free volume in rubber matrices was filled out with solvents. In general, the higher the swelling degree, the lower the chemical cross-link density. When equilibrium swelling degree was reached, the well-known Flory-Rehner equation modified by Krause<sup>[22]</sup> was used to calculate the cross-link density.

**Table 2.** Optimum cure times  $t_{c90}$  for rubber compounds based on NBR.

	S0 – P2	S0.5 – P1.5	S1 – P1	S1.5 – P0.5	S2 – P0
$t_{c90}$ (min)	16.5	17	16	11.5	10

**Table 3.** Optimum cure times  $t_{c90}$  for rubber compounds based on EPDM.

	S0– P2	S0.5 – P1.5	S1 – P1	S1.5 – P0.5	S2 – P0
$t_{c90}$ (min)	17.5	19	15	10.5	20.5

### 2.2.3. Evaluation of physical-mechanical and magnetic properties

The tensile properties of composites were evaluated in accordance with the valid technical standards by using Zwick Roell/Z 2.5 device (Zwick Roell Group, Ulm, Germany). The test samples were dumbbell-shaped with length 8 cm, width 6.4 mm and thickness 2 mm. The hardness in Shore A unit was measured with durometer.

Magnetic characteristics were determined by using magnetometer TVM-1 (Vúzort, Praha, Czech Republic) at maximum coercivity of  $H_m = 750$  kA/m. The measurement was based on induction method of scanning of scattering magnetic flux  $\phi$  induced by magnetic vibrating sample. The samples used for measurements were of square shape (8 x 4 x 4 mm).

### 2.2.4. Microscopic analysis

Scanning electron microscope JEOL JSM-7500 F (Jeol Ltd., Tokyo, Japan) was employed to investigate the surface morphology and microstructure of composites. The composites were frozen under glass transition temperature in liquid nitrogen and subsequently fractured into small fragments with uncovered surface fractures. Surface fractures were covered with a thin layer of gold by a sputter-coating device Balzers and samples were placed into SEM.

### 2.2.5. Thermo-oxidative aging

During thermo-oxidative aging tests the composite samples were kept in hot-air oven at 70°C and 100°C, respectively for 168 hours. Then, they were freely conditioned at a laboratory temperature for at least 24 hours and cross-link density as well as physical-mechanical properties were tested.

### 2.2.6. Thermogravimetric analysis

Thermogravimetric analysis was performed by using Derivatograph Q-1500D in temperature range 20-1000°C in ambient air atmosphere at a constant heating rate of 5°C/min.

### 3. Results and discussion

#### 3.1. Influence of curing system composition and aging on cross-link density

Both, sulfur and peroxide curing systems differ in their reaction mechanisms and lead to the formation of different cross-link types between elastomer chain segments. Thus, there is real presumption that they could significantly influence the cross-link density of composites, which is also clear from **Figures 1, 2**. As becomes apparent, the cross-link density was dependent not only on the composition of curing system but on the rubber matrix, too. The highest cross-link density exhibited both composite types cured with peroxide system (S0-P2), followed by the composites cured with sulfur system (S2-P0). By contrast, the lowest cross-linking degree showed the composites based on both rubbers cured in the presence of equivalent peroxide to sulfur ratio (S1-P1). Composites based on NBR exhibited much higher cross-link density when compared to equivalent composites based on EPDM. The biggest difference was recorded for composites cured with peroxide system (S0-P2). As shown, the cross-link density of the composite based on NBR with designation S0-P2 was nearly fivefold higher when compared to the corresponding composite based on EPDM. Higher cross-link density of the composite based on NBR cured with sulfur system (S2-P0), when compared to the equivalent EPDM based composite, can be attributed to the higher amount or reactive functional groups in the structure of acrylonitrile butadiene rubber. The structure of NBR consisting of cis-, trans-1,4-butadiene and 1,2-butadiene reveals that there are quantum of double bonds and allylic hydrogens present in the elastomer chains, which are both active in sulfur vulcanization. Ethylene propylene diene monomer rubber has saturated polymer backbone consisting of ethylene, propylene and randomly distributed non-conjugated diene monomer with pendant unsaturation. As the amount of 5-ethylidene-2-norbornene monomer in EPDM was kept under 5% it becomes clear that the amount of unsaturated double bonds in EPDM was much lower. Sulfur vulcanization is very complex process. Sequences of consecutive and parallel reactions run during this process in several stages. Although, the mechanism of sulfur vulcanization is very complicated and still not fully understood, it is generally known that the lower the amount of double bonds in elastomers, the lower the vulcanization rate and the lower the cross-link density.

The difference between the cross-link density of the composites based on both rubbers treated with peroxide system (S0-P2) was even higher. Based upon the above outlined facts about the functional groups in elastomers and suggested mechanisms for peroxide cross-linking of EPDM based rubber compounds <sup>[23-26]</sup> and NBR based rubber formulations <sup>[12,27-29]</sup> higher cross-link density of NBR based composites was expected. Higher crosslinking efficiency of sulfur and peroxide curing of NBR was subsequently reflected in higher cross-link density of corresponding composites cured with mixed curing systems (S0.5-P1.5, S1-P1, S1.5-P0.5) in comparison with their equivalents based on EPDM. It should be noted that for composites cured with peroxide, and mixed peroxide/sulfur systems, the contribution of coagent to the cross-link density must be involved, which is in more detail discussed later.

It is also shown in **Figures 1, 2** that the lowest crosslink density was found to have magnetic composites based on both rubbers cured with equivalent peroxide to sulfur ratio (S1-P1). It is supposed that some competitive reactions between vulcanization systems take place concurrently with the main cross-linking reactions and might exhaust peroxide radical species and/or sulfur fragments.

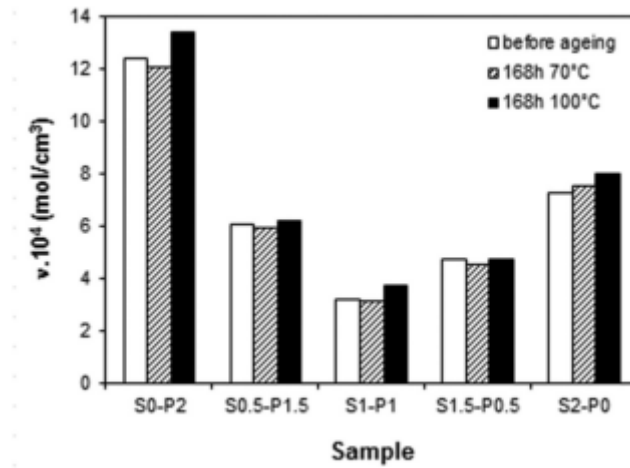


Figure 1. Influence of curing system composition and thermooxidative aging on cross-link density  $v$  of NBR based composites.

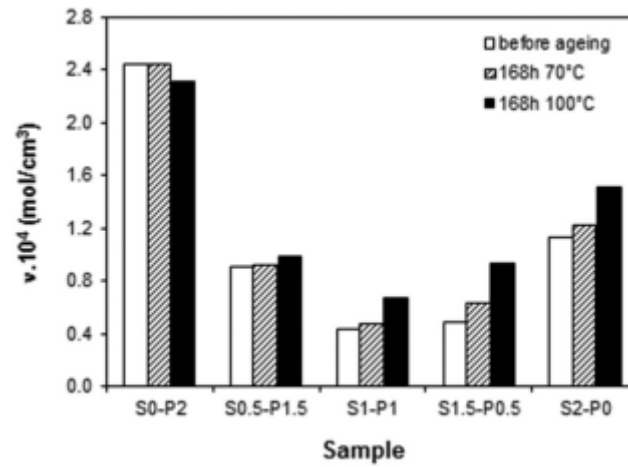


Figure 2. Influence of curing system composition and thermooxidative aging on cross-link density  $v$  of EPDM based composites.

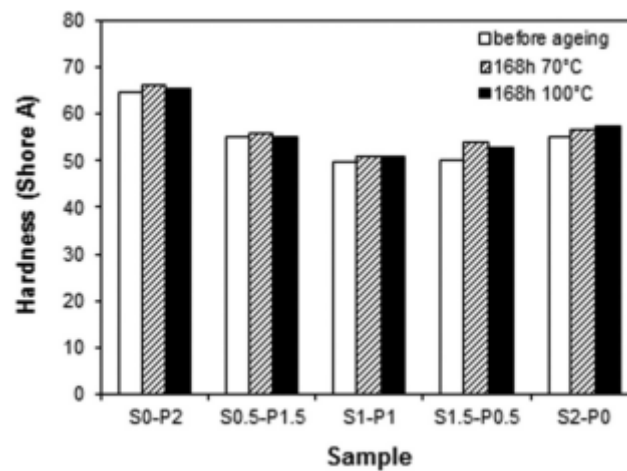


Figure 3. Influence of curing system composition and thermooxidative aging on hardness of NBR based composites.

When tested composites were exposed to thermooxidative aging at 70°C, the cross-link density changed only very few. The increase in aging temperature up to 100°C resulted in slight increase in cross-link density of composites based on NBR. The increase in cross-linking degree during aging can be attributed to the additional cross-linking of rubbers by free peroxide and/or sulfur species, which did not react during the main vulcanization course. Similarly, the cross-link density of composites based on EPDM, except for the composite cured with peroxide system (S0-P2), increased when temperature of aging increased up to 100°C. The increase in cross-link density was more pronounced with increasing amount of sulfur in the applied curing systems. It has been reported that several side reactions running concurrently with the main cross-linking reactions take place during peroxide vulcanization.<sup>[12,27]</sup> Among them, disproportionation and main polymer chain scission belong to the most frequent undesirable side reactions that may lead to the reduction of cross-linking yield.<sup>[30,31]</sup> Side reactions are usually promoted by radicals occurring on tertiary carbon atoms. It is assumed that the cross-linking efficiency of EPDM can be lowered mainly by scission reactions of macromolecular chains, which apparently occur on the tertiary carbons of polypropylene units. Outlining that, polypropylene segments can degrade via  $\beta$ -chain-scission with formation of lower molecular weight polymer chains.<sup>[32,33]</sup> Evidently, the destruction of elastomer chains by side reactions takes dominance over the formation of cross-links, resulting in the overall effect of decreased cross-link density of the composite based on EPDM cured with peroxide system (S0-P2). Side reactions run also during sulfur vulcanization. Following the achieved results, it might be stated that the amount of side reactions during sulfur curing is much lower compared to peroxide vulcanization.

In the case of NBR-based composites, more stable secondary radicals with less propensity to destructive side reactions are formed on rubber chains during peroxide curing.<sup>[34]</sup> Moreover, 1,2-butadiene structural units having side-chain vinyl unsaturation are much more prone toward radical addition reactions than double bonds in the main rubber chains. Thus, they can contribute to dominance of cross-linking and branching of the elastomer over degradation during first stages of aging.<sup>[9,27,35]</sup>

### *3.2. Influence of curing system composition and aging on physical mechanical properties*

The dependences of physical-mechanical properties of tested composites on curing system composition are graphically illustrated in **Figures 3-8**. It becomes evident that the hardness and elongation at break of both composite types are in close correlation with the cross-link density. The higher the cross-link density, the higher the hardness and the lower the elongation at break (**Figures 3-6**). The highest hardness exhibited composites cured with peroxide system (S0-P2) with the highest cross-linking degree, while composites cured with equivalent peroxide to sulfur ratio (S1-P1) having the lowest cross-link density were found to have the lowest hardness. The relation between cross-link density and hardness is also in good agreement with the results obtained in recent paper.<sup>[36]</sup> On the contrary, as seen in **Figures 5, 6** higher cross-link density was responsible for lower elongation at break, leading to lower molecular mobility and elasticity. From **Figures 7, 8** it becomes clearly apparent that the tensile strength showed increasing trend with increasing amount of peroxide and decreasing amount of sulfur in the applied curing systems. The lowest tensile strength exhibited composites cured with sulfur system (S2-P0), while the highest tensile strength were found to have composites cured with peroxide system (S0-P2). Generally, sulfur cured elastomers are characterized by higher tensile strength when compared to their peroxide cured equivalents. The reason for different tensile and elastic performance is attributed to the structure of the cross-links formed within rubber matrices. Longer and flexible sulfidic bridges facilitate micro-Brown motion of elastomer chain segments



between the cross-links that leads to the uniform stress redistribution onto higher amount of rubber chains. The relaxation of network stress results in higher tensile properties of sulfur cured elastomers.

On the other hand, shorter and more rigid carbon-carbon bonds restrain mobility and alignment of rubber chains under applied deformation strains. Due to less mobility of rubber chain segments, C-C bonds cause enhanced deformation stiffness and thus lower mechanical properties of peroxide cross-linked elastomers.<sup>[29,37]</sup> It becomes evident that the outlined theoretical predictions are against the experimental results. The application of zinc diacrylate as co-agent in peroxide curing system can be the best explanation for the improvement of tensile characteristics with increasing ratio of peroxide system. It has been proposed that during the curing process of rubbers with organic peroxide, zinc diacrylate undergoes the so-called „in-situ“ polymerization. The formed poly-ZDA molecules tend to form granular nanoscale aggregates that can be physically adsorbed or chemically grafted onto elastomer chains. These structures are considered as chemical or physical cross-linking points of the composites. In addition, co-agents with zinc ions contribute to the formation of ionic clusters within rubber matrices.<sup>[12, 38-41]</sup> It has also been revealed that zinc-based co-agents exhibit strong adhesion to polar materials.<sup>[42,43]</sup> It is well known that outside layers of ferrite magnetic crystals are formed by oxygen ions that are situated at the edge of structural units.<sup>[6,44]</sup> Polar physical interactions between ferrite and zinc ions of ZDA can be thus easily formed. Zinc ions from co-agents increase the polarity of elastomers by grafting of co-agents onto rubber chains on one hand, and on the other hand they physically interact with ferrite particles. This subsequently results in the improvement of compatibility and adhesion between the filler and the rubber on the filler-rubber interface. The outlined facts are suggested to be the reason for the enhancement of tensile strength with increasing proportion of peroxide curing system. By contrast, ferrite behaved as inactive filler in composites cured with sulfur systems as there were no additives in sulfur-based vulcanization system that could enhance the adhesion on the filler-rubber interfacial region.

The study of microstructure by SEM analysis suggested that the compatibility and adhesion between ferrite and the rubbers were higher for both composite types cured with peroxide system (S0-P2), perhaps due to zinc diacrylate forming interfacial layer between the rubber and the filler (**Figure 9**). From SEM images of composites cured with sulfur system (S2-P0) it was more evidently visible the presence of micro-cavities and voids on the interface filler - rubber. Surface morphology also demonstrated that the adhesion between the filler and the rubber was higher for NBR-based composites. This is likely due to the polarity of NBR. Strontium ferrite and zinc diacrylate are polar materials, therefore their affinity with polar elastomers is higher compared to nonpolar rubbers like EPDM.

From **Figure 6** it is possible to observe that the elongation at break of composites based on EPDM slightly decreased when test samples were exposed to thermooxidative aging at 70°C. The extension of aging to 100°C related to stronger decline of elongation at break, mainly for composites with higher sulfur amount (S1-P1, S1.5-P0.5, S2-P0). This can be attributed to the increase in cross-link density of the equivalent composites during aging due to additional cross-linking of the rubber matrix. In the case of composites based on NBR, the change of elongation at break in dependence on temperature of thermo-oxidative aging and curing system composition was variable (**Figure 5**). Therefore, it was not possible to clearly identify the influence of aging on elongation at break of these materials. Similarly, the influence of aging on tensile strength seemed to be ambiguous, as the tensile strength of both composite types slightly increased or decreased in comparison with corresponding composites before aging (**Figures 7, 8**). As shown in **Figures 3, 4**, the hardness of composites slightly increased during aging period, which could be ascribed to the increase in crosslinking degree.

### 3.3. Influence of curing system composition and aging on magnetic characteristics

It has been demonstrated in many scientific works that the incorporation of magnetic fillers into rubber matrices imparted magnetic properties to the composites considerably.<sup>[19,21, 45-47]</sup>

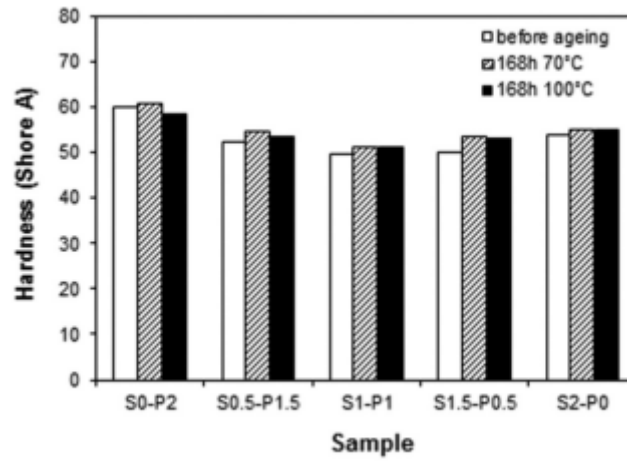


Figure 4. Influence of curing system composition and thermooxidative aging on hardness of EPDM based composites.

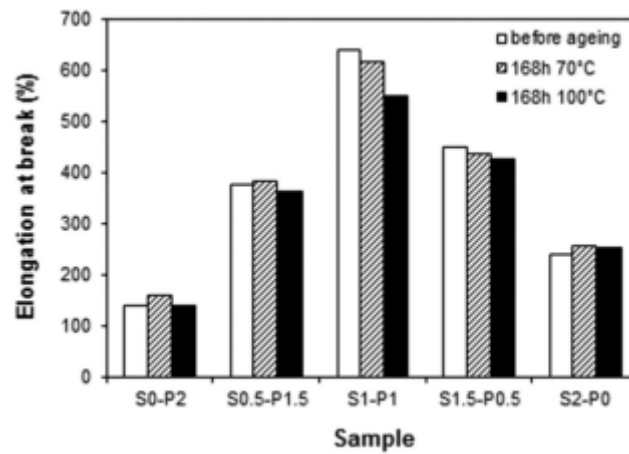


Figure 5. Influence of curing system composition and thermooxidative aging on elongation at break of NBR based composites.

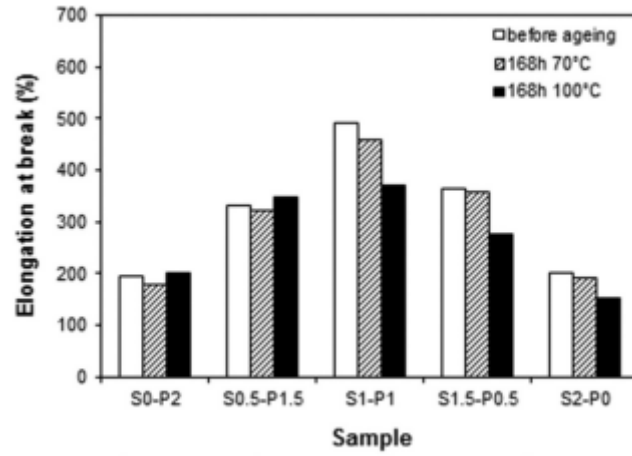


Figure 6. Influence of curing system composition and thermooxidative aging on elongation at break of EPDM based composites.

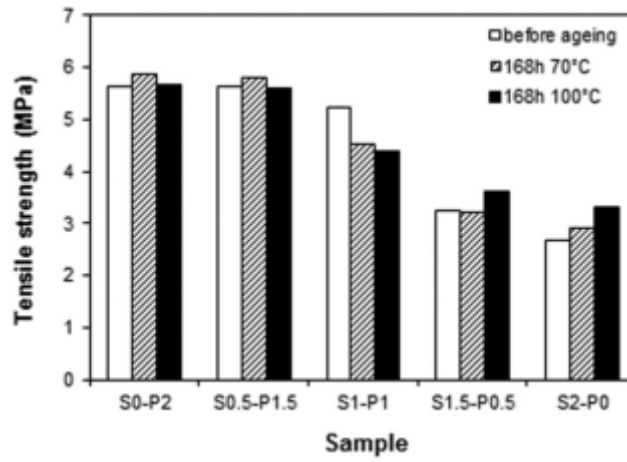


Figure 7. Influence of curing system composition and thermooxidative aging on tensile strength of NBR based composites.

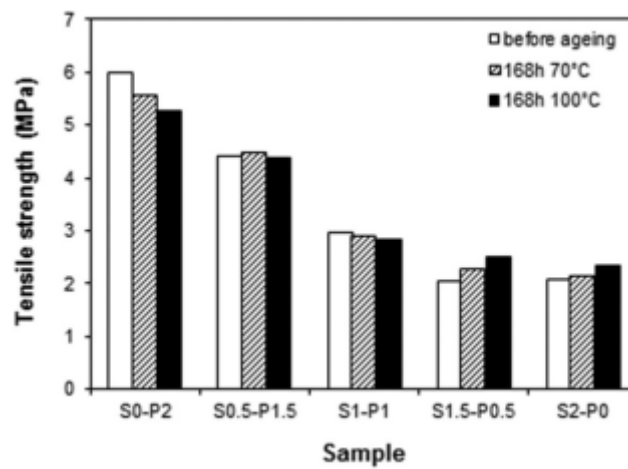


Figure 8. Influence of curing system composition and thermooxidative aging on tensile strength of EPDM based composites

In the present study, the content of magnetic filler was kept on constant loading, and there was concern whether the change in curing system composition could influence magnetic properties of composites. The possible changes in consequence of aging were also under observation. The remanent magnetic induction  $B_r$ , which represents the value of residual magnetization remained in the magnetic material when external magnetic field is removed and the coercivity  $H_c$ , presenting the intensity of external magnetic field needed to abolish the remanent magnetic induction in the material, belong to the most important parameters of all permanent magnets.

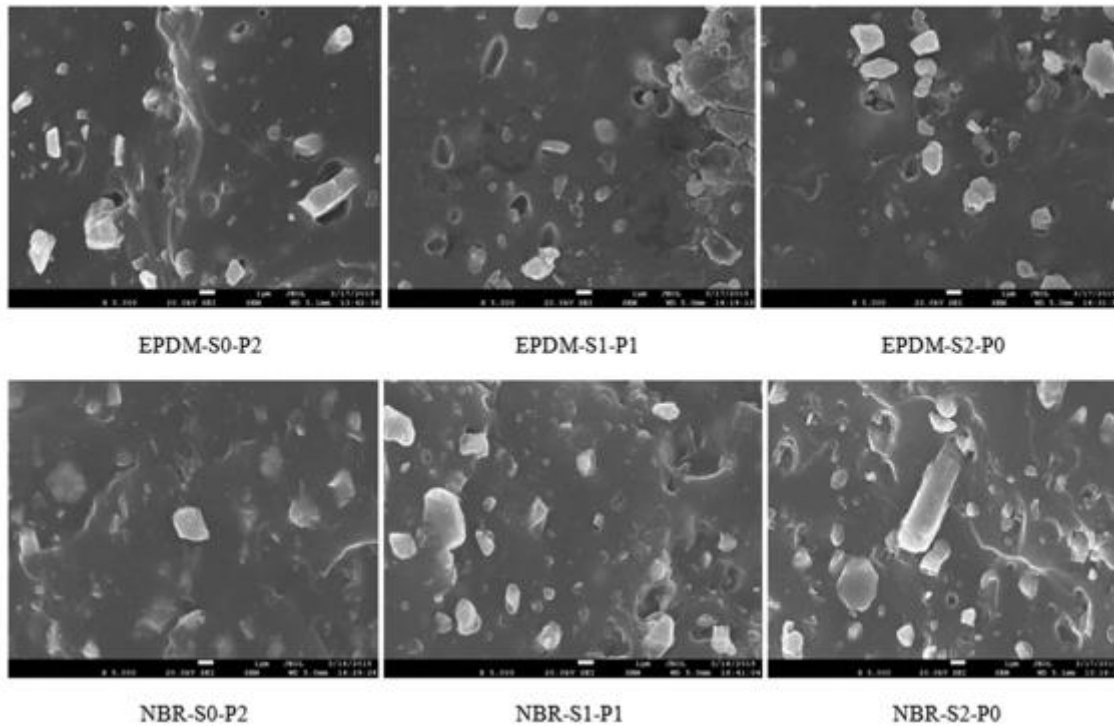


Figure 9. SEM images of composites.

From **Figures 10-13** it becomes obvious that magnetic characteristics of both type composites fluctuated only in the low range of experimental values, independently on the curing system composition or on the type of rubber matrix. There was also recorded almost no influence of thermo-oxidative aging on magnetic behavior. Based upon the achieved results it can be stated that only the content of magnetic fillers determined magnetic characteristics of rubber composites.

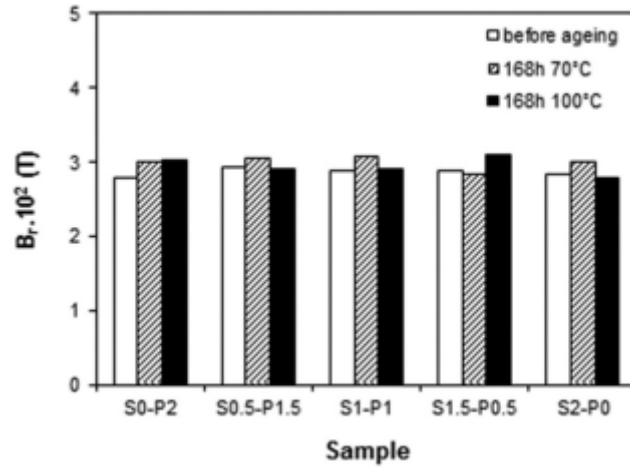


Figure 10. Influence of curing system composition and thermooxidative aging on remanent magnetic induction  $B_r$  of NBR based composites.

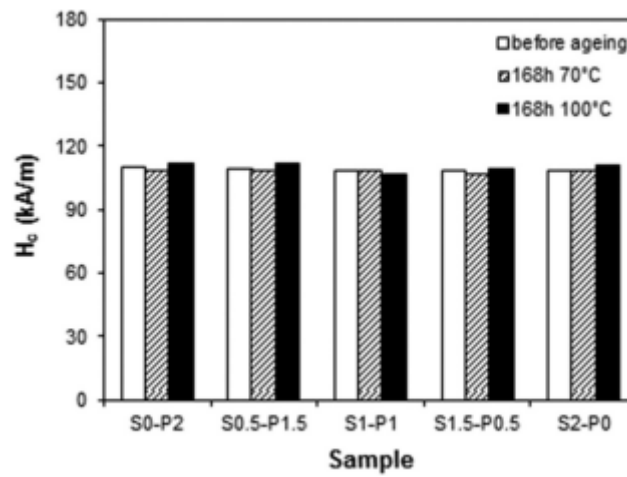


Figure 11. Influence of curing system composition and thermooxidative aging on coercivity  $H_c$  of NBR based composites.

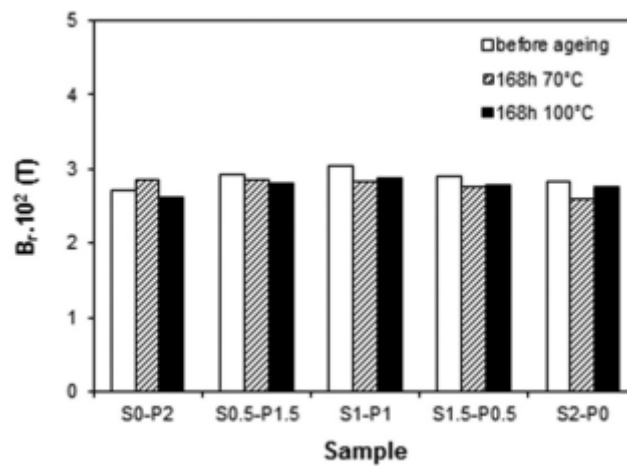


Figure 12. Influence of curing system composition and thermooxidative aging on remanent magnetic induction  $B_r$  of EPDM based composites.

### 3.4. Thermogravimetric analysis

The thermogravimetric tests in air atmosphere were obtained to evaluate the decomposition behavior of the composite materials. Thermogravimetric curves are illustrated in Figures 14, 15. From Figure 14 it is possible to observe that the decomposition process of composites based on NBR started at 380-390°C. The mass loss 35 wt.% at a given temperature was recorded. Above 400°C, an abrupt change in the TG curves occurred leading in faster mass loss in the temperature range between 400-500°C. This temperature interval can be identified as the main decomposition rate of the composites. The last step of decomposition occurred above 500°C leading to the constant mass of decomposition products that consisted of stable magnetic filler powder and inorganic substances from vulcanization systems, which were not burnt during the process.

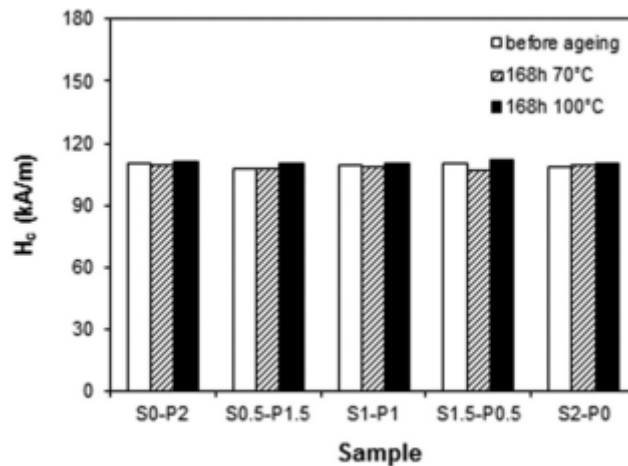


Figure 13. Influence of curing system composition and thermooxidative aging on coercivity  $H_c$  of EPDM based composites.

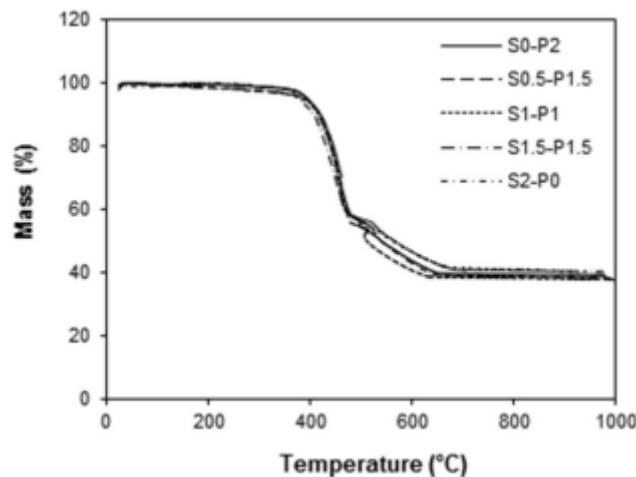
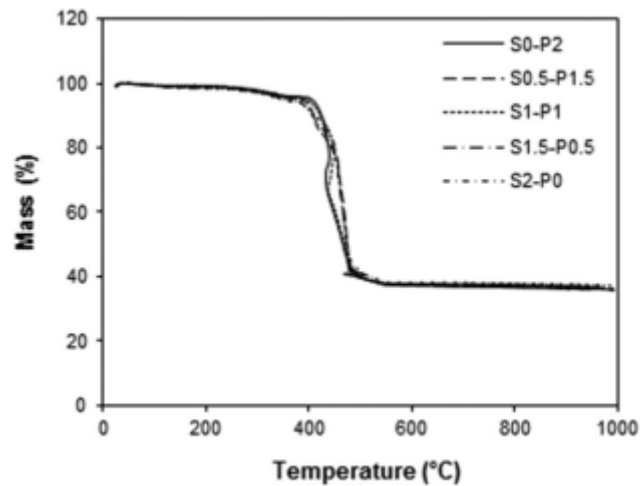


Figure 14. TG curves of NBR based composites.



**Figure 15.** TG curves of EPDM based composites.

The thermal stability of composites based on EPDM was a bit higher and initial temperature of thermal decomposition moved around 400-410°C (**Figure 15**). The mass loss 5-6 wt.% at this temperature was recorded. The fastest decomposition of composites occurred during the temperature range from 420 to 550°C indicating that more than 50 wt.% of the composites weight was incinerated within this interval. The residual unburned mass was strontium ferrite and inorganic substances of vulcanization systems, which were kept approximately at same level as in the case of NBR based composites (40 wt.%). From **Figures 14 and 15** it could be deduced that the degradation process of both composite types seemed not to be influenced by the composition of curing system. Though, after tabulating mass loss of composites according to the temperature range, slight differences were uncovered. As seen in **Table 4**, up to 400°C, the differences in mass loss of both composite types in dependence of curing system composition were rather low. This is in line with the results obtained by thermo-oxidative aging, where no significant changes in cross-link density and physical-mechanical properties were obtained. In the main degradation stage, between 400°C and 550°C, mass loss of composites cured with peroxide system (S0-P2) was a bit higher. Based upon the knowledge of the structure of formed cross-links, the opposite situation could be expected. Carbon-carbon cross-links have higher dissociation energy when compared to sulfidic cross-links, therefore it is assumed that the degradation stability of composites cured with peroxide system should be higher. The achieved results could be explained as follows. Sulfidic cross-links have lower thermal stability; thus, they are supposed to decompose as first. By their decomposition, not only sulfidic cross-links with lower sulfur atoms in sulfur bridges are formed, but also sulfur radical fragments can be easily oxidized in the presence of oxygen and hydroperoxides. Therefore, the mass loss of composites cured with sulfur system (S2-P0) needs not to fall rapidly. On the other hand, in the case of composites cured with peroxide system, at high temperatures, not only carbon-carbon cross-links, but also carbon-carbon bonds in the main rubber chains are decomposed. This can lead to higher mass loss of those composites. In the case of composites cured with mixed curing systems, different types and mixture of sulfur and carbon-carbon bonds are formed and changes in mass loss were therefore very low visible. However, in general it can be stated that the differences in degradation process of composites are very low, and the type of curing system applied in cross-linking of rubber matrices did not significantly influence the thermal stability of composites.

**Table 4.** Mass loss of the composites according to the temperature.

Temperature (°C)	Mass loss (%)			
	NBR		EPDM	
	S0-P2	S2-P0	S0-P2	S2-P0
200	0.4	0.2	0.9	1.3
300	1.1	1.2	2.4	2.8
400	5.8	5.9	4.7	5.1
450	25.7	24.5	40.4	38.2
500	44.3	43.4	59	57.3
550	51.3	48.8	62.5	61.8
600	56.5	53.8	62.7	61.9
700	60.5	58.6	63	61.9
800	60.6	59	63.3	62.2

#### 4. Conclusion

Strontium ferrite in constant loading level was incorporated into rubber matrices based on NBR and EPDM. The cross-linking of rubber matrices was performed in the presence of sulfur, peroxide, and mixed sulfur/per-oxide curing systems. The goal was to investigate the influence of curing system composition as well as thermo-oxidative aging on properties and cross-link density of rubber magnets.

The results demonstrated that the cross-link density of composites was dependent on the composition of curing system, which was subsequently reflected in typical dependencies of hardness and elongation at break. The tensile strength showed increasing trend with increasing amount of peroxide curing system, suggesting that zinc diacrylate as co-agent in peroxide vulcanization contributed to the improvement of adhesion between the rubber and the filler on the filler-rubber interface. Thus, it contributed to the higher reinforcing effect of ferrite in the rubber matrices. No significant changes in composite characteristics were recorded during thermo-oxidative aging. Magnetic characteristics were found to be influenced neither by composition of curing system nor by aging. The thermogravimetric analysis revealed that the decomposition process of composites was dependent only on the type of rubber matrix with almost no influence of curing system applied in cross-linking.

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