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Sulfur and peroxide curing of rubber magnetic composites with the application of zinc methacrylate

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Abstract

Rubber magnetic composites based on acrylonitrile butadiene rubber and strontium ferrite were cured with standard sulfur-based vulcanization systems as well as an organic peroxide. Zinc methacrylate (ZDMA) as a coagent was applied in both sulfur and peroxide vulcanization of rubber magnets. The aim was to evaluate the influence of ZDMA on curing characteristics and cross-link density of the prepared materials. Subsequently, physical-mechanical and magnetic properties were investigated. The results showed that ZDMA takes an active part in the cross-linking process of composites cured with an organic peroxide. Due to the presence of free radicals formed from peroxide decomposition, molecules of ZDMA polymerize into the nanostructures which can be physically adsorbed or chemically grafted onto rubber chains. Moreover, owing to zinc ions, ZDMA exhibits strong adhesion to ferrite filler and thus it contributes to the improvement of adhesion between the rubber and the filler on the interphase. The overall reinforcement of rubber magnetic composites was subsequently achieved. In the case of rubber magnets cured with the sulfur-based system, ZDMA acts as a conventional filler with a slight reinforcing effect due to the lack of free radicals required for its polymerization.

Keywords Rubber magnets, strontium ferrite, sulfur curing system, organic peroxide, zinc methacrylate

Introduction

Rubber composites filled with magnetic fillers have already been widely used in many applications because of their unique properties including good flexibility and elasticity, easy treatability, and excellent magnetic properties.^{1,2} Rubber magnets can absorb shocks and sound, thus they can be applied in motor parts, memory devices, and vibration absorbers, as sensors of magnetic and electromagnetic fields, also in microwave, radar technology, and in many others.^{3,4}

The final properties of rubber products are achieved in the process of vulcanization, simply termed as curing, during which physical and mainly chemical cross-links between rubber chain segments are formed. This leads to the formation of three-dimensional network structure within the rubber matrix.⁵⁻

⁷ The use of a specific curing system determines not only the quantity of the formed cross-links but also their structure or the quality. At present, sulfur and peroxide curing systems are most frequently used for the cross-linking of rubber compounds.

Sulfur vulcanization is a very complex process leading to the formation of different types of sulfidic cross-links between rubber chain segments, namely monosulfidic C-S-C, disulfidic C-S₂-C, and polysulfidic cross-links C-S_x-C ($x = 3-6$). The main features of sulfur-cured materials are good tensile properties, high tensile and tear strength, good dynamic characteristics, or good abrasion resistance. However, the negatives are poor resistance to aging and weak stability at high temperatures.⁸⁻¹²

By applying organic peroxides as curing agents for rubber formulations, rubber chain segments are cross-linked together with carbon-carbon bonds.^{13,14} Carbon-carbon cross-links exhibit higher bonding energy when compared to sulfidic cross-links, therefore peroxide-cured materials show higher thermal stability and improved resistance to thermo-oxidative aging.^{9,15,16} On the other hand, they usually have worse tensile and tear strength, inferior dynamic and elastic properties. For that reason, multifunctional low molecular weight organic compounds known as coagents are often added to rubber formulations cured with peroxides. Coagents contribute to increase of crosslinking efficiency of the vulcanization process and to increase of cross-link density of the final materials as well.^{9,12,17-20} As a result of this, physical-mechanical properties and treatability of peroxide-cured elastomers are improved.

Zinc salt of methacrylic acid or zinc methacrylate (ZDMA) belongs to the class of coagents typically used in peroxide vulcanization. Due to the unique structure and the presence of zinc ions in the molecules, it can form not only different types of linkages within the rubber matrix but also exhibits good adhesion to polar materials. Some studies were devoted to the preparation and curing of rubber magnetic composites with organic peroxide and ZDMA.²¹⁻²³ The results showed that the application of zinc-based coagent leads to the formation of various types of linkages within the rubber matrix (physical, chemical, and ionic) with improved adhesion to magnetic fillers. This was subsequently reflected in the modification of the physical-mechanical properties of rubber magnets. However, ZDMA has been used as a coagent in peroxide vulcanization. The goal of the present work was to investigate the influence of ZDMA on cross-linking and properties of rubber magnetic composites cured not only with organic peroxide but also with standard sulfur-based system and combined sulfur and peroxide curing systems.

Experimental

Materials

Acrylonitrile butadiene rubber (NBR) with trademark SKN 3345 and 31-35% content of acrylonitrile was supplied by Sibur International, Russia. As a magnetic filler, strontium ferrite (SrFe₁₂O₁₉), type FD 8/24 (Magnety, Světlá Hora, Czech Republic) was applied. Dicumyl peroxide (DCP) supplied from Merck Schuchardt OHG, Germany, was used as a free-radical initiator. Besides this, a standard sulfur curing system consisting of zinc oxide (Slovlak, Košeca, Slovakia) and stearic acid (Setuza, Ústí nad Labem, Czech Republic) as activators, *N*-cyclohexyl-2-benzothiazole sulfenamide (Duslo, Sala, Slovakia) as accelerator, and sulfur (Siarkopol, Tarnobrzeg, Poland) as curing agent was also used. ZDMA as coagent provided by Sigma-Aldrich, USA, was applied in both vulcanization systems.

Methods

Preparation and curing of rubber compounds. Compounding of rubber formulations was performed in a chamber of laboratory equipment (Brabender GmbH & Co., Germany) at 90°C and rotor speed of 50 r/min. First, NBR was plasticated for 2.5 min, then ferrite was added. After the next 2 min, ZDMA was introduced. The total time of first step mixing was 9 min at 90°C. The additives of peroxide or sulfur curing systems were added in the second step and compounded for 4 min. After that, the compounds were homogenized and shaped in two roll calender.

Rubber magnetic composites were prepared by the incorporation of a constant amount of ferrite—50 phr into the NBR-based rubber matrix. Organic peroxide and sulfur curing system were used for cross-linking of the rubber matrix. ZDMA was dosed to rubber formulations cured with organic peroxide or sulfur-based system in a concentration scale ranging from 10 phr to 50 phr. The structural and magnetic characteristics of applied magnetic filler are mentioned in Table 1. Table 2 summarizes the composition of rubber magnetic composites cured with a peroxide system, while Table 3 provides the composition of rubber magnets cured with the sulfur system.

The main objective of the second part of the study was to examine the amount of DCP on the behavior of rubber magnets with a constant level of coagents—30 phr and magnetic filler—50 phr. The composition of rubber magnetic composites with different amount of DCP is mentioned in Table 4. Table 5 summarizes the composition of rubber magnets with combined sulfur and peroxide curing systems with different amounts of DCP.

Table 1. Characteristics of SrFe₁₂O₁₉.

Characteristics	Value
Total porosity (%)	54.94
Specific surface area (m ² /g)	3.30
Total volume of pores (cm ³ /g)	0.264
Density (g/cm ³)	4.13
Remanent magnetic induction (T)	0.127
Coercivity (kA/m)	116

SrFe₁₂O₁₉: strontium ferrite.

Table 2. Composition of rubber magnets with peroxide curing system and different amount of

Component	NBR	Ferrite	DCP	ZDMA
Content (phr)	100	50	1	10–50

NBR: acrylonitrile butadiene rubber; DCP: dicumyl peroxide; ZDMA: zinc methacrylate.

Table 3. Composition of rubber magnets with sulfur curing system and different amount of ZDMA

Component	NBR	Ferrite	ZnO	Stearic acid	CBS	Sulfur	ZDMA
Content (phr)	100	50	3	2	1.5	1.5	10–50

ZDMA: zinc methacrylate; NBR: acrylonitrile butadiene rubber; ZnO: zinc oxide; CBS: N-cyclohexyl-2-benzothiazole sulfonamide.

Table 4. Composition of rubber magnets with peroxide curing system, constant amount of ZDMA, and different amount of DCP

Component	NBR	Ferrite	DCP	ZDMA
Content (phr)	100	50	2–10	30

ZDMA: zinc methacrylate; DCP: dicumyl peroxide; NBR: acrylonitrile butadiene rubber.

Table 5. Composition of rubber magnets with combined sulfur and peroxide curing systems, constant amount of ZDMA, and different amount of DCP.

Component	NBR	Ferrite	ZnO	Stearic acid	CBS	Sulfur	DCP	ZDMA
Content (phr)	100	50	3	2	1.5	1.5	2–10	30

ZDMA: zinc methacrylate; DCP: dicumyl peroxide; NBR: acrylonitrile butadiene rubber; CBS: N-cyclohexyl-2-benzothiazole sulfonamide.

The curing process of the prepared rubber compounds was performed by using a hydraulic press (Fontijne Holland BV, Holland) at 160° C based upon previously determined optimum curing time under a pressure of 15 MPa. The rubber compounds were cured into thin sheets with dimensions of 15 x 15 cm² and thickness of 2 mm.

Determination of cross-link density of composites. The cross-link density n was determined based on the equilibrium swelling of composite samples in acetone. The weighted dried samples were placed into acetone in which they swelled within time at a laboratory temperature. The weight of samples was measured every hour until the equilibrium swelling was reached. The Flory-Rehner equation modified by Krause²⁴ was then used to calculate the cross-link density based upon the equilibrium swelling state:

$$\nu = - \frac{V_{r0} \ln(1 - V_r) + V_r + \chi V_r^2}{V_s \left(V_r^{1/3} V_{r0}^{2/3} - 0.5 V_r \right)}$$

where ν is the cross-link density (mol/cm³), V_{r0} is the volume fraction of rubber in equilibrium swelling sample of vulcanizate in the absence of fillers, V_r is the volume fraction of rubber in equilibrium swelling sample of a filled vulcanizate, V_s is the molar volume of solvent (for acetone = 73.52 cm³/mol), and χ is the Huggins interaction parameter (for NBR-acetone, $\chi = 0.3692$).

Evaluation of physical-mechanical properties. Z 2.5 (Zwick Roell, Zwick GmbH & Co., Germany) appliance was used to evaluate the tensile properties of composite materials. The tests were performed in accordance with the valid technical standards and the crosshead speed of the measuring device was set up to 500 mm/min. Dumbbell-shaped test samples (width 6.4 mm, length 80 mm, and thickness 2 mm) were used for measurements. The hardness was measured by using the durometer and was expressed in Shore A.

Determination of magnetic characteristics. Magnetic characteristics of the composites were evaluated at a laboratory temperature and maximum coercivity of $H_m = 750$ kA/m. Magnetometer TVM-1 (Vúzort,

Praha, Czech Republic) equipped with Weiss electromagnet was used. The basic principle of measurement is the induction method of scanning of scattering magnetic flux F induced by magnetic vibrating sample. The samples for the determination of magnetic characteristics were of prism shape ($8 \times 4 \times 2 \text{ mm}^3$).

Microscopic analysis of composites. The surface morphology and microstructure of composite materials were observed using a scanning electron microscope (SEM; JEOL JSM-7500F, Jeol Ltd., Japan) at an accelerating voltage ranging from 10 kV to 50 kV. The samples were first cooled down in liquid nitrogen under glass transition temperature and then fractured into small fragments with a surface area of $3 \times 2 \text{ mm}^2$. The fractured surface was covered with a thin layer of gold and put under the microscope objective.

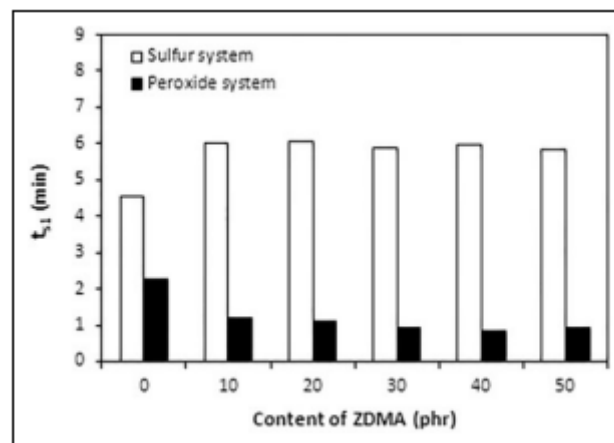


Figure 1. Influence of ZDMA content on scorch time t_{s1} of composites. ZDMA: zinc methacrylate.

Results and discussion

Influence of ZDMA content on cross-linking and properties of rubber magnetic composites

In the first part of the study, rubber magnetic composites with a constant level of magnetic filler were cured either with DCP or with a standard sulfur-based vulcanization system. The composition of both curing systems was kept constant and the main aim was to investigate the amount ZDMA on cross-linking and properties of the prepared composites. ZDMA was incorporated into the rubber formulations in a concentration scale ranging from 10 phr to 50 phr. The composition of rubber formulations tested in the first part of the research is specified in Tables 2 and 3.

Curing process and cross-link density. The influence of ZDMA on the curing process of rubber magnets was assessed based on the evaluation of vulcanization characteristics, scorch time t_{s1} , optimum cure time t_{c90} , and torque difference DM. From Figure 1, it is possible to observe that scorch time, the reference composite without ZDMA cured with the sulfur system, was nearly twofold longer in comparison with equivalent composite cured with DCP. While the application of ZDMA leads to the shortening of scorch time in peroxide-cured composites, an extension of t_{s1} values was recorded in the case of sulfur-cured rubber magnets. It also becomes apparent that the scorch time of composites cured with the sulfur system is much longer when compared to those cured with the peroxide system. The results follow the general findings, according to which the regulation of scorch time in peroxide-cured rubber compounds is complicated. It is determined mainly by the type of peroxide and its ability

to decompose into free radicals at vulcanization temperature. Peroxide free radicals then rapidly react with rubber chains to form cross-links.⁹⁻¹⁵

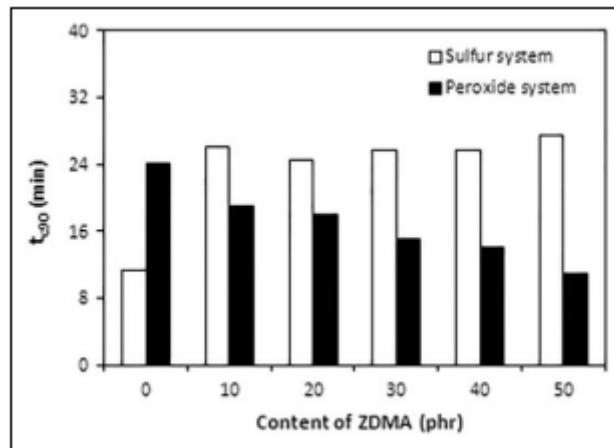


Figure 2. Influence of ZDMA content on optimum cure time t_{c90} of composites. ZDMA: zini methacrylate.

The regulation of scorch safety can only hardly be influenced by peroxide concentration or by using inhibitors of radical reactions, because their presence in rubber compounds usually leads to the lowering of cross-linking efficiency.^{12,25} On the other hand, controlling of scorch time and also the whole sulfur vulcanization process are much easier. It can be simply adjusted by proper type and content of accelerator and also by the overall composition of the curing system. As seen in Figure 2, the optimum cure time of reference composites showed the opposite tendency and was longer in the case of composite cured with DCP. The presence of ZDMA resulted in the shortening of the optimum cure time of peroxide-cured composites. The shortest time required for optimal curing exhibited composite cured with maximum ZDMA content. By application of 10 phr ZDMA into the rubber formulation cured with the sulfur system, optimum cured time prolonged in almost 16 min when compared to the reference. But then there was almost no change in the t_{c90} values with the next increasing content of ZDMA. From the graphical dependences of torque difference (Figure 3) and cross-link density (Figure 4) on ZDMA content, it is possible to observe similar behavior. As seen, there was almost no change in torque difference and cross-link density in dependence on ZDMA content in the case of rubber magnets cured with the sulfur system. On the other hand, a significant increase in both characteristics was recorded with an increasing amount of ZDMA in peroxide-cured rubber magnetic composites.

Based on the achieved results, it becomes apparent that ZDMA takes an active part in the vulcanization process of composites cured with an organic peroxide. In general, peroxide curing of rubber process proceeds via a radical mechanism. The first step is a homolytic dissociation of peroxides into free radicals at high temperatures, their possible fragmentation, and subsequent reactions of peroxide radicals with rubber chain segments.^{25,26} It has been reported in scientific studies²⁷⁻²⁹ that the in situ radical polymerization of ZDMA takes place during the curing process of rubber matrix with organic peroxides. Poly-ZDMA generated by this reaction aggregates to form the granular nanoparticles which can be physically adsorbed chemically grafted onto rubber chains. These structures can be considered as the chemical or physical cross-linking points of the composites.

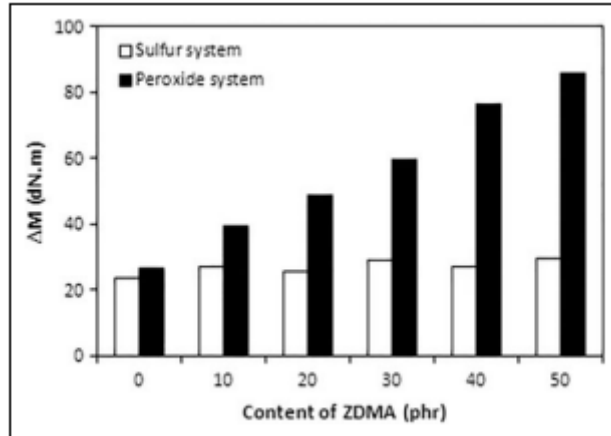


Figure 3. Influence of ZDMA content on torque difference DM of composites. ZDMA: zinc methacrylate.

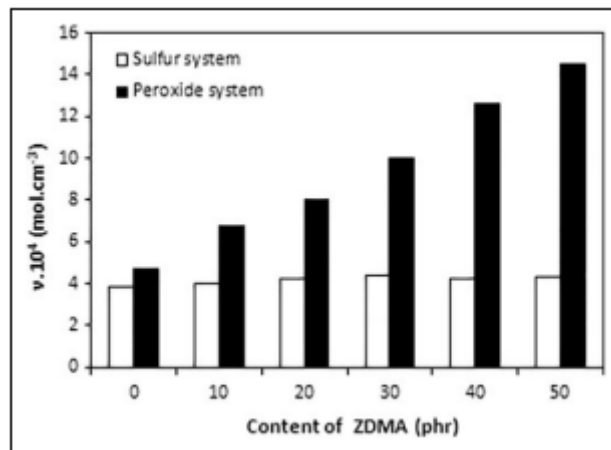


Figure 4. Influence of ZDMA content on cross-link density ν of composites. ZDMA: zinc methacrylate.

Additionally, the formation of ionic clusters through static electronic attractions with the contribution of zinc ions from coagent molecules was also observed.^{25,30-33} Thus, ZDMA as a coagent in peroxide vulcanization contributes to the formation of a more complex cross-link structure within the rubber matrix and leads to the increase of cross-link density.

On the other hand, although the cross-linking of rubber compounds with sulfur curing systems has been known for over 150 years, the chemistry of sulfur vulcanization is very complex and still not fully understood. It is even not clear whether it proceeds via ionic or free-radical intermediates. Several reaction pathways have been proposed considering ionic or radical mechanisms, eventually, both mechanisms may run concurrently.^{9,10,12}

As was already outlined, for activation and polymerization of coagents, free radical intermediates are required. During the curing process of rubber compounds with organic peroxide, free radicals are formed from thermal decomposition of the peroxide at a vulcanization temperature. By contrast, based upon the general knowledge as well as achieved results, it can be deduced that the concentration of free radicals is very low in the rubber matrix during the sulfur vulcanization process.

Moreover, even if some free radicals are present in the rubber matrix, they could be depleted for activation and polymerization of ZDMA, but then there would be a lack of their efficiency during reactions of sulfur curing systems with rubber chains. These presumptions could be the reason for the extension of scorch time and mainly optimum cure time of rubber composites cured with sulfur vulcanization system and ZDMA.

Microscopic analysis and properties. The evaluation of surface morphology of composites confirmed the above-outlined aspects showing that more homogenous structure exhibited composites cured with the peroxide system (Figure 5). This seems to be a clear evidence that ZDMA undergoes polymerization forming nanostructures and ionic clusters in the rubber matrix. On the other hand, from SEM images of composites cured with the sulfur system (Figure 6), it is possible to observe inhomogeneous structure, which can be caused by aggregation or agglomeration of nonpolymerized particles of ZDMA. It becomes apparent that due to the lack of free radicals during sulfur vulcanization, polymerization of ZDMA does not take place and particles of ZDMA tend to agglomerate. Such agglomeration is typical for conventional fillers pointing out to their bad distribution in the rubber matrix. Based upon this it can be stated that ZDMA acts as a conventional filler in the sulfur-cured composites. From Figures 5 and 6 showing the morphology of reference composites cured in the absence of ZDMA (REF), it is also possible to observe the agglomerates of $\text{SrFe}_{12}\text{O}_{19}$ which seem to be not well dispersed in the rubber matrix. The incorporation of ZDMA leads to better dispersion of the magnetic filler.

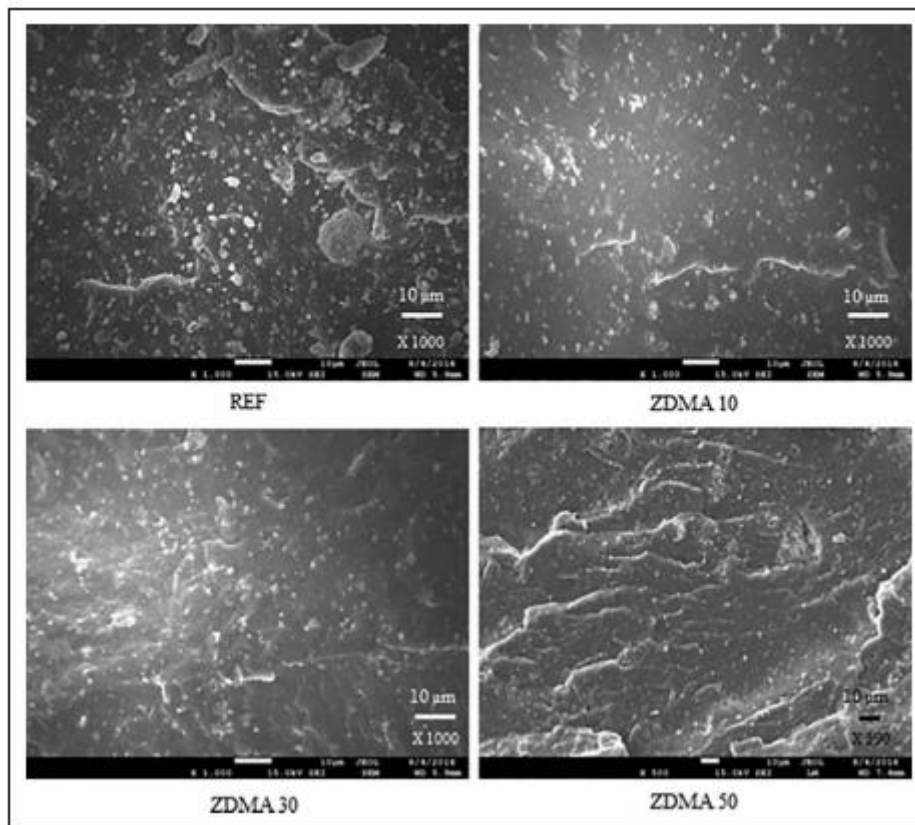


Figure 5. SEM images of composites cured with peroxide system and different content of ZDMA. SEM: scanning electron microscope; ZDMA: zinc methacrylate.

This can be attributed to a higher viscosity of the rubber matrix and thus higher shear rates during compounding on one hand, and to good adhesion of ZDMA to magnetic filler on the other hand. This effect is more visible in the case of composites cured with a peroxide system. Figures 7 and 8 provide SEM images of surface fractures of composites with higher magnification. Figure 7 reveals the morphology of the composite cured with organic peroxide and 30 phr of ZDMA, while Figure 8 demonstrates the morphology of the composite cured with sulfur system and 30 phr of ZDMA. The following SEM images again confirm that mutual compatibility and homogeneity is higher in the case of composite cured with the peroxide system. In Figure 7, it can be seen particles of magnetic filler, polymerized molecules of ZDMA and white areas attributed to particles of ZDMA, which did not participate in polymerization process. By contrast, the SEM image of the composite cured with a sulfur system (Figure 8) demonstrates a nonuniform structure formed from particles of ferrite and aggregates or agglomerates of nonpolymerized particles of ZDMA.

The values of physical-mechanical properties of composites cured with peroxide as well as sulfur vulcanization systems are graphically illustrated in Figures 9-11. The hardness of composites showed an increasing tendency with an increasing amount of ZDMA (Figure 9). Higher hardness of composites cured with DCP and ZDMA can be attributed to higher cross-link density of the equivalent composites when compared to those cured with the sulfur system.

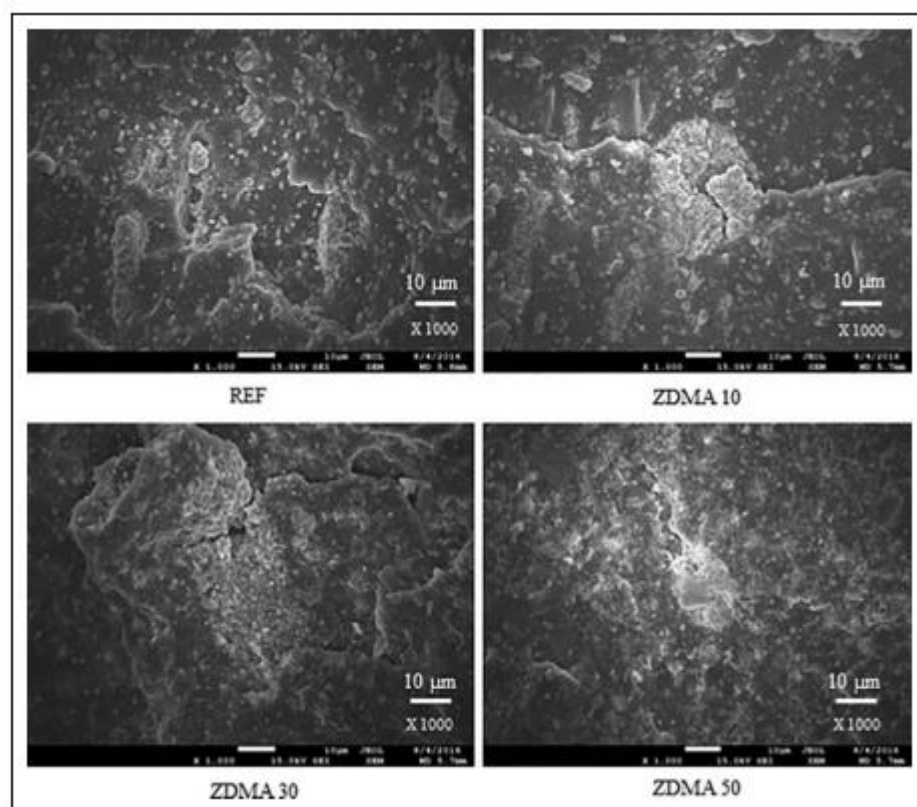


Figure 6. SEM images of composites cured with sulfur system and different content of ZDMA. SEM: scanning electron microscope; ZDMA: zinc methacrylate.

Despite the fact that the cross-link density of sulfur-cured composites was almost not influenced by the presence of ZDMA, the hardness of these composites also increased with an increasing amount of ZDMA. As already mentioned, even if ZDMA is not effectively involved in the sulfur curing process of

the composites, it acts as a conventional filler in the rubber matrix. The hardness of fillers is usually higher than that of the rubber matrix and this seems to be the most likely reason for the increase in hardness of sulfur-cured composites. On the other hand, a higher cross-linking degree of peroxide-cured composites is responsible for lower elongation at break of the equivalent composites (Figure 10). The higher is the cross-link density, the higher is restricted the rubber chains mobility and thus the elasticity and flexibility decrease. From Figure 11, it becomes apparent that the tensile strength of peroxide-cured rubber magnets showed a significantly increasing tendency with an increasing amount of ZDMA. The tensile strength increased in more than 20 MPa when the content of ZDMA increased from 0 phr up to 50 phr (from over 3 MPa for the reference to almost 25 MPa for the composite with 50 phr of ZDMA). As already described, during the curing process of rubber matrix with organic peroxide, polymerization of ZDMA takes place leading to the formation of nanostructures and ionic clusters which are physically adsorbed or chemically grafted onto rubber chains.²⁷⁻³⁰

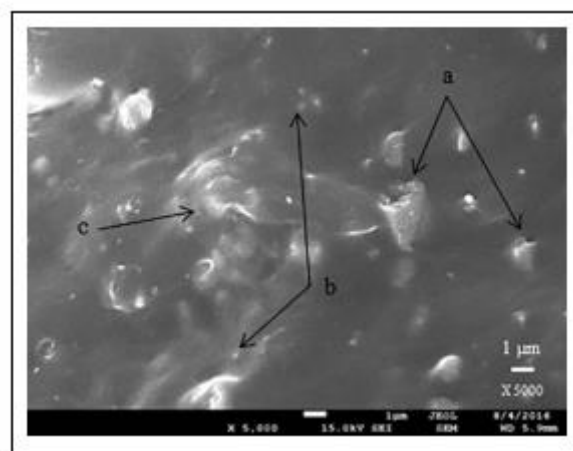


Figure 7. SEM image of composite cured with organic peroxide and 30 phr of ZDMA: (a) particles of ferrite, (b) polymerized particles of ZDMA (poly-ZDMA), and (c) non-polymerized particles of ZDMA. SEM: scanning electron microscope; ZDMA: zinc methacrylate.

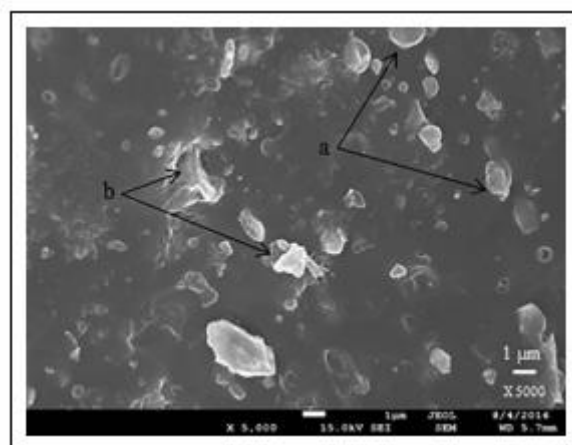


Figure 8. SEM image of composite cured with sulfur system and 30 phr of ZDMA: (a) particles of ferrite and (b) aggregates of nonpolymerized particles of ZDMA. SEM: scanning electron microscope; ZDMA: zinc methacrylate.

Thus, ZDMA contributes to the formation of more complex cross-link structure within the rubber matrix, which causes the reinforcement of the rubber matrix. Secondly, it has been found that zinc-based coagents can establish a strong bond to polar substrates, similar to ferrite fillers.^{34,35} By grafting of ZDMA onto rubber chains, zinc ions of coagents increase the polarity of rubber matrix on one hand, and they strongly interact with ferrite particles on the other hand. Thus, the improvement of compatibility and adhesion between the filler and the rubber on the interphase is achieved by means of ZDMA physically adsorbed or chemically grafted onto rubber chains and physically bonded to ferrite particles. The above-mentioned aspects are responsible for significant improvement of the tensile strength of rubber magnetic composites cured with a peroxide system.

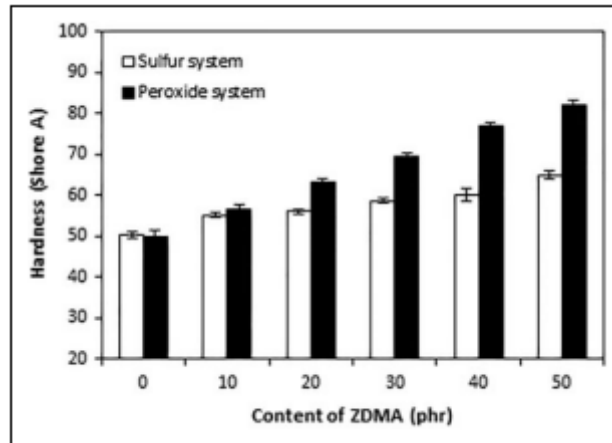


Figure 9. Influence of ZDMA content on hardness of composites. ZDMA: zinc methacrylate.

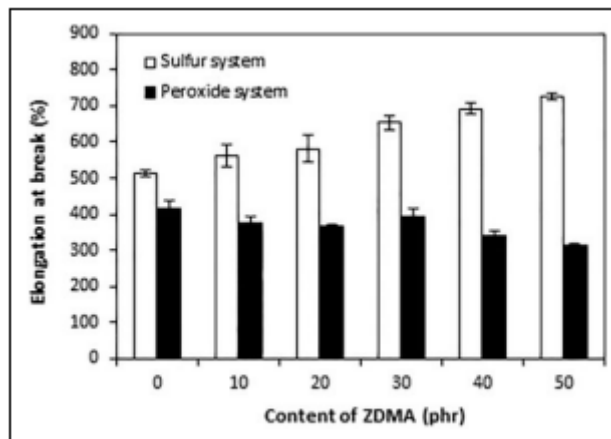


Figure 10. Influence of ZDMA content on elongation at break of composites. ZDMA: zinc methacrylate.

SEM analysis of composites cured with DCP and ZDMA (Figure 5) confirmed the outlined statements revealing very good adhesion and compatibility between the rubber matrix and $\text{SrFe}_{12}\text{O}_{19}$. It is also possible to observe that the homogeneity and compatibility on the interphase filler-rubber are improved with an increasing amount of ZDMA.

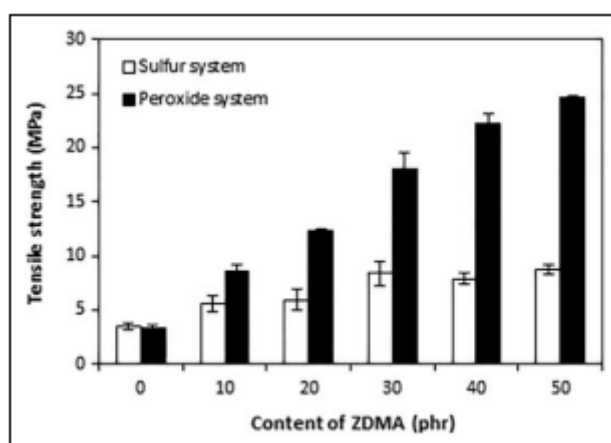


Figure 11. Influence of ZDMA content on tensile strength of composites. ZDMA: zinc methacrylate.

The application of ZDMA also leads to a slight improvement in the tensile strength of sulfur-cured rubber magnets. However, the difference between the tensile strength of the reference composite and maximally ZDMA filled composite was only about 5 MPa. Due to the lack of free radicals during the sulfur vulcanization process, polymerization of ZDMA does not take place, which was also revealed by SEM analysis (Figure 6). Despite the fact that ZDMA does not become involved in the cross-link network structure, as already outlined, it can act as a conventional filler with a low reinforcing effect. It is supposed that there can be formed physical interactions between polar acrylonitrile groups of NBR and zinc ions of ZDMA as well as between zinc ions of ZDMA and $\text{SrFe}_{12}\text{O}_{19}$ in sulfur-cured rubber magnetic composites. Thus, improved adhesion between the components of sulfur-cured composites can also be achieved, which results in slight reinforcement of the rubber magnets.

The influence of the composition of curing system on the remanent magnetic induction B_r and coercivity H_c was also investigated. The remanent magnetic induction B_r , representing the value of residual magnetization retained in the magnetic material after magnetizing it in the external magnetic field, showed a slightly decreasing trend with an increasing amount of ZDMA in both type composites (Figure 12). The possible explanation might be the presence of nonmagnetic zinc ions of ZDMA which might act as a shield against magnetic flow through the composites. The higher the amount of ZDMA, the higher was the amount of zinc ions and the more was the shielded magnetic flow through the composites. The remanent magnetic induction thus decreased. From Figure 12, it is also possible to see that slightly higher values of B_r showed composites cured with a peroxide system. The values of coercivity, which represent the intensity of the external magnetic field required to abolish the remanent magnetic induction in the material, fluctuated from 109 kA/m to 113 kA/m with no evident influence on the amount of ZDMA or the type of curing system applied.

Influence of peroxide content on cross-linking and properties of rubber magnetic composites

The obtained results revealed that ZDMA significantly influences the cross-linking process and properties of rubber magnets cured with a peroxide system. On the other, due to the absence of free radicals necessary for polymerization, ZDMA does not participate in the cross-linking process during sulfur vulcanization and behaves as a filler. Therefore, the following study aimed to increase the amount of DCP in both types of composites.

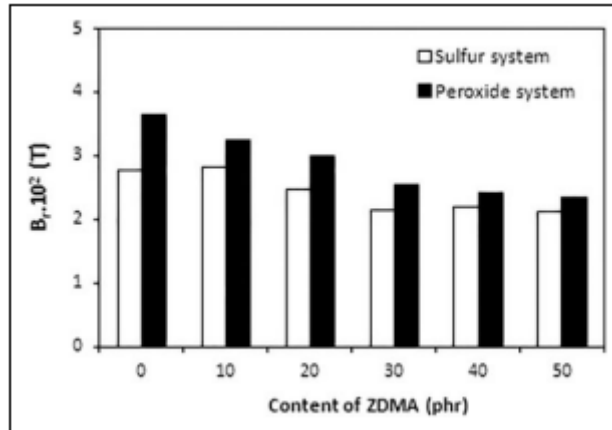


Figure 12. Influence of ZDMA content on remanent magnetic induction B_r of composites. ZDMA: zinc methacrylate.

The content of ZDMA and also $SrFe_{12}O_{19}$ was kept on a constant level in all composites, 30 or 50 phr, respectively, while DCP was dosed to the rubber formulations in a concentration scale ranging from 2 phr to 10 phr. The more was the amount of DCP, the more free radicals were generated from its thermal dissociation at a vulcanization temperature. The composition of rubber magnetic composites cured with a peroxide system is summarized in Table 4, while Table 5 provides the composition of rubber magnets cured with a combined sulfur vulcanization system and an organic peroxide. The composites cured only with the sulfur system, or with 1 phr DCP, are in graphical illustrations marked as reference (REF).

Curing process and cross-link density. As possible to observe from Figure 13, the scorch time of the reference composite cured with sulfur vulcanization system was more than 5 min longer in comparison with reference composite cured with an organic peroxide. While only a small difference in scorch time with the change of peroxide content in composites cured with peroxide system was observed, increasing content of peroxide in composites cured with combined sulfur and peroxide systems resulted in the lowering of the scorch safety. The biggest difference in optimum cure time of both type composites was also possible to observe in the case reference composites cured either with the sulfur system or organic peroxide (Figure 14).

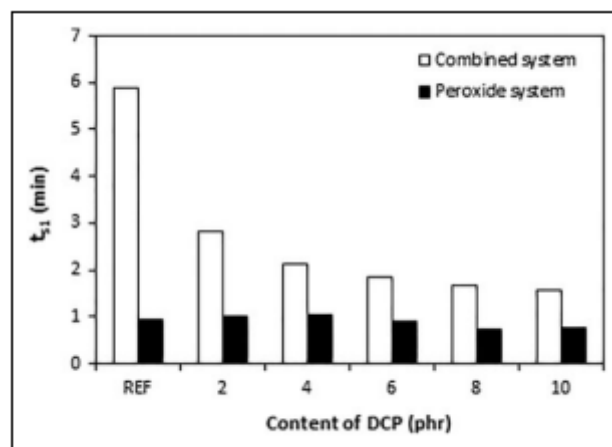


Figure 13. Influence of the peroxide content on scorch time t_{s1} of composites.

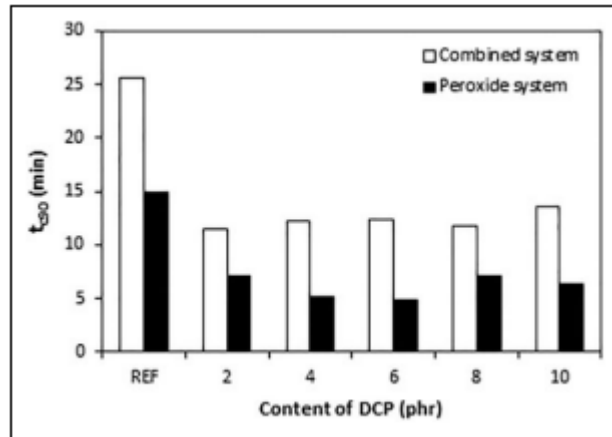


Figure 14. Influence of the peroxide content on optimum cure time t_{c90} of composites.

With the increasing content of DCP, the difference in optimum cure time of both type composites became less visible. As also seen in Figures 13 and 14, composites cured with combined vulcanization systems exhibited longer scorch time and also longer optimum cure time in comparison with the composites cured with a peroxide system. The achieved results revealed that the sulfur curing process of rubber composites proceeds more slowly, as it becomes obvious mainly from the comparison of curing characteristics of reference composites.

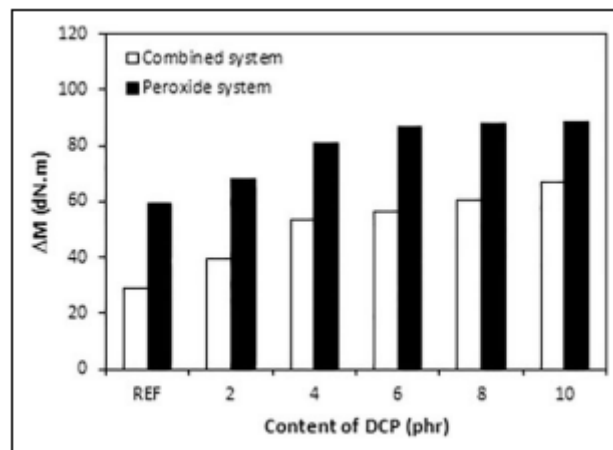


Figure 15. Influence of the peroxide content on torque difference DM of composites.

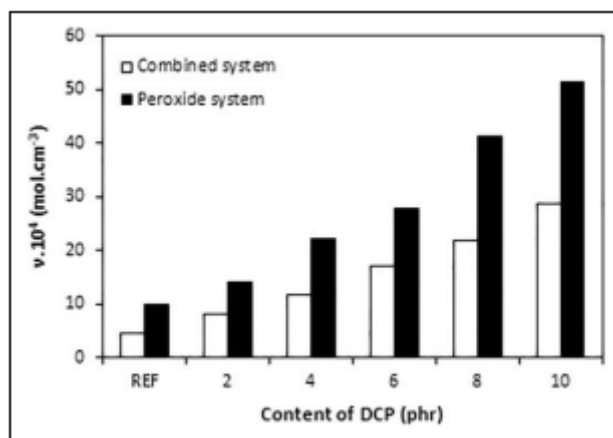


Figure 16. Influence of the peroxide content on cross-link density n of composites.

As already outlined, the slower vulcanization process of the reference sulfur-cured composite might be caused by the presence of ZDMA, which could react with radical fragments of sulfur curing systems, leading to the lack of their efficiency in cross-links formation. This leads to the deceleration of the sulfur vulcanization process. With increasing content of DCP both, scorch time and optimum cure time of composites cured with combined systems become shorter, which indicates that the curing process proceeds faster and ZDMA involves in cross-linking. The results obtained from the determination of torque increment (Figure 15) and cross-link density (Figure 16) confirmed the presumption, showing that ΔM values and cross-link density of both type composites showed an increasing tendency with increasing content of DCP. The higher the amount of peroxide, the more free radicals derived from peroxide could participate in the formation of cross-links between rubber chains. On the other hand, as already mentioned, peroxide free radicals could support polymerization of coagent molecules into nanostructures and ionic clusters and their couplings onto rubber chains which could contribute to the increase of cross-link density as well.

Microscopic analysis and properties. From an observation of surface morphology of both type composites, it becomes obvious that dimensions of coagent structures decrease with an increasing amount of peroxide (Figures 17 and 18).

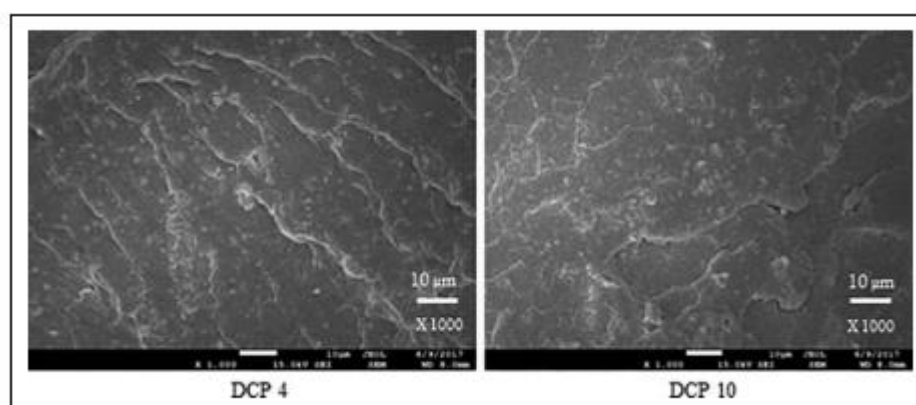


Figure 17. SEM images of composites cured with the peroxide system and different content of peroxide. SEM: scanning electron microscope.

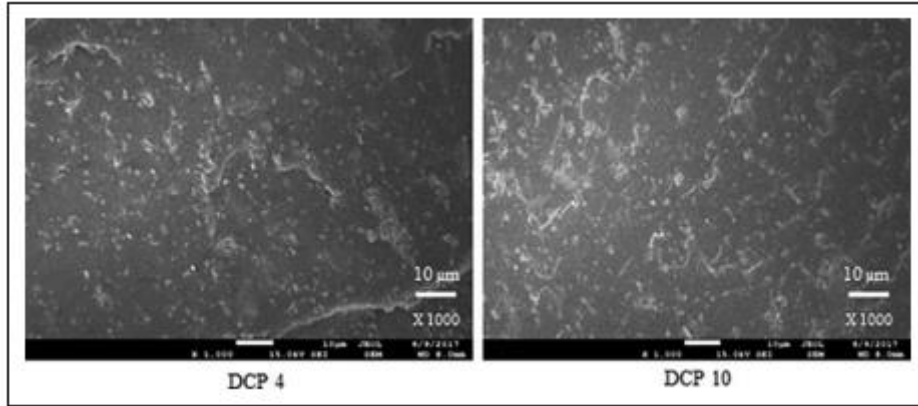


Figure 18. SEM images of composites cured with combined sulfur and peroxide systems and different content of peroxide. SEM: scanning electron microscope.

The higher the amount of DCP, the more monomers from ZDMA took part in the in situ polymerization, causing the decrease of the molecular weight and size of polymerized molecules of the coagent. The dependences of hardness and elongation at break of composites followed the dependences of cross-link density, showing that higher cross-link density of composites cured with peroxide system was reflected in higher hardness and lower elongation at break of the equivalent composites (Figures 19 and 20). From Figure 21, it is possible to observe that the tensile strength of composites cured with peroxide system first slightly increased by an increasing amount of DCP from 1 phr to 2 phr, then a decreasing trend of tensile strength was observed by further increasing the content of DCP. The tensile strength of composites cured with combined systems also increased with an increasing amount of DCP, reached a maximum value at 4 phr DCP, followed by the drop to lower values. The reason for the decrease in tensile strength can be attributed to a very high cross-linking degree. Due to the low mobility of rubber chain segments at high cross-link density, the applied deformation strains cannot be distributed uniformly on the whole spatial cross-linked network structure of the rubber matrix. This leads to the formation of local stresses within the rubber matrix, causing inception and cracks growing. The tensile strength of composites subsequently decreases.

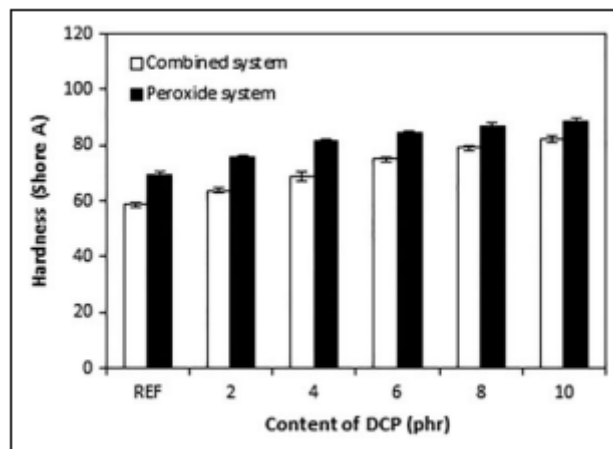


Figure 19. Influence of the peroxide content on hardness of composites.

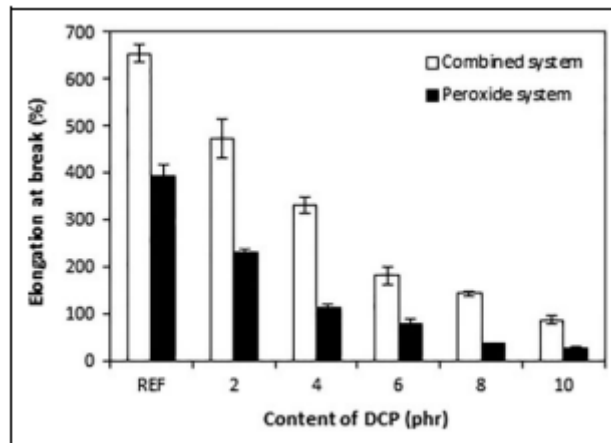


Figure 20. Influence of the peroxide content on elongation at break of composites.

Magnetic characteristics of composites were found not to be influenced by the amount of peroxide as their values moved in a close experimental range.

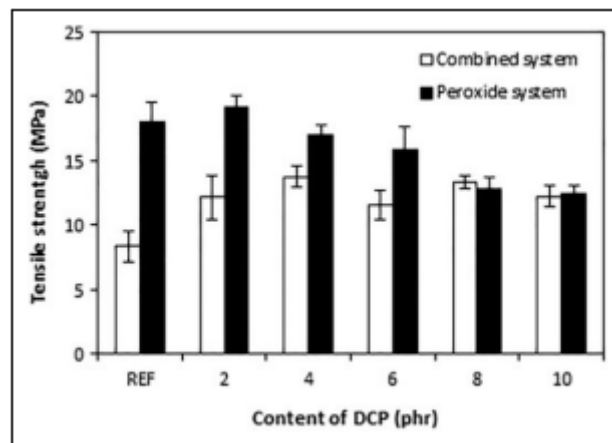


Figure 21. Influence of the peroxide content on tensile strength of composites.

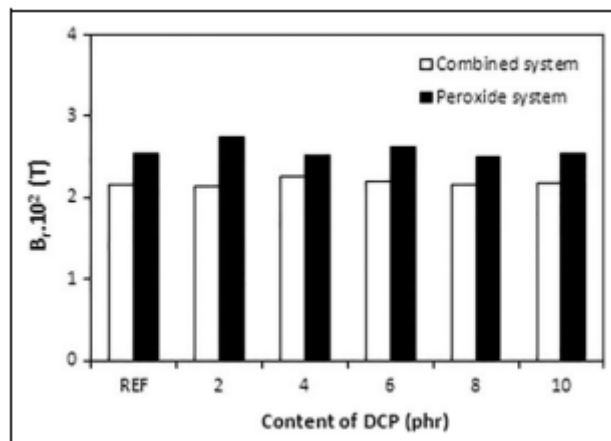


Figure 22. Influence of the peroxide content on remanent magnetic induction B_r of composites.

From Figure 22, it is shown that slightly higher values of remanent magnetic induction exhibited composites cured with a peroxide system. However, based on the present outputs and results demonstrated in our previous research, it can be generally stated that magnetic characteristics of composites are dependent mainly on the type and content of applied magnetic filler.³⁶⁻³⁸

Conclusion

Rubber magnetic composites based on NBR and SrFe₁₂O₁₉ were cured with sulfur and peroxide curing system with the introduction of ZDMA. The goal of the work was to investigate the influence of curing system composition on the cross-linking and properties of tested composites with a constant level of magnetic filler.

The achieved results revealed that ZDMA plays an important role in the vulcanization process of rubber magnetic composites cured with an organic peroxide. Due to the presence of free radicals formed from peroxide decomposition, polymerization of ZDMA in the rubber matrix takes place leading to the formation of more complex crosslink structures within the rubber matrix and the increase in cross-link density. Moreover, ZDMA improves the adhesion to applied SrFe₁₂O₁₉. The adhesion and compatibility between the rubber and the filler on the interphase are subsequently achieved, resulting in the increase of tensile strength of composites. The increase of cross-link density was reflected in the increase of modulus and hardness of rubber magnets and the decrease of elongation at break. By contrast, ZDMA acts as a conventional filler in composites cured with the sulfur system, due to a lack of free radicals required for the activation and polymerization of ZDMA. Magnetic characteristics of composites were found to be almost not influenced by the composition of curing system.

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