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Influence of Combined Sulfur and Peroxide Curing Systems and Ageing on the Properties of Rubber Magnets

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ABSTRACT

Strontium ferrite in constant loading is incorporated into acrylonitrile butadiene rubber in order to prepare rubber magnetic composites. Sulfur, peroxide and combined sulfur/peroxide curing systems are applied for cross-linking of rubber composites. The work is focused on the investigation of curing system composition and thermo-oxidative ageing on cross-link density, physical-mechanical and magnetic properties of rubber magnets. The results revealed that the cross-link density and the structure of the formed cross-links within the rubber matrices affect the property spectrum of vulcanizates.

Keywords: Ageing, peroxide curing, rubber magnetic composites, sulfur curing

1. Introduction

Rubber magnetic composites are group of smart materials combining elastic properties of rubber matrices and magnetic properties of suitable fillers. Due to their unique properties, they have been widely used as permanent flexible magnets, shielding devices, microwave absorbers or sensors of magnetic and electromagnetic fields.[1,2]

Sulfur vulcanization of rubber compounds is a complex process, which leads to the formation of different types of sulfidic cross-links between macromolecules of rubber. Sulfur cured vulcanizates are characterized by high tensile and tear strength, good dynamic properties, but poor resistance to ageing and weak high temperature stability.[3]

On the other hand, carbon-carbon linkages are formed between rubber chain segments by application of organic peroxides as curing agents. The main features of peroxide cured vulcanizates are good heat-ageing stability, good electrical properties, low compression set or no discoloration of the finished products.[4] However, compared to sulfur systems, they usually exhibit worse tensile and tear strength and inferior elastic properties.

Cross-linking ofrubber compounds with peroxides can be effectively improved by using of co-agents. Co-agents are multifunctional low molecular weight organic compounds, which are used to increase the cross-linking efficiency and physical-mechanical properties of peroxide cured elastomers.[5]

As different types of cross-links are formed within rubber matrices by application of sulfur and peroxide curing systems, different propensity of rubber magnetic composites to thermo-oxidative ageing might be expected. Moreover, ferrites as magnetic fillers are complex compounds of iron oxides with oxides of some other metals. The application of ferrites into rubber matrices leads also to the incorporation of an ample amount of oxygen and iron ions into rubber compounds. Ions of transition metals, as iron, belong to the so called “rubber toxicants.” Thus, the presence offerrite could contribute to the enhanced inclination of rubber magnetic composites to degradation factors, mainly to the thermo-oxidative ageing.

2. Experimental Section

Acrylonitrile butadiene rubber NBR (SKN 3345, content of acrylonitrile 31-35%, Sibur International, Russia) was used as rubber matrix. Strontium ferrite SrFe12O19 (Magnety, Světlá Hora, Czech Republic) was used as magnetic filler. Peroxide curing system consisted of dicumyl peroxide DCP (Merck Schuchardt OHG, Germany) as peroxide curing agent and acrylic acid zinc salt ZDA (zinc acrylate, Sigma-Aldrich, USA) as co-agent. Sulfur curing system consisted of zinc oxide (Slovlak, Košeca, Slovakia) and stearic acid (Setuza, Ústí nad Labem, Czech Republic) as activators, N-cyclohexyl-2-benzothiazole sulfenamide CBS (Duslo, Šala, Slovakia) as accelerator and sulfur (Siarkopol, Tarnobrzeg, Poland) as curing agent. The composition of the rubber magnets is summarized in **Table 1**.

The two steps mixing of rubber compounds were carried out in a laboratory mixer Brabender. The rubber and the filler were compounded in the first step (9 min, 90 °C), while the curing system was introduced in the second step (4 min, 90 °C). After that the blends were homogenized in two roll calender.

The cross-link density v was determined based on equilibrium swelling of the composite samples in acetone. After reaching the equilibrium state, the Flory-Rehner equation modified by Krause was introduced to calculate the cross-link density.

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

	S0-P2	S0.5-P1.5	S1-1	S1.5-P0.5	S2-P0
NBR	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

The tensile properties of tested composites were evaluated by using Zwick Roell/Z 2.5 appliance. Magnetic characteristics were determined by using magnetometer TVM^{-1} at maximum coer-civity of Hm = 750 kA m^{-1}.

For thermo-oxidative ageing, composites were kept in the hotair oven chamber in form of test specimens. The ageing was carried out in air atmosphere at 70 °C and 100 °C, exposure time was equal to 168 h.

3 Results and Discussion

The influence of curing system composition and ageing on cross-link density of rubber magnets is graphically illustrated in **Figure 1**a. As shown, the highest cross-link density exhibited the composite cured only with peroxide system (S0-P2), followed by the composite cured only sulfur system (S2-P0). The lowest degree of cross-linking showed the composite cured with equivalent sulfur to peroxide ratio (S1-P1). The possible explanation of this phenomenon might be some competitive reactions, which may deplete peroxide radicals and/or sulfur fragments, running concurrently with the main cross-linking reactions. The different character of cross-link density dependences relates with the different reaction mechanisms of both type curing systems with the rubber matrix. Also, in the case of composites cured only with peroxide, or mixed sulfur/peroxide systems, the contribution of co-agent to the cross-link density must be included, which is discussed in the following section.

After exposure of composites to the conditions of thermooxidative ageing at 70 °C, the cross-link density of both types composites changed only very little. The rise of ageing temperature to 100 °C resulted to a slight increase in cross-link density of composites. The increase in cross-link density after ageing can be attributed to the additional cross-linking of rubber matrices by free sulfur and/or peroxide species, which were not reacted during the vulcanization process.

The dependences of modulus M100 and hardness on the curing system composition were in close connection with the dependences of cross-link density. This means that the highest modulus and hardness exhibited composite cured only with peroxide system (S0-P2) with the highest cross-ink density. On the contrary, the lowest cross-link density of the composite cured with equivalent sulfur to peroxide ratio (S1-P1) was reflected in the lowest values of both characteristics. It can also be stated that the increase in cross-linking degree after ageing was connected with higher hardness and modulus of composites. On the other hand, higher the cross-link density, higher is restricted elastomer chains elasticity and mobility leading to decrease of the elongation at break. Thus, the composite cured with equivalent ratio of sulfur and peroxide with the lowest cross-link density showed the highest elongation at break.

From graphical dependence of tensile strength on the curing system composition (**Figure 1**b) it becomes apparent that the tensile strength of composites was improved with increasing amount of peroxide and decreasing amount of sulfur in the applied curing systems. The highest tensile strength showed the composites with higher amount of peroxide curing system (S0-P2, S0.5-P1.5), while the lowest tensile strength was found to have composite cured only in the presence of sulfur system (S2-P0). The results are not in correlation with the general theoretical predictions, as outlined in the introduction part. The composition of peroxide curing system with the presence of zinc acrylate as co-agent is the best explanation for the increase of tensile strength with increasing amount of peroxide system.

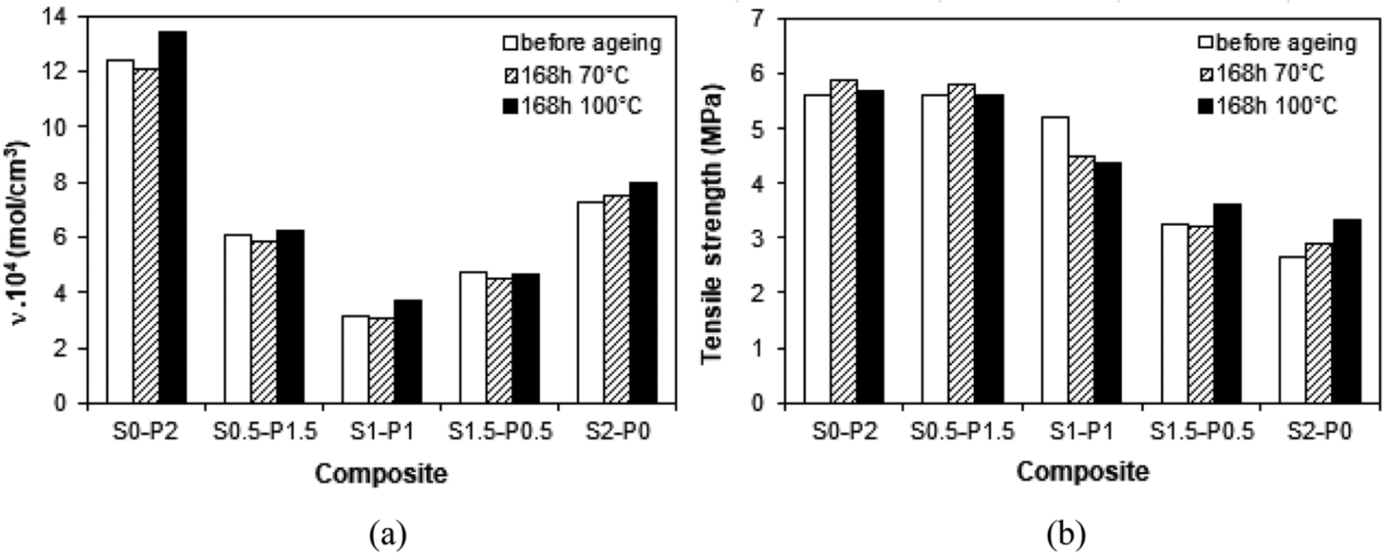

Figure 1. Influence of curing system composition and thermo-oxidative ageing on cross-link density v (a) and tensile strength (b) of composites.

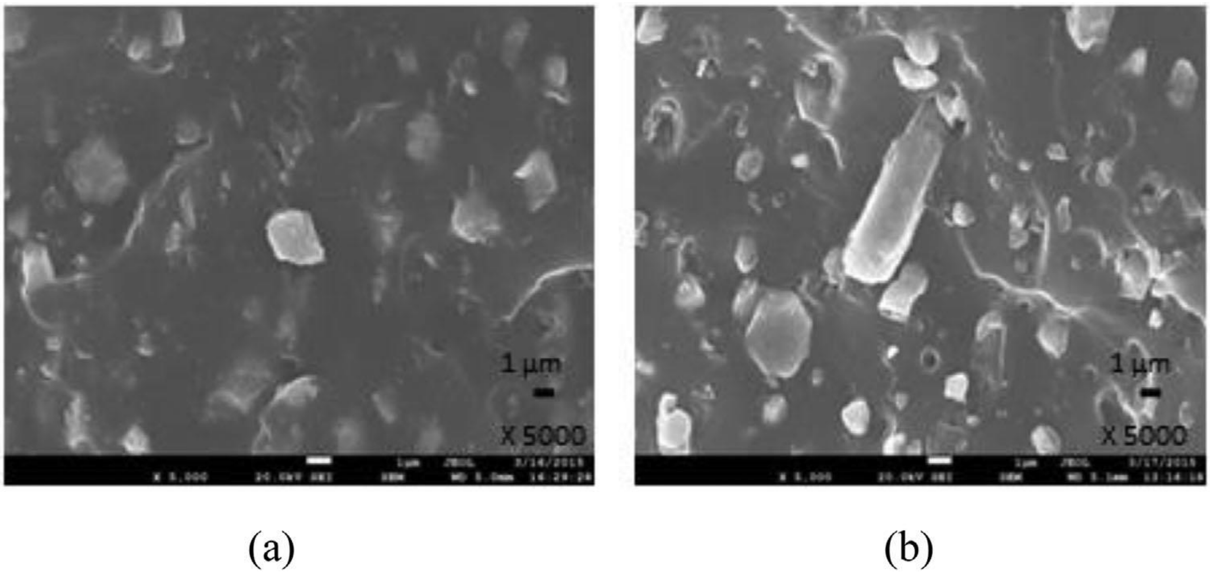

Figure 2. SEM images of composite cured only with peroxide system S0-P2 (a) and composite cured only with sulfur system S2-P0 (b).

It has been reported that during the curing process of rubber matrix with peroxide, co-agent ZDA undergoes the in situ polymerization. Poly-ZDA formed during this reaction tends to aggregate to form the granular nanodispersions, which can be chemically grafted or physically adsorbed onto elastomer chains. These structures are considered as the chemical or physical cross-linking elements of the composites.[6] Moreover, it has also been demonstrated that zinc based co-agents exhibit strong adhesion to polar materials, as to ferrite fillers.[7] Based upon the achieved results it can be stated that by grafting of co-agents onto rubber chains, zinc ions of co-agents increase the polarity of elastomer on one hand, and on the other hand, strongly interact with ferrite particles. Thus also the improvement of compatibility and adhesion between the filler and the rubber on the interphase is achieved, by means of ZDA physically adsorbed or chemically grafted onto rubber chains and physically bonded to ferrite particles. The mentioned aspects are suggested to be the reason for the increase of tensile strength with increasing amount of peroxide curing system. SEM analysis confirmed the above outlined presumptions and revealed that the adhesion and compatibility between ferrite and the rubber is higher in the case of composite cured only with peroxide system (S0-P2), just because of zinc acrylate forming interfacial layer between the rubber matrix and the filler (**Figure 2**). In the case of composite cured only with sulfur system (S2-P0), there is more evidently visible the presence of microcavities and voids on the interphase filler - rubber.

The influence of ageing on the tensile strength of composites seems to be ambiguous, as the tensile strength slightly increased or decreased in comparison with the original values of non-aged composites.

The remanent magnetic induction Br, which represents the value of residual magnetization remained in the magnetic material when external magnetic field, is one of the most important magnetic characteristics of permanent magnets and the experimentally determined values of Br for the tested composites are presented in **Figure 3**. As it is shown, remanent magnetic induction of composites moved only in the low range of experimental values, independently on the curing system composition. There was also recorded almost no influence of thermo-oxidative ageing on the magnetic characteristics of the prepared composites.

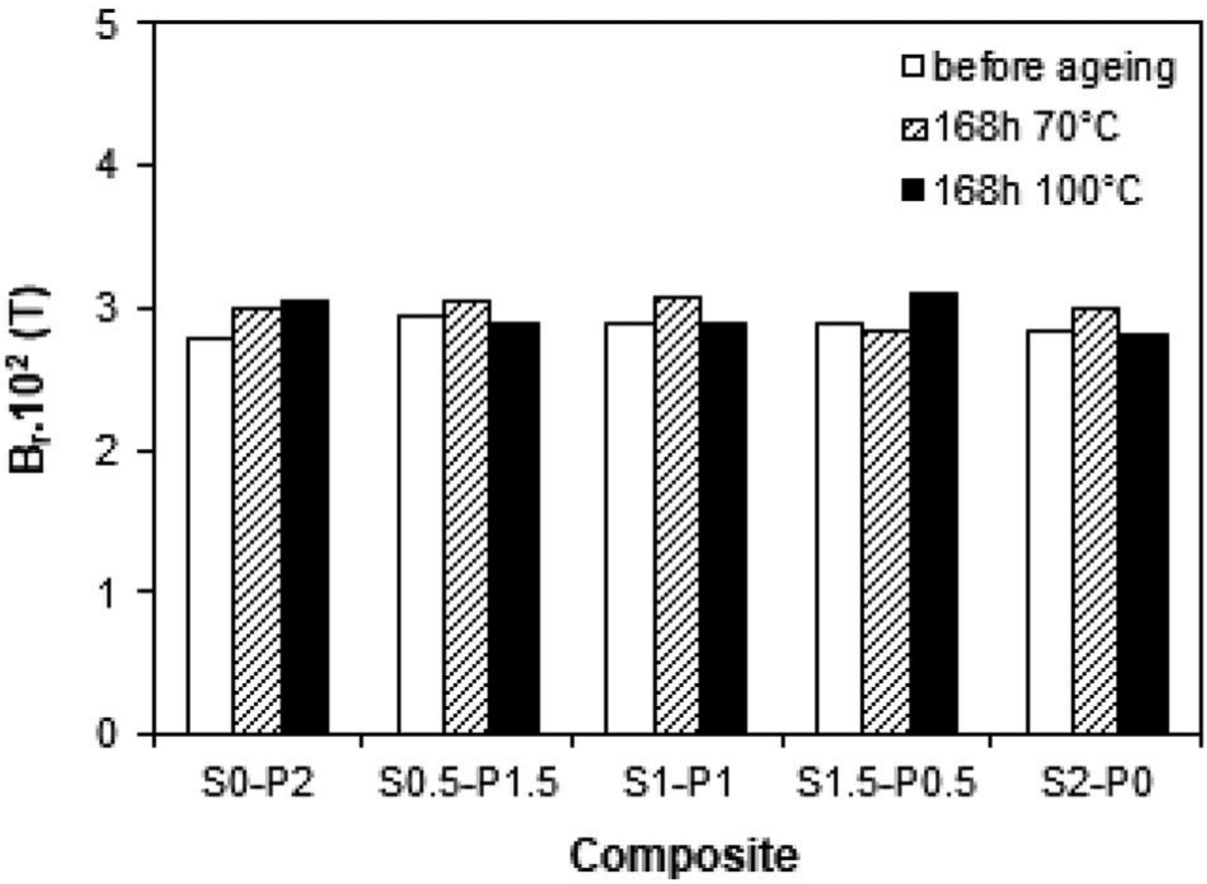

Figure 3. Influence of curing system composition and thermo-oxidative ageing on remanent magnetic induction Br of composites.

4. Conclusion

The results of the study revealed that the dependences of physical-mechanical properties of composites on curing system composition were in close correlation with the dependences of cross-link density, while the tensile strength of rubber magnets showed increasing tendency with increasing amount of peroxide in the applied curing systems. The influence of curing system composition and ageing on magnetic characteristics was negligible.

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