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Elastomeric composites with magnetorheological and magnetic properties conaining nano-sized iron oxide

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Outline:

Introduction

The interest in elastomer magnetorheological materials results from the strong linkage between their rheological properties with the external magnetic field. Change of material stiffness in various operating conditions is the basis for many MRE applications, such as self-adapting engine casings, dampers [1]. Such materials can be applied both in space industry, and electrical engineering, as equipment for vibration attenuation, as well as in the automotive industry for production of variable stiffness mounts (dampers which can be tuned, characterised with variable stiffness). Such materials can serve as deflection sensors [2-4].

Current challenges include designing and production of multifunctional materials that are “smart” at the material level. Reference to material intelligence images three basic functions: sensation of changes, processing the information obtained and response to such changes [5]. Innovative functions of smart materials are, in many cases, equivalent to natural behaviour of live organisms. Biological systems continuously adapt to continuous dynamic changes caused to the natural environment by the development of inherent homeostasis capacity. “Smart” materials should also reveal similar characteristics [6].

Magnetorheological materials (MR): liquids, foams, and elastomers, belong to a class of smart materials that can, as a result of magnetic field impact, change rheological properties in the continuous, sudden and reversible manner. MR materials are based on the suspension of magnetically polarised particles, usually iron compounds, in a non-magnetic medium [7]. MR liquid analogues responding to magnetic field are magnetorheological elastomers (MRE), where oil has been replaced with polymer medium or gel. Similarly as in the case of liquids, physical phenomenon responsible for sensitivity of magnetorheological elastomers to magnetic field is very similar. In fact, the “strength” of liquids responding to the magnetic field depends on the degree of ordering. In turn, the “strength” of elastomers responding to the magnetic field is typically characterised by the change of shear modulus and dissipation in the magnetic field. The response of magnetorheological liquid to the magnetic field is the shift in the flow limit, while of magnetorheological elastomer – increase in flexibility module [7-11]. The main advantage of MRE is the possibility of controlled change of the shear modulus and shape under the impact of the magnetic field. Such materials comprise the elastomer medium where ferromagnetic particles are distributed, which causes that under the impact of the magnetic field, the structure gets ordered and elastomer properties change [12]. Magnetorheological elastomers can be divided into two types:

- anisotropic, particles of which are grouped in column structures resembling a chain,
- isotropic, where magnetic particles are evenly distributed in the entire volume of the medium [13].

Properties of magnetorheological elastomers depend on the intensity and direction of the magnetic field. This may affect stiffness and distribution of chain structures. If the magnetic field is active during crosslinking of the rubber material, ferromagnetic particles are ordered into chains (anisotropy). However, if there is no field, particles are distributed randomly (isotropy). If the composite is subjected to the impact of the magnetic field, ferromagnetic particles are not ordered, the networked elastomer medium prevents it [7].

The analysis of literature clearly indicates that with the same volume share of particles, MRE with anisotropic microstructure shaped at the phase of generation in the magnetic field, they are characterised with a much greater magnetorheological effect than MRE with isotropic particle distribution. Some doubts are, however, raised by information on the impact of microstructure of magnetic particles on the MR effect of isotropic elastomers [14-16]. A more thorough analysis is needed on the impact of magnetic nanoparticles with various sizes with elastomer medium in reference to rheological properties of MRE composites. It is also important to investigate how the filler dispersion, and the contribution of auxiliary agents, impacts on magnetorheological properties of vulcanisates. It is also worth to refer the above research related to formation of specific filler "structure" to mechanical properties, which are of major importance from the point of view of later properties of composites.

Basic physical properties, which are often operating parameters of rubber products, depend on the degree of filler dispersion [17-19]. The improvement in the degree of filler dispersion is a resulting effect of aggregation, including assessment of agglomeration, as well as even distribution of the filler in rubber matrix [20,21]. Increase in the degree of dispersion of products filled below the percolation threshold is accompanied with increased mechanical strength, electric resistance and abrasion resistance of vulcanisates. It is also necessary to investigate how filler dispersion affects magnetic and magnetorheological properties of MRE composites.

Transition metal ions are the most widely used group of polymer degradation accelerators. Interest in these additives is related to their ability to catalyze the decomposition of hydroperoxides to free radicals [22]. The most commonly used are the transition metals iron of cobalt and magnesium. Iron is particularly effective for accelerating the process of photodegradation, while magnesium and cobalt are particularly sensitive to thermal degradation [23]. Analysis of the literature shows that metals with variable valences affect the acceleration of aging processes: thermo-oxidizing, UV and weathering. In the case of magnetorheological materials, high iron content is necessary in order to achieve the desired magnetorheological effect however, it may adversely affect the long-term oxidative stability of these materials and hence their subsequent long-term performance.

The aim of the study was to obtain elastomer composites with improved magnetic, magnetorheological and mechanical properties. Moreover, examination whether the high content of ferromagnetic materials, which is essential in order to achieve the desired magnetorheological effect of MRE, adversely affects the acceleration of aging processes: thermo-oxidizing and ultraviolet.

Materials and methods

Materials

Elastomers

- Ethylene-octene rubber (POE) – ENGAGE 8150, crystallinity degree: 27%, Mooney viscosity (ML(1+4) 121^0C): 16, producer: The Dow Chemical Company, USA
- Ethylene-propylene rubber (EPM) – DUTRAL CO 054, propylene unit content: 40 %, Mooney viscosity (ML(1+4) 125^0C): 44, producer: Montedison Ferrara, Italy.
- Acrylonitrile-butadiene rubber (NBR) – PERBUNAN 2845 F, acrylonitrile unit content: 28%, Mooney viscosity ML 45, producer: Lanxess, Germany.
- Methyl-vinyl silicone rubber (MVQ) – POLYMER MV 007, vinyl unit content: 0,07%, Mooney viscosity (ML(1+4) 100^0C): 15, producer: „Silikony Polskie" Chemical Company, Nowa Sarzyna, Poland.

Crosslinking agnets

- ➢ dicumyl peroxide (DCP), purity: 99,0%,
  M_{mol}=270,37 g/mol.
  Producer: Sigma Aldrich Chemie GmbH, Germany
- ➢ triallyl-1,3,5-triazine-2,4,6(1H,3H,5H) (TAC), producer: Sigma Aldrich Chemie GmbH, Germany
- ➢ sulfuric crosslinking complex:
- ✓ rhombic sulphur S_8, producer: Siarkopol, Poland
- ✓ zinc oxide (ZnO), producer: Huta Będzin, Poland
  mercaptobenzothiazole MBT, producer: Organika Chemical Company, Poland
- ✓ stearin, producer: POCH, Poland

Filler

- ➢ Nono-sized iron oxide (II,III) Fe_3O_4, magnetite, magnetization saturation ca. 100 Am^2/kg, particie size <5µm, iron content 95%, density 4.8-5.1 g/mL in 25 °C, producer Sigma Aldrich Chemie GmbH, Germany

Composition of typical elastomer mixture: rubber – 100 phr, DCP - 2 phr, TAC – 0.5 phr, ZnO - 5 phr, MBT - 2 phr, S - 2 phr, filler 20-100 phr.

Methods

Elastomer mixtures, based on ethylene-octene, ethylene –propylene, acrylonitrile-butadiene and silicone rubber filled with nano-sized iron oxide powder were prepared by common manufacturing procedures for elastomers. Magnetoactive particles were mixed with the rubber and vulcanisation system using two – roll mills at 30 ºC or Brabender measuring mixer N50 (temp. 50 ºC, speed range 40 min-1, time of the process 10 min). Then, the mixtures were vulcanised at 160 ºC and, 15 MPa pressure for 30 min. The vulcanisates were produced in two different ways: under the influence of a magnetic field – to align the magnetic particles in the elastomer matrix and without the presence of a magnetic field.

The mechanical properties were examined with a Zwick static materials testing machine, according to ISO 37 standards. The magnetic properties of the samples were measured with a vibrating sample magnetometer VSM LakeShore 7410, with a the field of 960 kA/m. The magnetorheological properties were studied with an Ares Rheometer (plate-plate system, plate diameter, 20 mm; gap 2 mm; magnetic field range, 0-300 mT). The cross-linking density of the vulcanisates was calculated based on rapid solvent-swelling measurements (in toluene and in toluene with ammonium vapours) using the Flory-Rehner equation. Microstructural observations were made using scanning electron microscopy (SEM). A heat ageing process was performed with an FD series dryer (Binder) according to PN-82/C04216 standards. An ultraviolet ageing process was performed with UV2000 equipment (Atlas).

Results and discussion

Rheological properties of elastomer mixtures

Determination of rheological properties of elastomer blends technology gives direct benefits (determination of the optimal time of vulcanization, blends flow) and provides preliminary information on the effect of filler on the properties of the elastomer and the tendency to form the structure of the filler in the elastomer. Increasing the minimum and the maximum torque due to the filler effect, is an indirect measure of the hydrodynamic effect and/or structure of the filler and/or increase of the crosslink density.

The hydrodynamic effect results from the introduction of a rigid polymer of the solid phase, which is not deformed. Consequently, internal stresses of the polymer network are greater than those applied from the outside, resulting in an independent contribution to the deformation of the torque or the Young's modulus in the measurement of mechanical properties.

The structure of the filler also influence the rheometric properties of vulcanizates. It is related not only to the construction of the filler particles, particularly to the anisotropy, but also the ability to specific interactions.

Rheometric properties of elastomer mixtures containing nano-sized magnetite

Tables 2.1-4 show the results of rheological properties of the elastomeric compounds (rubbers: ethylene-propylene, ethylene-octene, butadiene-acrylonitrile, and silicone) filled with nanometric magnetite in different contents (0-100 phr).

TABLE 2.1
Rheometric properties of ethylene-propylene blends filled with nano-sized magnetite

Nanometric magnetite [phr]	$M_{min.}$ [dNm]	ΔM [dNm]	τ_{09} [min]
0	18,0	47,1	20
20	34,7	50,5	13
40	39,3	50,9	6
60	44,4	54,1	5
80	53,0	57,6	4
100	59,3	57,6	3

M_{min} - minimum torque;
ΔM - increase in torque during crosslinking;
τ_{09} - curing time.

TABLE 2.2
Rheometric properties of ethylene-octene blends filled with nano-sized magnetite

Nanometric magnetite [phr]	M_{min} [dNm]	ΔM [dNm]	τ_{09} [min]
0	15,0	28,8	15
40	29,3	30,7	3
60	36,7	37,3	3
80	45,5	39,4	3
100	53,5	40,0	3

TABLE 2.3
Rheometric properties of acrylonitrile-butadiene blends filled with nano-sized magnetite

Nanometric magnetite [phr]	$M_{min.}$ [dNm]	ΔM [dNm]	τ_{09} [min]
0	6,4	49,2	9
20	8,9	54,4	15
40	11,2	67,6	17
60	11,5	73,6	17
80	12,6	86,9	16
100	13,8	89,6	14

TABLE 2.4
Rheometric properties of silicone blends filled with nano-sized magnetite

Nanometric magnetite [phr]	M_{min} [dNm]	ΔM [dNm]	τ_{09} [min]
0	24,1	30,1	6
60	36,8	33,9	9
80	44,3	34,3	9
100	48,6	35,4	10

The addition of nano-sized iron oxide increases the torque increment and minimum torque values when compared with unfilled blends. Regardless of the type of rubber used, ΔM and M_{min} values increases with increasing nanometric magnetite content. The highest values of the rheometric torque gain during crossilinking were obtained for acrylonitrile-butadiene rubber compositions (Table 2.3). Increasing torque increments for filled compounds can attest to the increased crosslinking density of vulcanizates. Nano-sized magnetite seems to be an active filler, showing an influence on the modules growth during vulcanization. There is also significant hydrodynamic effect which results from the introduction of the rigid phase to the solid elastomer, which in turn may result in strengthening elastomeric mixtures.

The addition of the filler cause a decrease in the time of vulcanization of ethylene-propylene and ethylene-octene compounds. In other cases, τ_{09} values increased - which may indicate an increased tendency to agglomerate of the nanometric magnetite in higher contents. Moreover NBR mixtures are crosslinked by sulphur crosslinking complex instead of dicumyl peroxide, what can explain the differences.

Comparing the rheometric properties of composites based on the same elastomers (EPM, POE, NBR, MVQ) filled with nanometer magnetite, it can be seen that there are no significant differences in the characteristics of the individual compounds. Generally maintains the same trend - addition of fillers increases the ΔM and M_{min} values compared with unfilled systems. Moreover, as the amount of filler increases, viscosity also increases in almost all of the elastomeric composition.

Crosslinking density of magnetorheological composites

Crosslinking density of elastomer vulcanizes containing nano-sized magnetite

The crosslinking density and the concentration of crosslinking nodes disintegrating under ammonia vapor of vulcanizates made of: ethylene-propylene, ethylene-octene, acrylonitrile-butadiene and silicon rubbers filled with nanometeric iron oxide (0-100 phr) are posted in tables 2.5-2.8.

TABLE 2.5
Crosslinking density of EPM vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	$v_e \cdot 10^{-5}$ (T)	$v_e \cdot 10^{-5}$ (T+A)	$\Delta v \cdot 10^{-5}$
0	7,5	4,9	2,6
20	14,9	5,5	9,4
40	17,6	6,3	11,3
60	20,3	9,8	10,5
80	26,3	7,0	19,3
100	29,3	9,8	19,5

v_e - crosslinking density measured in toluene (T) or in toluene with ammonia vapour (T+A),
Δv – non-covalent crosslinking nodes content

TABLE 2.6
Crosslinking density of POE vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	$v_e \cdot 10^{-5}$ (T)	$v_e \cdot 10^{-5}$ (T+A)	$\Delta v \cdot 10^{-5}$
0	3,5	3,2	0,3
40	15,6	10,7	4,9
60	24,3	14,6	9,7
80	31,9	19,7	12,2
100	36,4	24,8	11,6

TABLE 2.7
Crosslinking density of NBR vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	$v_e \cdot 10^{-5}$ (T)	$v_e \cdot 10^{-5}$ (T+A)	$\Delta v \cdot 10^{-5}$
0	6,8	6,4	0,4
20	8,0	6,8	1,2
40	9,0	6,6	2,4
60	11,0	7,4	3,6
80	9,1	6,9	2,2
100	11,8	7,7	4,1

TABLE 2.8
Crosslinking density of MVQ vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	$v_e \cdot 10^{-5}$ (T)	$v_e \cdot 10^{-5}$ (T+A)	$\Delta v \cdot 10^{-5}$
0	8,6	6,1	2,5
60	54,8	27,1	27,7
80	69,3	35,7	33,6
100	80,7	44,4	36,3

Analysis of equilibrium swelling in toluene and toluene with ammonia vapors seem to confirm the results of rheological properties of rubber blends filled with nano-sized magnetite. The presence of the filler resulted in an increase in crosslink density of the composites, which was reflected by an increase in value of the torque gain. As is apparent from the study, regardless of the type of rubber used there is an increase in network density compared to the unfilled systems.

It can be assumed that the change of crosslinking density under the influence of the ammonia is an indirect measure of elastomer - filler interactions. The increase in the value of Δv (for all vulcanizates filled with nanometer magnetite compared to reference samples) may therefore indicate that the interaction at the interface of the elastomer - filler also will increase, which should manifest itself into improved mechanical properties.

Additionally, it is noted that, with the increase of the filler content, there is an increase of network nodes concentration in ethylene-octene and silicone vulcanizates (Table 2.6 and 2.8). Equilibrium swelling studies confirmed the results of the rheological properties of POE/nano-sized magnetite and MVQ/nano-sized magnetite composites - with increasing filler content, also the rheometric torque increased.

Mechanical properties of magnetorheological composites

Obtaining the elastomer composites with improved mechanical properties, may create the opportunity to produce materials with unique functional properties, which can present both scientific and market novelty.

Mechanical properties of elastomeric vulcanizates containing nano-sized iron oxide

The values of the stresses at 100% elongation, tensile strength, elongation at break, thermo-oxidizing (Kterm) and ultraviolet (Kuv) aging factors of: ethylene-propylene, ethylene-octene, acrylonitrile-butadiene, and silicone composites, filled with nano-sized iron oxide (0-100 phr) are shown in Tables 2.9-2.12 and in Figures 2.2.2.1-4.

TABLE 2.9
Mechnical properties of ethylene-propylene vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	**SE_{100} [MPa]**	**TS [MPa]**	**EB [%]**
0	0,9	1,3	324
20	0,9	2,9	675
40	0,9	4,5	655
60	1,0	4,9	654
80	1,1	4,7	668
100	1,2	4,9	695

SE_{100} - stress at 100% elongation,
TS - tensile strength,
EB - elongation at break.

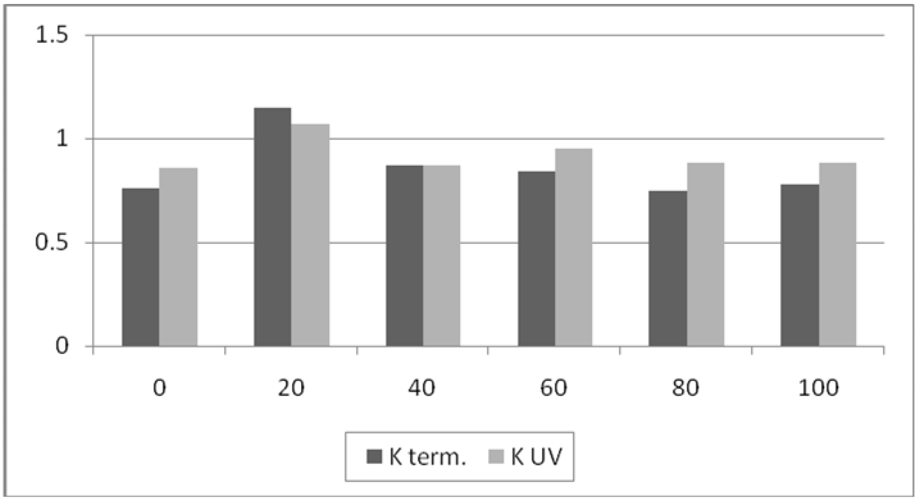

FIGURE 2.1
Aging factors - thermal (K term) and UV (K UV) of ethylene-propylene vulcanizates containing nano-sized magnetite

TABLE 2.10
Mechnical properties of ethylene-octene vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	**SE $_{100}$ [MPa]**	**TS [MPa]**	**EB [%]**
0	2,8	4,9	482
40	2,4	6,2	556
60	3,1	8,0	663
80	3,2	9,8	678
100	3,8	9,9	631

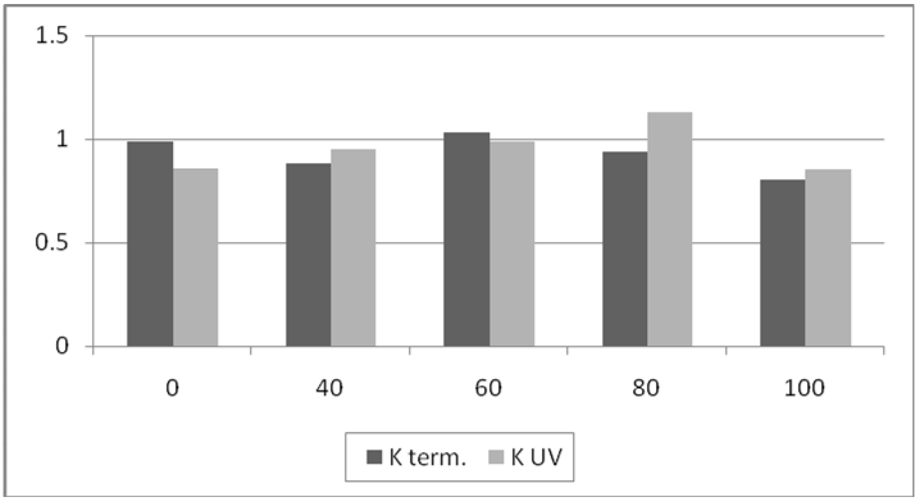

FIGURE 2.2
Aging factors - thermal (K term) and UV (K UV) of ethylene-octene vulcanizates containing nano-sized magnetite

TABLE 2.11
Mechnical properties of acrylonitrile-butadiene vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	**SE$_{100}$ [MPa]**	**TS [MPa]**	**EB [%]**
0	1,5	4,1	394
20	1,2	4,5	563
40	1,5	4,9	504
60	1,7	7,1	507
80	1,7	5,6	528
100	3,0	5,7	308

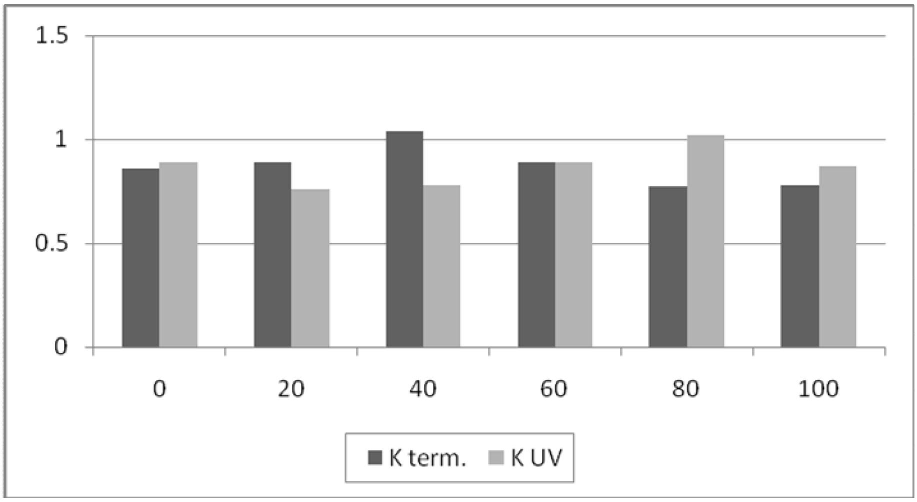

FIGURE 2.3
Aging factors - thermal (K term) and UV (K UV) of acrylonitrile-butadiene vulcanizates containing nano-sized magnetite

TABLE 2.12
Mechnical properties of silicone vulcanizates containing nano-sized magnetite

Nanometric magnetite [phr]	SE_{100} [MPa]	TS [MPa]	EB [%]
0	0,8	2,7	468
60	1,1	4,1	585
80	1,1	4,2	565
100	1,2	3,8	492

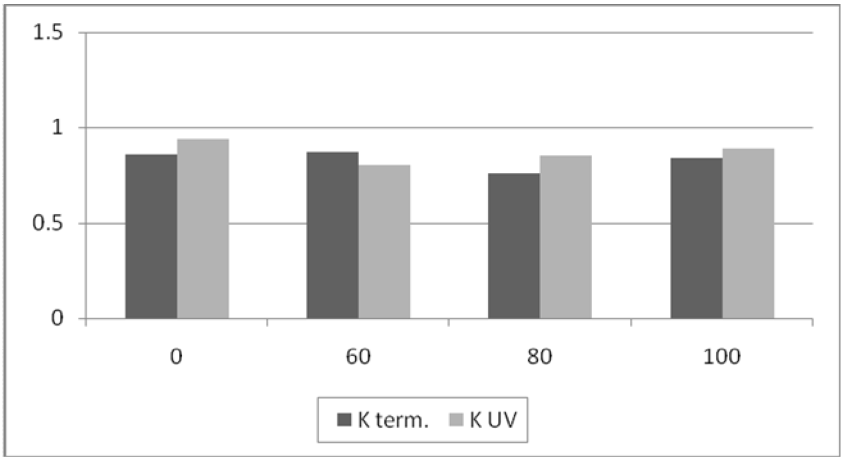

FIGURE 2.4
Aging factors - thermal (K term) and UV (K UV) of silicone vulcanizates containing nano-sized magnetite

Increased activity of nano-sized magnetite manifested by improved mechanical properties of the filled vulcanizates (regardless of the type of rubber) is the confirmation of previous studies about rheological properties and equilibrium swelling of the composites. The improvement of mechanical properties results in an increased stress at 100% elongation and tensile strength of the vulcanizates filled with nano-sized magnetite, compared to the unfilled samples.

In most cases, namely: the vulcanizates of the ethylene-propylene (Table 2.9), acrylonitrile-butadiene (Table 2.11) and silicon (Table 2.12) rubber, the tensile strength increases with increasing amount of filler up to 60 phr in the composite, then decrease in TS values is observed. The reduction in tensile strength is probably associated with the increase in crosslinking density of vulcanizates, especially that it is accompanied by an increase in the module. It seems also possible that as a result of poor dispersion of nanometric iron oxide, elastomers may degrade the mechanical properties. Exceptions are vulcanizates made of POE rubber, wherein with increasing amount of nanometric magnetite SE_{100} and TS values also increased (Table 2.10). In such a state of things in addition to the increased activity of the filler may also affect the stiffness of the polymer chain.

The values of elongation at break oscillate at a similar level and range from 300 - 700%, and always the EB values of unfilled vulcanizates are the lowest.

Very interesting were the results of mechanical properties of composites subjected to the processes of aging. Regardless of the type of rubber and the amount of filler used, all of the vulcanizates proved resistant to both thermo-oxidizing and ultraviolet degradation. This means no effect of aging on the mechanical properties of composites, which may be a positive aspect in terms of usability for this type of materials.

Scanning electron microscopy of magnetorheological composites

SEM images of vulcanizates breakthroughs allow to estimate the distribution of the filler with an elastomer. Provide adequate dispersion of the particles have a substantial impact on the obtained certain properties of composites. Reducing the degree of agglomeration of the filler affects its activity, which can be manifested in improved mechanical properties.

Using SEM images it is also possible to observe the microstructure of magnetic particles in both iso- and anisotropic elastomer composites, which is extremely important for determining magnetic and magnetorheological properties of the vulcanizates. The domain of the anisotropic composite is formation of the characteristic structures of the filler (chain-like), which occurs during crosslinking in the magnetic field. Interactions between ferromagnetic particles in a magnetic field causing them to approach each other and as a result increase the stiffness of the material.

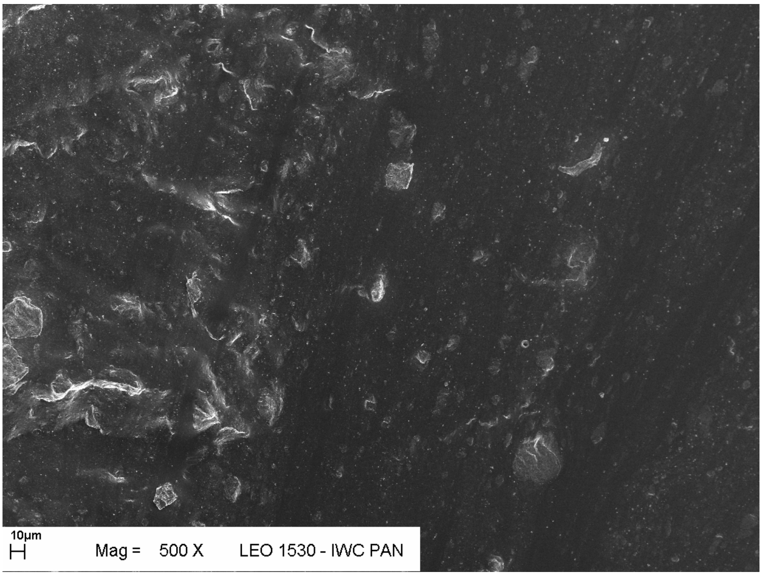

FIGURE 2.5
SEM image of ethylene-propylene vulcanizate containing nanometric magnetite (80 phr)

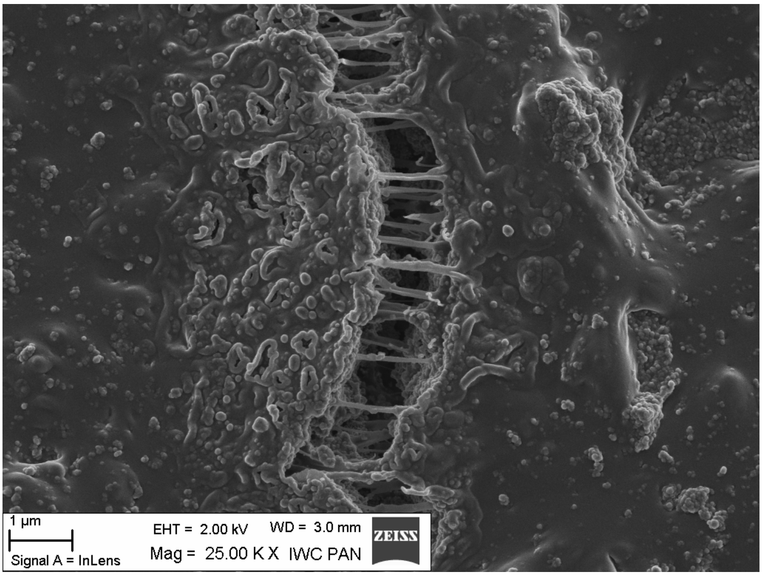

FIGURE 2.6
SEM image of ethylene-octene vulcanizate containing nanometric magnetite (80 phr)

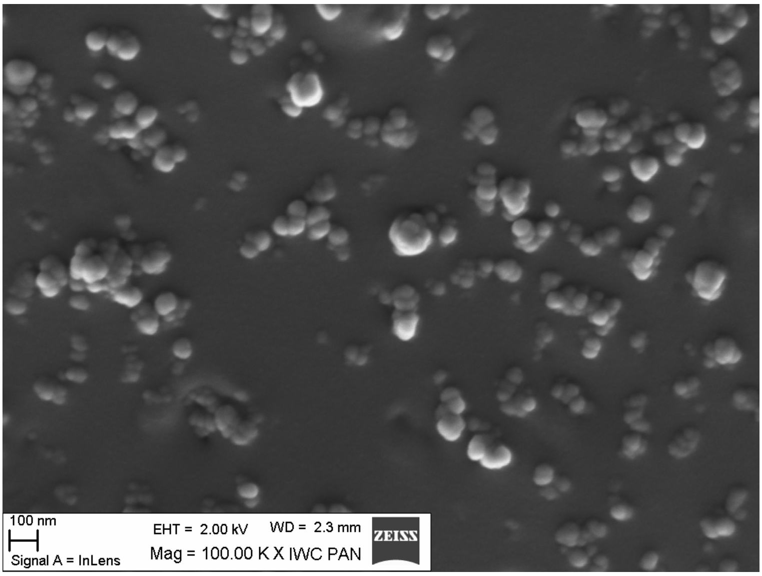

FIGURE 2.7
SEM image of acrylonitrile-butadiene vulcanizate containing nanometric magnetite (60 phr)

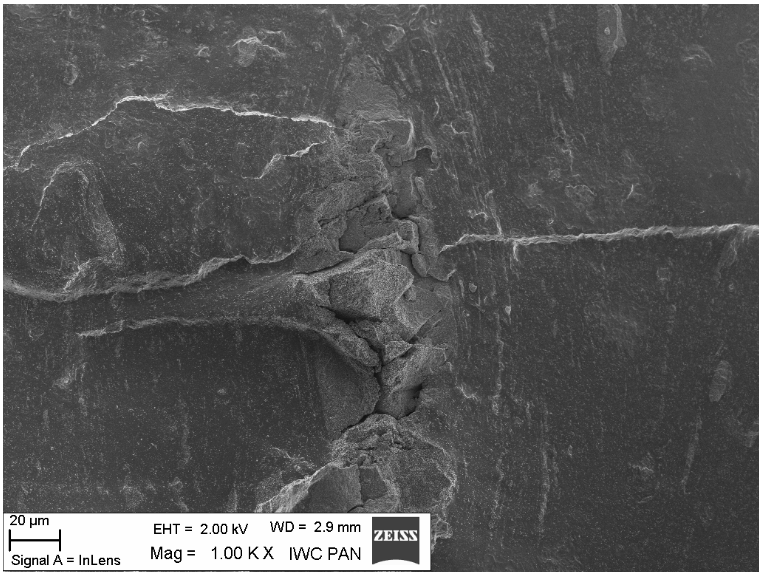

FIGURE 2.8
SEM image of silicone vulcanizate containing nanometric magnetite (100 phr)

Magnetic properties of MRE composites containing nano-sized magnetite

Magnetization hysteresis loops diagrams of MRE vulcanizates as well as the maximum saturation magnetization, remanence and coercivity values of: ethylene-propylene, ethylene-octene, acrylonitrile-butadiene and silicone rubber composites, filled with nanometric magnetite (60 and 100 phr) are presented in the figures 2.9 – 2.12 and table 2.13.

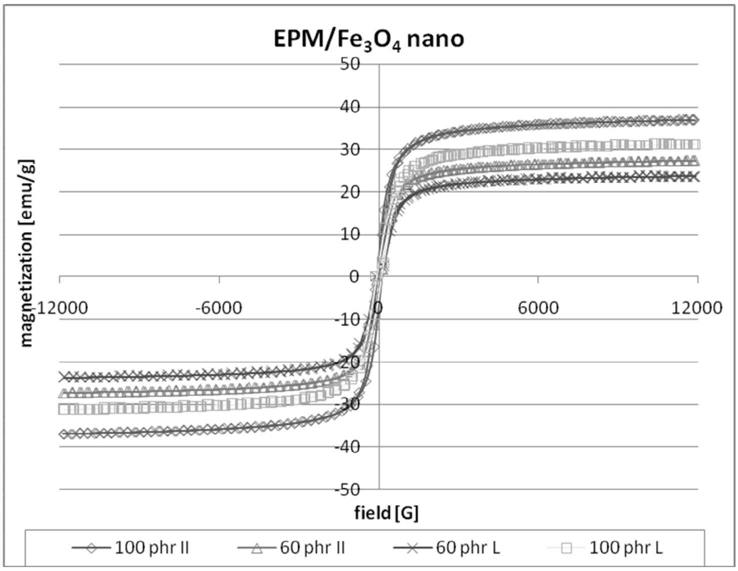

FIGURE 2.9
Magnetization hysteresis loops of ethylene-propylene vulcanizates filled with nanometric magnetite (60 and 100 phr) cured in 1.2 T magnetic field oriented parallel "II" and perpendicular "L" to a sample surface

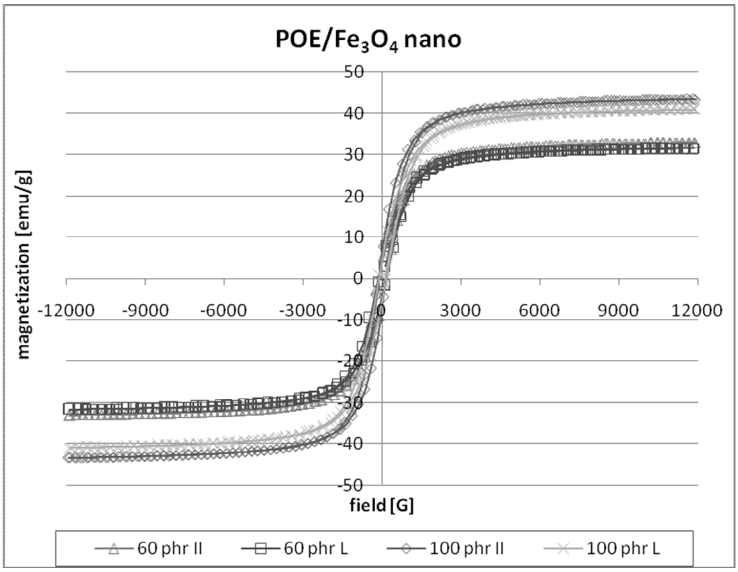

FIGURE 2.10
Magnetization hysteresis loops of ethylene-octene vulcanizates filled with nanometric magnetite (60 and 100 phr) cured in 1.2 T magnetic field oriented parallel "II" and perpendicular "L" to a sample surface

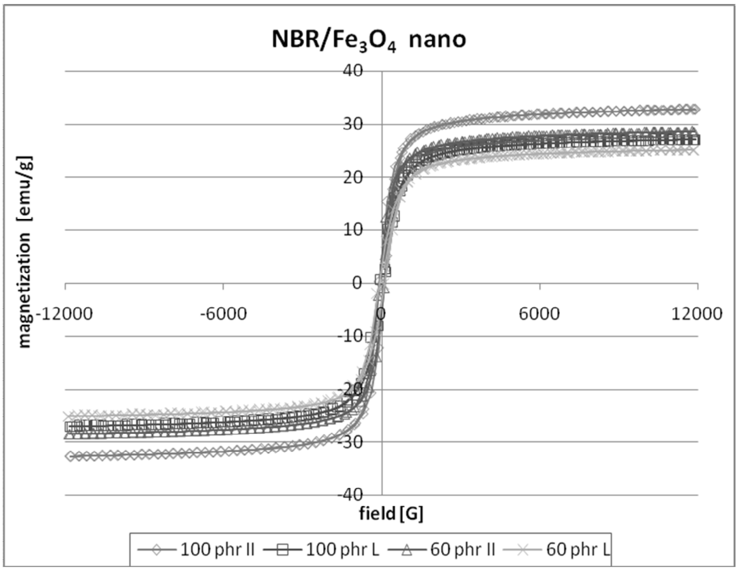

FIGURE 2.11
Magnetization hysteresis loops of acrilonitrile-butadienie vulcanizates filled with nanometric magnetite (60 and 100 phr) cured in 1.2 T magnetic field oriented parallel "II" and perpendicular "L" to a sample surface

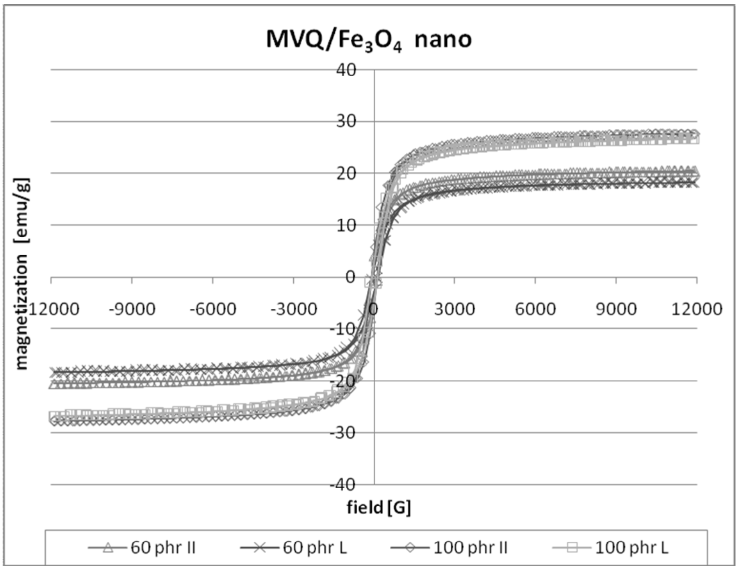

FIGURE 2.12
Magnetization hysteresis loops of silicone vulcanizates filled with nanometric magnetite (60 and 100 phr) cured in 1.2 T magnetic field oriented parallel "II" and perpendicular "L" to a sample surface

TABLE 2.13
Magnetic properties of acrylonitrile-butadiene vulcanizates filled with nano-sized magnetite (60 phr)

Composite	**Coercivity (Hci) [G]**	**Magnetization (Ms) [emu/g]**	**Retentivity (Mr) [emu/g]**
isotropic	26,84	27,27	5,55
anisotropic	23,46	23,14	4,68

High magnetic susceptibility of nano-sized magnetite (about 100 Am^2/kg) causes all vulcanizates exhibit magnetic properties, regardless of the type of rubber. Furthermore, with the increase of the filler content in composites, the maximum magnetization grow. The maximum magnetization values depend on the elastomer type and vary in the range of 18 to 43 emu/g.

The highest values of Ms have been designated for etylene-octene/nanometric magnetite (100 phr) and acrylonitrile-butadiene/nanometric magnetite (100 phr) vulcanizates. This demonstrates the ease of formation of specific chain-like structures in these elastomers.

The values of the magnetization in the case of the magnetic field applied parallel to the sample in each cases was greater than the values received for samples with perpendicular applied field. A similar correlation can also be observed in the case of the coercivity and remanence. This indicates the preferred arrangement of filler particles, thereby facilitating the penetration of the magnetic flux field and as a consequence magnetise the composites. Magnetic anisotropy can also be seen by analyzing the magnetization curves shapes - a steeper curves obtained for the samples cured in magnetic field oriented parallel confirm the specific arrangement of the filler particles in the elastomer.

Magnetic properties comparative characteristics of the ethylene-propylene composites prepared in and without the presence of magnetic field during crosslinking was carried out (Table 2.13). Isotropic

composite has a much lower saturation magnetization compared to the anisotropic vulcanizate, which result from the differences in the microstructure of the filler particles. Moreover, maximum magnetization of an isotropic composite is very close to the Ms value obtained of the anisotropic composite, where magnetic field was oriented perpendicular to the sample surface.
Both the remanence and coercive change in a small range, suitably from 2 to 7 emu/g for Mr and from 20 to 120 G for Hci what classificate obtain vulcanizates as soft magnetic composite materials.

Magnetorheological properties of mre composites containing nano-sized magnetite

Figures 2.13-2.18 present storage (elastic) G’ and loss modulus G’’ change as a function of sample deformation frequency ω (in the field and without the magnetic field) of ethylene-propylene, acrylonitrile-butadiene and silicone vulcanizates containing nanometric iron oxide (60 and 100 phr).

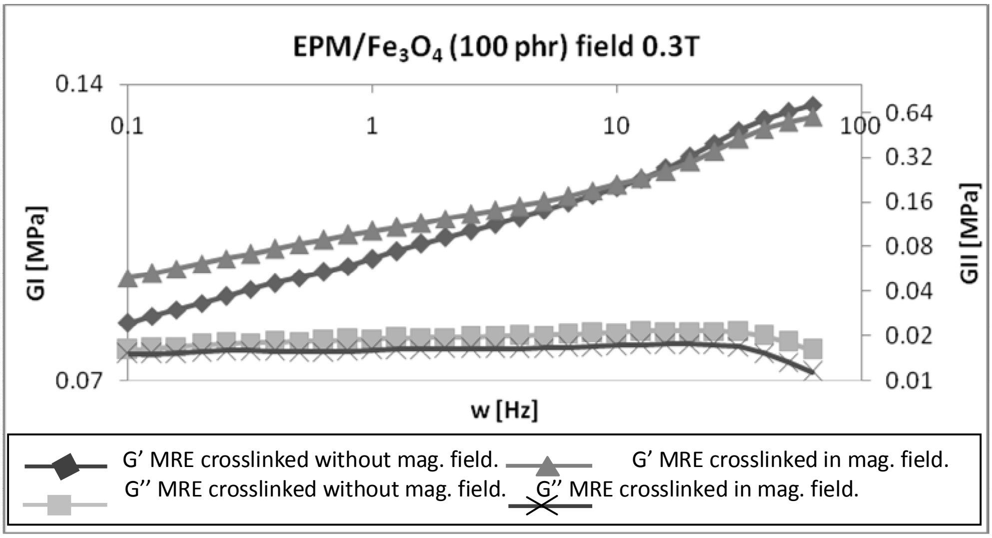

FIGURE 2.13
Dependance of the elastic (storage) modulus (G') and loss modulus (G'') of the MRE composites on deformation frequency (ω)

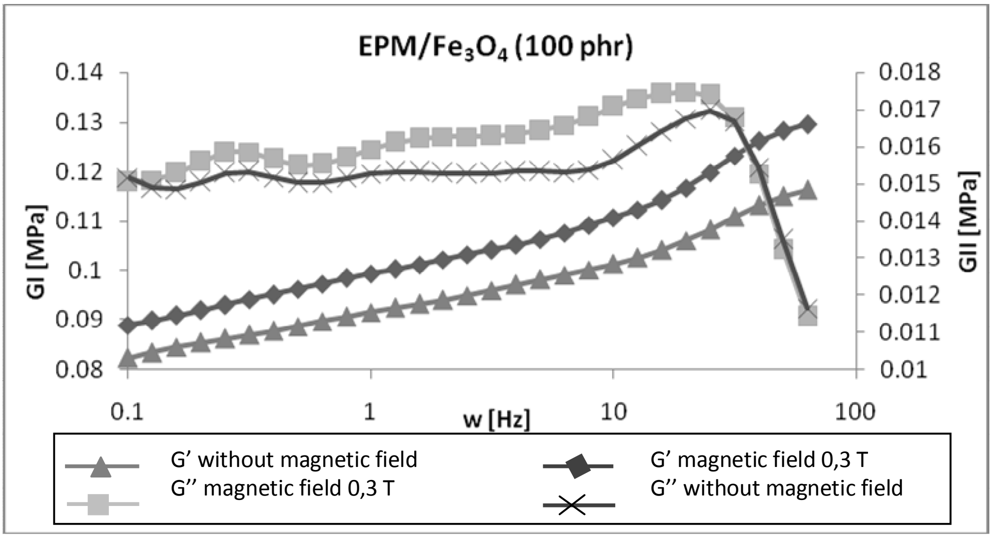

FIGURE 2.14
Dependance of the elastic (storage) modulus (G') and loss modulus (G'') of the MRE composites (crosslinked in the presence of magnetic field) on deformation frequency (ω)

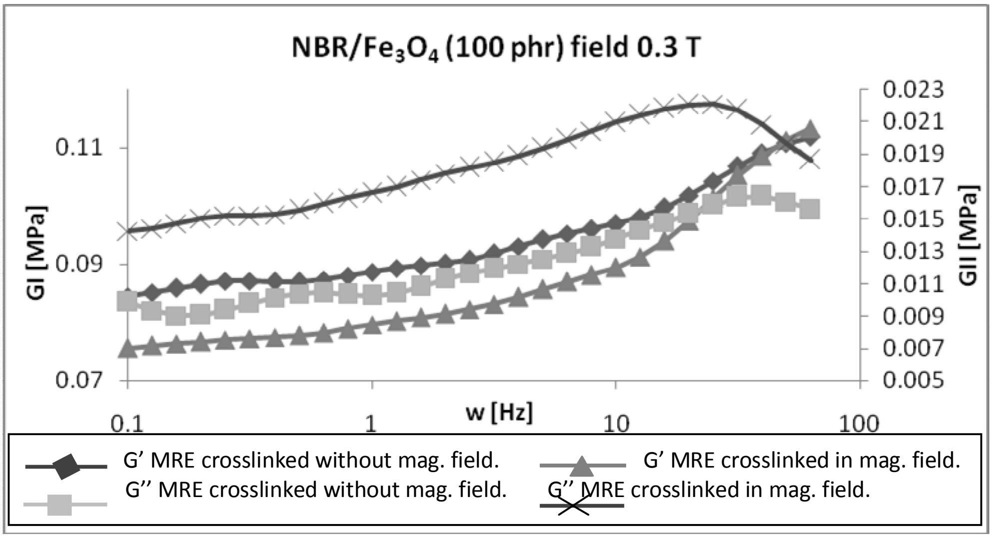

FIGURE 2.15
Dependance of the elastic (storage) modulus (G') and loss modulus (G'') of the MRE composites on deformation frequency (ω)

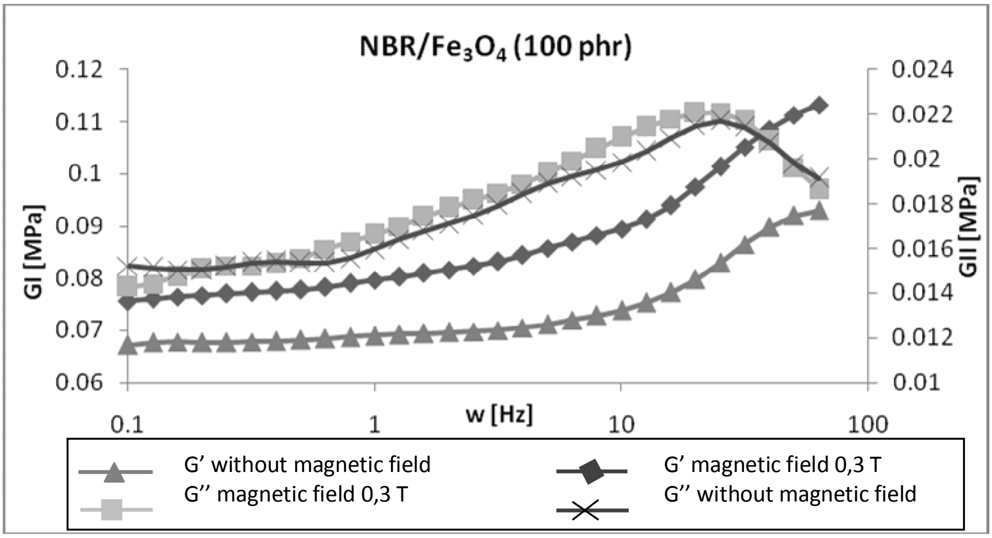

FIGURE 2.16

Dependance of the elastic (storage) modulus (G') and loss modulus (G'') of the MRE composites (crosslinked in the presence of magnetic field) on deformation frequency (ω)

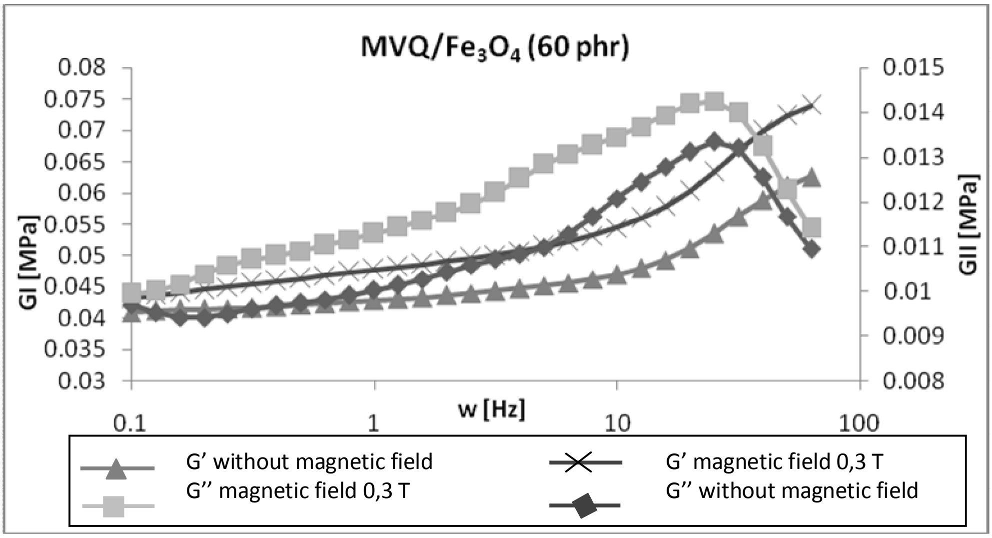

FIGURE 2.17

Dependance of the elastic (storage) modulus (G') and loss modulus (G'') of the MRE composites (crosslinked in the presence of magnetic field) on deformation frequency (ω)

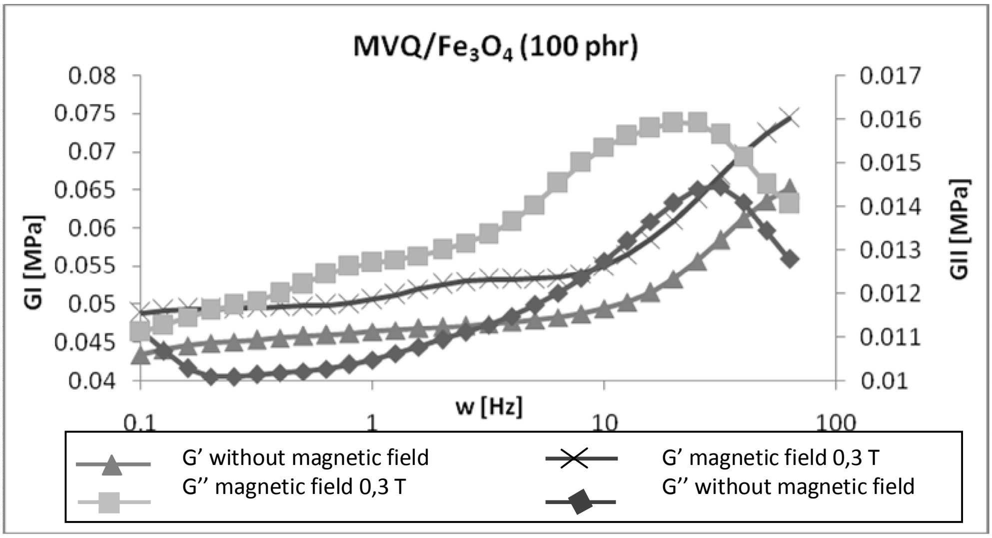

FIGURE 2.18

Dependance of the elastic (storage) modulus (G') and loss modulus (G'') of the MRE composites (crosslinked in the presence of magnetic field) on deformation frequency (ω)

TABLE 2.14

Magnetorheological effect (ΔG') of MRE compostes containing nano-sized Fe_3O_4

Composite	ΔG' [MPa]
EPM/magnetite/100 phr	0,11
NBR/magnetite/100 phr	0,22
MVQ/magnetite/60 phr	0,18
MVQ/magnetite/100 phr	0,14

Based on the changes in storage modulus of iso- and anisotropic composites, magnetorheological effect values have been calculated and summarized in Table 2.14.

The highest magnetorheological effect present composites made of acrylonitrile-butadiene, then silicone and then ethylene-propylene rubber. Analysis of MVQ/nano-sized magnetite systems prove that increasing the amount of filler from 60 to 100 phr, has no effect on increasing the magnetorheological effect. Perhaps this is related to the aggregation of nanoparticles and hence some difficulty to organize a specific chain-like structure.

Values of elastic and storage modules of the samples, for each frequency deformation show large variations with respect to the tested composites. The highest capacity for storage as well as to disperse the deformation energy demonstrate ethylene-propylene rubber. Slightly lower rigidity present acrylonitrile-butadiene and silicone rubber.

Comparative characterization of magnetorheological properties for ethylene-propylene and butadiene-acrylonitrile composites cured in the field and without magnetic field was carried out (Fig. 2.13 and 15). Isotropic composite reaches the lower values of G' and G'' as a function of ω compared to the anisotropic vulcanizate, which is strongly connected to the differences in the microstructure of the filler particles.

Conclusions

The addition of nano-sized iron oxide, regardless of the type of the elastomeric medium (EPM, EPDM, NBR, POE, MVQ) causes an increase of the minimum torque and the increase in torque during curing, relative to the unfilled mixtures. This demonstrates the activity of magnetic filler that create own lattice in the elastomer and an increase of the hydrodynamic effect, which results in greater stress in the elastomer network.

Equilibrium swelling analysis in toluene and toluene with ammonia vapors confirm the results of rheological properties. The presence of the filler resulted in an increase in crosslink density of the composites. Regardless of the type of rubber used there is an increase in network density compared to the unfilled vulcanizates.

The increased activity of magnetite manifests by vulcanizates mechanical properties improvement (regardless of the type of rubber). It is also the confirmation of previous studies about the rheological properties of the composites and equilibrium swelling. Mechanical properties improvement results in an increased stress at 100% elongation and tensile strength of all MRE.

A very interesting from the point of existing scientific data seems to be the mechanical properties analysis of vulcanizates subjected to the processes of aging both thermo-oxidizing and ultraviolet. Nanofiller does not cause deterioration of the mechanical properties of vulcanizates, as evidenced by the values of the aging factors oscillating around unity, regardless of the type of rubber.

Nano-sized magnetite forms a characteristic filler particles paths, which are able to convey a higher stress compared to the "regular" composites. After application of a magnetic field such composites exhibit greater rigidity.

High susceptibility of nano-sized magnetite (about 100 Am2/kg) causes all vulcanizates exhibit magnetic properties, regardless of the type of rubber. Very essential during the study was to focus the magnetic flux - parallel or perpendicular to the sample surface, and hence to the filler particles in the elastomer matrix arranged in order to achieve adequate magnetic anisotropy. The method used: cross-linking in a magnetic field causes the preferred orientation of ferromagnetic materials (chain-like structures) and thus improve the magnetic properties of composites. Regardless of the type of composite, there are observed differences in the magnetization hysteresis curves, due to the different arrangement of the magnetic flux. The magnetic flux directed parallel to the sample surface and therefore to the particles filler chain, result in increasing the saturation magnetization of the composites. Magnetic anisotropy can also be seen by analyzing the shape of magnetization curves - a steeper curves, support the hypothesis of a specific arrangement of the filler particles in the elastomer. Composites of ethylene propylene rubber filled with nanometer magnetite, non-activated in magnetic field have a much lower saturation magnetization compared to the anisotropic vulcanizates.

All vulcanizates exhibit magnetorheological properties. Composites activated in the magnetic field reaches much higher values of G 'and G'' as a function of ω as compared to vulcanizates crosslinked without the field. It is the result of a specific (columnar) orientation of filler particles in the elastomer. The theory about improved magnetorheological properties of anisotropic composites compared to isotropic is confirmed.

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