Magnetorheological materials based on ethylene-octene elastomer

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Abstract: Magnetorheological elastomer composites based on several magnetoactive fillers such as: carbonyl iron powder, gamma iron oxide, micro- and nano-sized Fe_3O_4 in ethylene-octene elastomer are reported and studied. To improve the dispersion of the applied fillers in a polymer matrix, ionic liquids were added during the process of composite preparation. To align the particles in the elastomer, the crosslinking process took place in a magnetic field. The effect of the amount of ferromagnetic particles and their arrangement on the microstructure and properties in relation to the external magnetic field was examined. It was found that the microstructure isotropy and anisotropy has a significant effect on the properties of the magnetorheological elastomers. Moreover, different amounts of magnetoactive fillers influence the mechanical properties (increase the tensile strength) of the composites compared to unfilled samples. The magnetic flux directed parallel to the sample surface increases the saturation magnetization of the composites. Magnetic anisotropy can also be seen by analyzing the shape of magnetization curves — steeper curves obtained for anisotropic samples support the hypothesis of a specific arrangement of the filler particles in the elastomer. The addition of ionic liquids improve the dispersion of the applied magnetoactive fillers (CIP and γ-Fe_2O_3) in the elastomer matrix, which in turn favorably affected the network density, tensile properties and magnetorheological effect of the composites.

Keywords: magnetorheological elastomers, magnetic fillers, ethylene-octene elastomer, microstructure, ionic liquids, magnetic properties, magnetorheological properties, smart materials.

Magnetoreologiczne materiały na bazie elastomeru etylenowo-oktenowego

Streszczenie: Wytworzono magnetoreologiczne kompozyty elastomerowe (MRE) na bazie kopolimeru etylenowo-oktenowego z udziałem napełniaczy magnetoaktywnych: żelaza karbonylkowego (CIP), tlenku żelaza gamma (γ-Fe_2O_3), mikro- lub nanometrycznego tlenku żelaza (Fe_3O_4). W celu zwiększenia stopnia zdyspergowania zastosowanych napełniaczy do układu dodawano różne ciecze jonowe. Kompozyty sieciowane pod wpływem pola magnetycznego wykazywały silną anizotropię cząstek napełniaczy spowodowaną ich specyficznym ułożeniem w matrycy elastomerowej. Stwierdzono, że dodatek napełniaczy magnetycznych wpływa na poprawę właściwości mechanicznych kompozytów; nastąpiło zwiększenie wytrzymałości na rozciąganie wulkanizatów w porównaniu z wytrzymałością próbek nienapełnionych. Stwierdzono również, że strumień magnetyczny ukierunkowany równolegle do powierzchni próbek, a tym samym do łańcuchów cząstek napełniaczy, powoduje zwiększenie magnetyzacji nasycenia kompozytów. Zastosowane ciecze jonowe z grupy soli alkiloamoniowych zwiększają stopień zdyspergowania magnetyków w matrycy elastomerowej, co wpływa na ich większą aktywność. W konsekwencji, napełniacze tworzą rozbudowaną strukturę w elastomerach. Dodatek cieczy jonowych wpływa także na zwiększenie gęstości sieci przestrzennej, poprawę właściwości wytrzymałościowych oraz na wielkość efektu magnetoreologicznego kompozytów.

Słowa kluczowe: elastomery magnetoreologiczne, napełniacze magnetyczne, elastomer etylenowo-oktenowy, mikrostruktura, ciecze jonowe, właściwości magnetyczne, właściwości magnetoreologiczne, materiały inteligentne.

Magnetorheological (MR) materials belong to a class of functional and smart materials whose rheological properties can be changed continuously, rapidly and reversibly by an applied magnetic field. Since the first discovery by Rabinow in 1948 [1], magnetorheological materials have attracted considerable interests in both indus-

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trial and academic areas. They include three categories: MR fluids, MR elastomers, and MR foams [2].

MR fluids (MRFs) are a kind of colloidal suspension that can change their phase between liquid and solid under the control of a magnetic field. They are composed of oil with low permeability and micrometer sized ferrous particles. When a MR fluid is exposed to a magnetic field, the ferrous particles are magnetized and attracted by each other to form chains and columns in the direction of the external magnetic field, and the phase changes to solid. When it is sheared under a stress above its yield stress, it will show characteristics of the liquid phase again and the yield stress is determined by the external magnetic field. When the external field is removed, it will recover its liquid phase [3]. Over the past two decades, MR fluids have been applied as dampers, brakes and engine mounts [3]. However, MRFs also exhibit some shortcomings, such as deposition, environmental contamination and sealing problems, which hinder useful applications of MRFs.

MR elastomers (MREs), the structural solid analogues of MRFs, may be a good solution to overcome the disadvantages of MRFs. The physical properties of MR elastomers are very similar to those of MR fluids. However, the particle chains within the elastomer composite are intended to operate in the pre-yield regime, whereas MR fluids typically operate within a post-yield continuous shear or flow regime [2]. Thus, a typical MRE consists of viscoelastic materials, powdery solids (metals), and viscous liquids. The MR effect of MREs is described as a reversible change in modulus in an applied magnetic field [4]. This has been confirmed in several studies in terms of both anisotropic (*e.g.* Wang *et al.* [5]; Danas *et al*. [6], Rudykh *et al*. [7]) and isotropic (*e.g.* Kaleta *et al*. [8]; Lu *et al.* [9]) MREs. Conventional methods to prepare MREs under an external magnetic field have many shortcomings, *e.g.* conventional rubber-producing equipment must be modified to provide a magnetic field during crosslinking, thick MREs cannot practically be performed because the magnetic flux density will decrease sharply as the thickness of the MRE increases, the chain direction of the anisotropic MRE must be considered when it is to be used in a particular device. However, according to current research, anisotropic MREs have a much larger MR effect than isotropic MREs [2]. There have also been attempts undertaken to prepare isotropic MREs without external fields. As a result of magnetic particle addition with high particle volume concentration, the absolute MR effect in the isotropic MR rubbers is larger than that previously reported. However, these materials with such high iron particle concentrations have a high zero-field modulus, which is why the relative MR effect is low [2].

Due to their properties, ferromagnetic composites with an elastomer matrix have already found many applications, for example in tunable vibration absorbers and damping components (*e.g.* [10], noise barrier system and sensors [11, 12]). The capability of fast, reversible, and large deformation has made these materials promising candidates for next-generation actuators or artificial muscles (*e.g.* [13, 14]). The large, field-induced volumetric strain of a porous magneto-active polymer may also be used in drug delivery systems [15].

Deagglomeration means breaking filler agglomerates in rubber. The pace of this process is affected both by the viscosity of the elastomer mixture and size of agglomerates. It is very hard to achieve completely deagglomerated filler in rubber. The magnetic [16], thermodynamic [17] and catalytic [18] properties of nanoparticles, as well as many other properties, largely depend on their size. Nanoparticles of metals have a typical tendency to reduce their very high surface energy, which is a manifestation of their thermodynamic instability. They are susceptible to mutual stabilization by sorption of molecules from the environment or by a reduction in surface energy as a result of coagulation, aggregation and agglomeration. It is exactly to prevent such processes that the nanoparticles must be kinetically stabilized [19]. The literature points to three main concepts for stabilization: electrostatic, steric and a combination thereof. The idea aimed at using strongly charged adsorbents in the stabilization of nanoparticles, instead of neutral stabilizers, leads to electrostatic stabilization. The best nanoparticle stabilizers are ionic ones, strongly adsorbing, which fit the concept of surface and electrostatic stabilization at the same time. Ionic liquids (ILs) provide surplus ions favorable for coordination. Strong coordination is required in the case of applications such as catalysis, where access of substrate molecules to the metal surface is required. It must be added that nanoparticles with strongly adsorbing ligands can be isolated from the stabilizers and isolated as a powder, owing to which a stabilizing layer on the surface is sustained [20].

Analysis of the literature clearly indicates that, with the same volume share of particles, MREs with anisotropic microstructure are characterized with a much greater magnetorheological effect than MREs with isotropic particle distributions. However, there are some doubts, raised by information on the impact of the microstructure of magnetic particles on the MR effect of isotropic elastomers. Moreover, a review of the literature data clearly stresses the importance of particle dispergation, which significantly affects the properties of smart materials, including their mechanical or magnetorheological properties. Metal particles reveal an intensified tendency to aggregate and agglomerate, which has an unfavorable impact on the properties of elastomer composites, principally with regards their mechanical properties. Their stabilization is necessary [21]. The addition of ionic liquids may prove effective in the context of counteracting aggregation and agglomeration of ferrofiller particles. These are the major objectives of our research.

The studies presented here involve the development of MREs based on several different magnetoactive fillers in new, non-polar, ethylene-octene elastomer, which also present good ageing resistance. The addition of ionic liquids can improve the dispersion of applied magnetoactive fillers in elastomer matrices. The influence of the number of ferromagnetic particles and their arrangement in relation to the external magnetic field was investigated. Scanning electron microscopy was used to observe MRE microstructure. The particles' orientation and their arrangement in both iso- and anisotropic composites were also investigated with a vibrating sample magnetometer (VSM).

EXPERIMENTAL PART

Materials

Engage polyolefin elastomer: ethylene-octene copolymer was produced by DOW Chemical Company USA [comonomer octene content: 25 wt %, ML (Mooney Viscosity) (1+4) at 121 °C: 35, crystallinity: 27 %]. Crosslinking agent: dicumyl peroxide DCP (purity: 98 %) was obtained from Sigma-Aldrich. Fillers: gamma-iron(III) oxide (γ-Fe_2O_3) — average particle size of 650 nm, magnetite (Fe_3O_4) both micro- and nano- size (av. particle size of 1100 nm for micro-sized and 450 nm for nano-sized magnetite) were obtained from Sigma-Aldrich, carbonyl iron powder (CIP) — av. particle size of 3100 nm, was purchased from BASF. Ionic liquids: 1-ethyl-3-methylimidazolium diethylphosphate (EMIMDEP), 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$), 1-hexyl-3-methylimidazolium chloride (HMIMCl), 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM OTf), 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$), trihexyltetradecylphosphonium chloride (HPCl) and 1-butyl-3-methylimidazolium chloride (BMIMCl) were supplied by Sigma-Alrdich.

The composition of a typical elastomer mixture: ENGAGE copolymer — 100 phr, DCP — 2 phr, ionic liquid — 3 phr, fillers (CIP, γ-Fe_2O_3, micro- and nano-sized Fe_3O_4) — 40—100 phr.

Sample preparation

Elastomer mixtures, based on ethylene-octene copolymer filled with micro- and nano- size iron oxides (Fe_3O_4), carbonyl iron powder (CIP) and gamma-iron oxide (γ-Fe_2O_3) were prepared in a Brabender measuring mixer N50 (temp. 50 °C, rotor speed range 40 min^{-1}, time of the process 10 min). Then, the mixtures were cured at 160 °C, at 15 MPa pressure for 30 min. To align the magnetic particles in the elastomer matrix, crosslinking was carried out in the presence of a magnetic field produced by high temperature resistant samarium-cobalt magnets. The magnetic properties of the magnets: retentivity: 1100— 1200 mT, normal coercivity (bH_{ci}): 438—517 kA/m, intrinsic coercivity (jH_{ci}): 454—597 kA/m, maximum energy stored within the magnet (BH_{max}): 223—255 kJ/m^3.

Methods of testing

— The mechanical properties were examined by static materials testing machine Zwick, according to ISO 37 standards.

— The network density of cured samples was calculated based on rapid solvent-swelling measurements (in toluene) using the Flory-Rehner equation (elastomer-solvent interaction parameters, $\mu_0 = 0.478$, $\beta = 0.404$ — calculated in the Institute of Polymer and Dye Technology).

— The magnetic properties of the samples were measured with vibrating sample magnetometer VSM Lakeshore 7410, in the range of the field up to 960 kA/m.

— Magnetorheological properties were studied with the application of an ARES Rheometer (plate-plate system, plate diameter, 20 mm; gap 2 mm; magnetic field range, 0—300 mT). Magnetorheological effect (ΔG, MPa) values of the composites were calculated based on the equation (1).

$$\Delta G = \frac{G(H) - G(H=0)}{G(H=0)} \tag{1}$$

where: $G(H)$ — a composite storage modulus determined under a magnetic field strength equal to 0.3 T (measured at the highest frequency of sample deformation ω = 60 Hz), $G(H=0)$ — a composite storage modulus determined without the magnetic field (measured at the highest frequency of sample deformation ω = 60 Hz).

— Microstructure observations were carried out using a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Magnetic properties of MRE

The orientation of particles and their arrangement were investigated by VSM. Studies of the magnetic properties of the MREs were conducted parallel and perpendicular (corresponding to the magnetic field direction during curing) to the sample long axis. Four different types of composites were investigated. ENGAGE/CIP (60 phr) and ENGAGE/γ-Fe_2O_3 (60 phr), all containing ionic

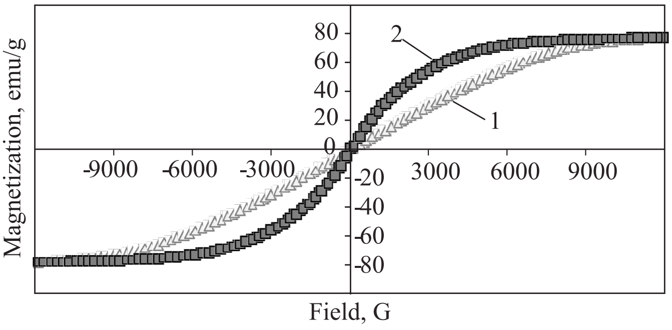

Fig. 1. Magnetic properties — hysteresis curves of MRE samples — ENGAGE/CIP cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

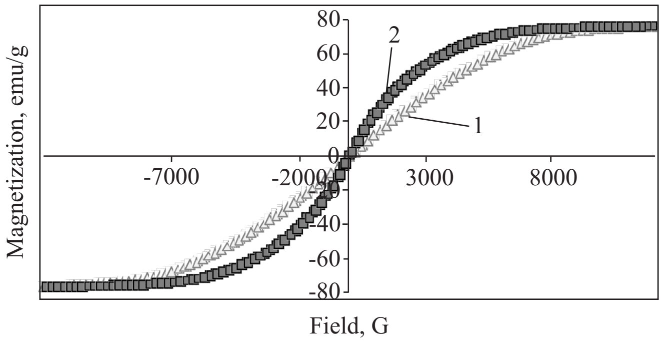

Fig. 2. Magnetic properties — hysteresis curves of MRE samples — ENGAGE/CIP (60 phr)/HPCl cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

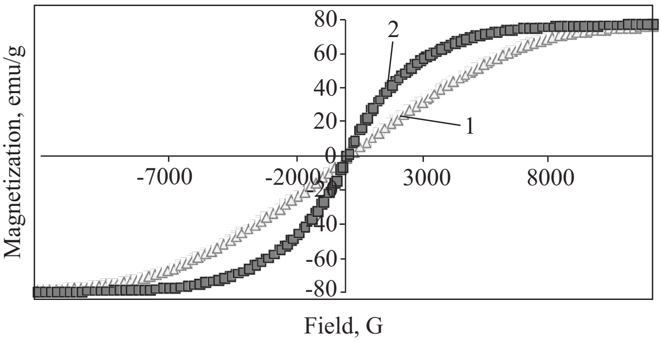

Fig. 5. Magnetic properties — hysteresis curves of MRE sample — ENGAGE/CIP (60 phr)/BMIMPF$_6$ cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

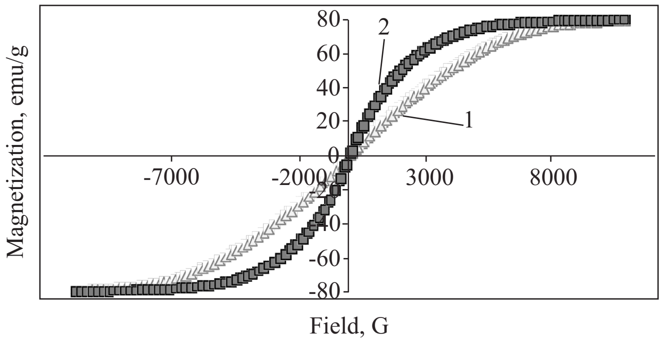

Fig. 3. Magnetic properties — hysteresis curves of MRE sample — ENGAGE/CIP (60 phr)/HMIMCl cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

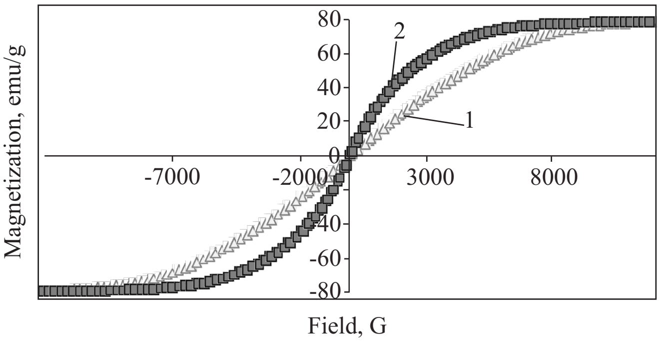

Fig. 6. Magnetic properties — hysteresis curves of MRE sample — ENGAGE/CIP (60 phr)/BMIM Otf cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

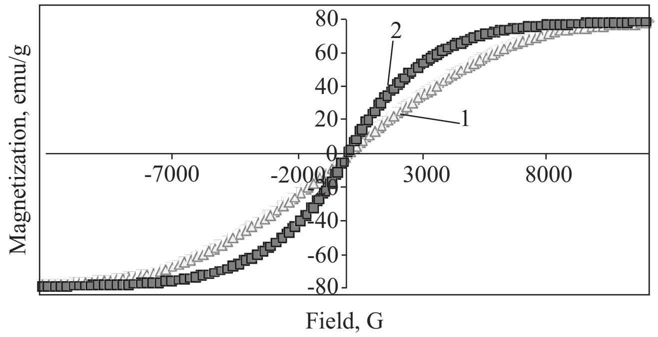

Fig. 4. Magnetic properties — hysteresis curves of MRE sample — ENGAGE/CIP (60 phr)/BMIMCl cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

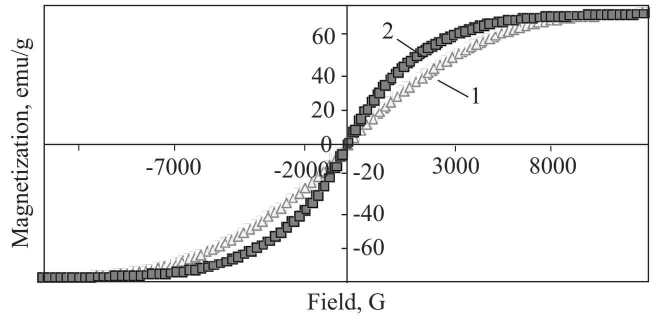

Fig. 7. Magnetic properties — hysteresis curves of MRE sample — ENGAGE/CIP (60 phr)/EMIMDEP cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

liquids added as dispersing agents (3 phr). ENGAGE/micro-sized Fe_3O_4 (60 phr) and ENGAGE/nano-sized Fe_3O_4 (60 phr) without addition ionic liquids, for comparison with other systems.

Examinations of ENGAGE/CIP/ILs systems confirmed that all composites were found to be anisotropic (Figs. 1—9). Significant differences (even 20 emu/g at *ca.* 5000 G — ENG/CIP/BMIMPF$_6$) occur between individual hysteresis curves of MRE samples cured with and without the use of an external magnetic field. This is undeniably due to the strong anisotropy of ferromagnetic particles and their arrangement in the elastomer matrix. Remanence values for all prepared composites filled with carbonyl iron powder vary from 0.2 to 0.7 emu/g, regardless of magnetic field direction. Coercivity values obtained for the MREs with CIP particles vary from 20 to 22 G,

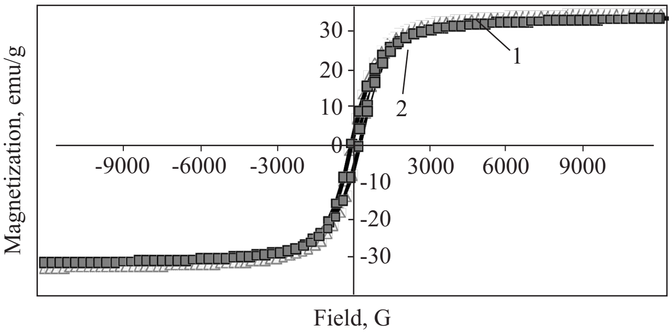

Fig. 8. Magnetic properties — hysteresis curves of MRE sample — ENGAGE/Fe_3O_4 micro (60 phr) cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

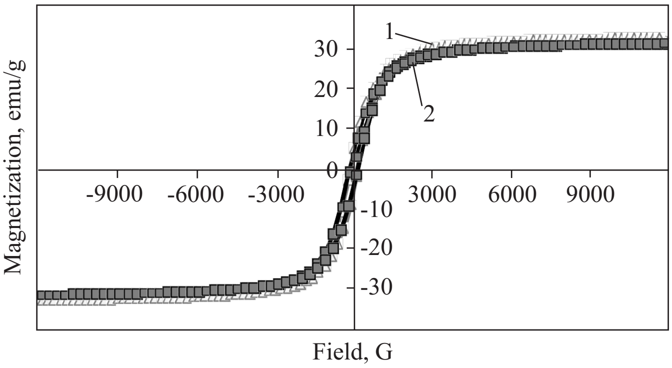

Fig. 9. Magnetic properties — hysteresis curves of MRE sample — ENGAGE/Fe_3O_4 nano (60 phr) cured under magnetic field of 1.2 T applied parallel or perpendicular to the sample long axis; 1 — perpendicular, 2 — parallel

indicating magnetically soft materials. Analysis of ENGAGE/γ-Fe_2O_3/ILs systems proved that all composites are isotropic. Differences between the magnetisation saturation (M_s) for samples examined in a parallel and perpendicular magnetic field were insignificant (less than 0.4 emu/g). Thus Table 1 collects individual values for several magnetic characteristics — M_s, M_r, H_c. Cured samples with γ-Fe_2O_3 were found also to be magnetically soft materials, with a coercivity field from 98 to 106 G. The addition of ionic liquids did not cause diametrical changes in the magnetic properties of cured ethylene-octene elastomer composites containing gamma iron oxide or CIP — all samples represent very good magnetic properties. The maximum magnetization of all cured samples remains at the same level regardless of the type of dispersant.

As expected, composites without the addition of ionic liquids: ENGAGE/micro-sized Fe_3O_4 (60 phr) and ENGAGE/nano-sized Fe_3O_4 (60 phr) exhibit magnetic characteristics. They present a slightly anisotropic nature as evidenced by the differences in the maximum magnetization.

High magnetic susceptibility of used fillers: micro- and nano-sized magnetite (100 Am^2/kg), gamma iron oxide (80 Am^2/kg) and carbonyl iron (200 Am^2/kg) causes all cured samples to exhibit magnetic properties. The higher the magnetic susceptibility of magnetic materials, the better the magnetic properties of the composites.

Mechanical properties and crosslinking density of MRE

The influence of different magnetoactive filler particles (micro- and nano-sized Fe_3O_4, γ-Fe_2O_3 and CIP) in the crosslinking of ethylene-octene elastomers was estimated based on the mechanical properties (tensile strength and elongation at break) and network density of cured samples. The results are given in Tables 1 and 2 and Fig. 10. From the compiled data, it follows that applying ferromagnetic fillers considerably increased the tensile strength of ENGAGE composites. Concerning micro- and nano-sized Fe_3O_4, tensile strength increases at least 2 times in each case, independent of the filler content in the 60—100 phr range, compared to unfilled system. The best mechanical properties characterize cured samples with 60 phr of microsized magnetite. As far as the tensile

Table 1. Network density, mechanical and magnetic properties of cured ethylene-octene copolymer composites containing γ-Fe_2O_3 and ionic liquids

γ-Fe_2O_3, phr	Ionic liquid	$\nu_e \cdot 10^5$, mol/cm³	TS_b, MPa	E_b, %	H_c, G	M_s, emu/g	M_r, emu/g
0	—	3.22	4.87 (±0.18)	482	—	—	—
60	—	4.01	5.14 (±0.22)	432	102.4	24.5	4.0
100	—	4.52	5,71 (±0.16)	375	109,1	30,1	4.1
60	HPCI	4.58	6.92 (±0.33)	455	103.8	25.0	4.0
60	HMIMCI	4.42	5.62 (±0.14)	410	101.0	24.9	4.2
60	BMIMCI	4.63	5.99 (±0.25)	418	103.1	24.8	4.2
60	$BMIMPF_6$	5.41	5.16 (±0.20)	331	98.4	24.5	4.0
60	EMIMDEP	4.91	5.18 (±0.28)	370	101.9	25.3	4.3
60	BMIM Otf	5.26	4.94 (±0.16)	322	104.5	25.1	4.2

ν_e — network density, TS_b — tensile strength, E_b — elongation at break, H_c — coercivity, M_s — magnetization, M_r — retentivity of the composites.

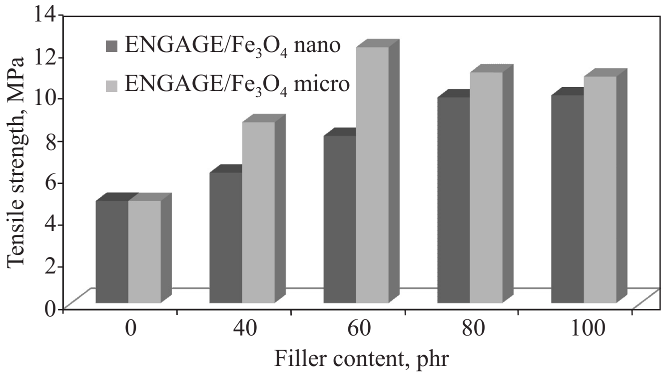

Fig. 10. Tensile strength (TS_b) of ENGAGE vulcanizates containing nano- or micro-sized Fe_3O_4 with the given phr contents

strength of composites is concerned, tensile strength values increase until 80 phr of iron oxides are reached. Due to mechanical properties, 60—80 phr of iron oxides were found to be the optimal filler content.

T a b l e 2. Network density and mechanical properties of cured ethylene-octene copolymer composites containing carbonyl iron powder and ionic liquids

CIP, phr	Ionic liquid	$\nu_e \cdot 10^5$ mol/cm^3	TS_b, MPa	E_b, %
0	—	3.22	4.87 (±0.18)	482
60	—	18.0	6.02 (±0.22)	376
100	—	31.2	4.69 (±0.26)	475
60	HPCI	24.8	10.6 (±0.33)	412
60	HMIMCI	27.4	7.1 (±0.19)	414
60	BMIMCI	34.8	9.1 (±0.15)	427
60	BMIMPF$_6$	27.4	8.4 (±0.36)	464
60	EMIMDEP	26.9	10.6 (±0.32)	422
60	BMIM Otf	32.6	9.0 (±0.29)	485

The influence of ionic liquids on the ability of γ-Fe_2O_3 and CIP powders particles in the crosslinking of ENGAGE elastomers was estimated based on the tensile properties and network density of cured samples. From the results given in Table 1 and 2 it follows that the application of ionic liquids, together with γ-Fe_2O_3 and CIP particles, increased the tensile strength of the composites compared to those produced without ionic liquids as dispersing agents. Applying ILs also favorably affected the network density of the MREs. The calculated values confirmed that all of the applied ionic liquids increased cross-link density, the most effective dispersing agents were 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM Otf) for composites filled with γ-Fe_2O_3 and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$) and 1-butyl-3-methylimidazolium chloride (BMIMCl) for composites filled with carbonyl ion powder. In the case of the ENGAGE/CIP/ILs system it is worth noting a significant increase in the value of tensile strength for composites containing ionic liquids compared to a reference sample. This demonstrates the effective impact of the use of the dispersants. It is likely that the chosen ionic liquids improve the dispersion of the magnetic fillers, which in turn increases their activity and translates into a reinforcing effect.

Magnetorheological properties of MRE

The elastic (storage) modulus *G′* and loss modulus *G″* of ethylene-octene composites containing ionic liquids γ-Fe_2O_3 or CIP were measured as a function of angular frequency ω under magnetic field (Figs. 11—16). The storage modulus *G′* represents the ability of the viscoelastic material to store the energy of deformation, which contributes to the material stiffness. The loss modulus *G″* represents the ability of the material to dissipate the energy of deformation. The influence of chain-like structures on the rheological properties was investigated with an external magnetic field of 0.3 T and without applied magnetic

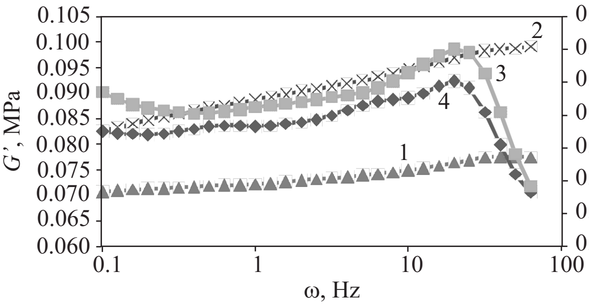

Fig. 11. Dependence of the elastic (storage) modulus (*G′*) and loss modulus (*G″*) of MRE sample — ENGAGE/γ-Fe_2O_3 (60 phr) (crosslinked in the presence of magnetic field) as a function of deformation frequency (ω); 1 — *G′* without magnetic field, 2 — *G′* magnetic field 0.3 T, 3 — *G″* magnetic field 0.3 T, 4 — *G″* without magnetic field

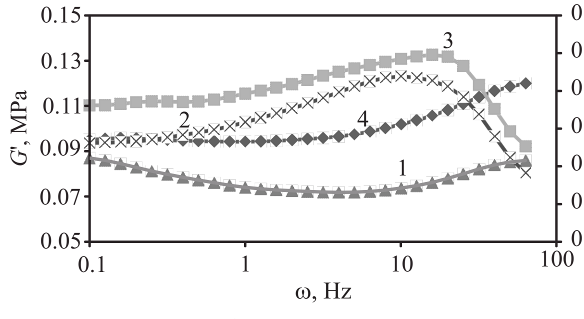

Fig. 12. Dependence of the elastic (storage) modulus (*G′*) and loss modulus (*G″*) of MRE sample — ENGAGE/γ-Fe_2O_3 (crosslinked in the presence of magnetic field) as a function of deformation frequency (ω); 1 — *G′* without magnetic field, 2 — *G′* magnetic field 0.3 T, 3 — *G″* magnetic field 0.3 T, 4 — *G″* without magnetic field

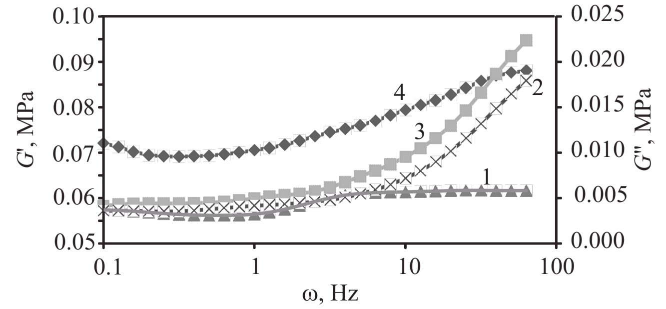

Fig. 13. Dependence of the elastic (storage) modulus (*G′*) and loss modulus (*G″*) of MRE sample — ENGAGE/γ-Fe$_2$O$_3$/BMIMPF$_6$ (crosslinked in the presence of magnetic field) as a function of deformation frequency (ω); 1 — *G′* without magnetic field, 2 — *G′* magnetic field 0.3 T, 3 — *G″* magnetic field 0.3 T, 4 — *G″* without magnetic field

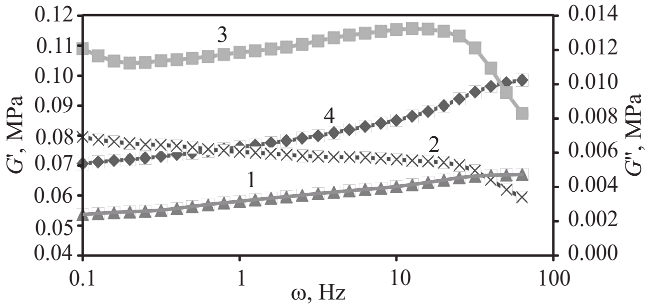

Fig. 15. Dependence of the elastic (storage) modulus (*G′*) and loss modulus (*G″*) of MRE sample — ENGAGE/CIP/HMIMCl (crosslinked in the presence of magnetic field) as a function of deformation frequency (ω); 1 — *G′* without magnetic field, 2 — *G′* magnetic field 0.3 T, 3 — *G″* magnetic field 0.3 T, 4 — *G″* without magnetic field

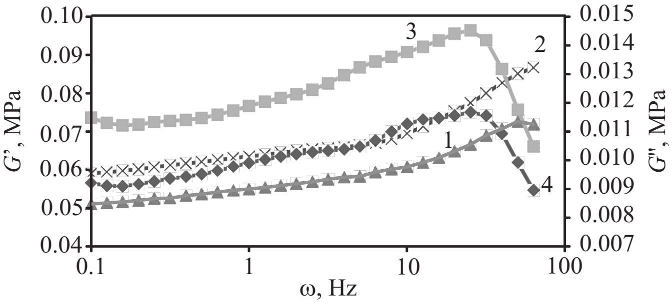

Fig. 14. Dependence of the elastic (storage) modulus (*G′*) and loss modulus (*G″*) of MRE sample — ENGAGE/CIP (60 phr) (crosslinked in the presence of magnetic field) as a function of deformation frequency (ω); 1 — *G′* without magnetic field, 2 — *G′* magnetic field 0.3 T, 3 — *G″* magnetic field 0.3 T, 4 — *G″* without magnetic field

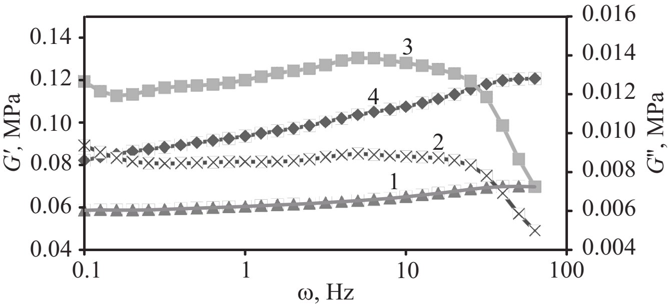

Fig. 16. Dependence of the elastic (storage) modulus (*G′*) and loss modulus (*G″*) of MRE sample — ENGAGE/CIP/BMIMPF$_6$ (crosslinked in the presence of magnetic field) as a function of deformation frequency (ω); 1 — *G′* without magnetic field, 2 — *G′* magnetic field 0.3 T, 3 — *G″* magnetic field 0.3 T, 4 — *G″* without magnetic field

field. As expected, all cured samples exhibit magnetorheological properties. The elastic modulus increased with strain frequency no matter what kind of magnetoactive filler and ionic liquid was used. Similarly, the same behavior, with smaller intensity, occurs when analyzing the loss modulus as a function of strain frequency. Higher initial values of the storage modulus for composites containing carbonyl iron powder indicate more appropriate alignment in the elastomer matrix and larger magnetic susceptibility. It should be mentioned that the differences between *G″* values recorded for MREs containing the remaining fillers were insignificant.

All values of storage *G′* and loss *G″* modulus of the composites measured under the influence of magnetic field are greater than those without applied magnetic field which indicates the occurrence of the magnetorheological effect. Tables 3 and 4 contain a comparison of MR effect values for each composite. It is worth noting that

Table 3. Magnetorheological effect of cured composites ENGAGE/γ-Fe$_2$O$_3$ (60 phr)/ILs with different ionic liquids

Composite	Δ*G*, MPa
ENGAGE/γ-Fe$_2$O$_3$	0.28
ENGAGE/γ-Fe$_2$O$_3$/HPCl	0.31
ENGAGE/γ-Fe$_2$O$_3$/BMIMCl	0.18
ENGAGE/γ-Fe$_2$O$_3$/HMIMCl	0.40
ENGAGE/γ-Fe$_2$O$_3$/BMIM Otf	0.34
ENGAGE/γ-Fe$_2$O$_3$/BMIMPF$_6$	0.43
ENGAGE/γ-Fe$_2$O$_3$/EMIMDEP	0.28

Table 4. Magnetorheological effect of cured composites ENGAGE/CIP (60 phr)/ILs with different ionic liquids

Composite	Δ*G*, MPa
ENGAGE/CIP	0.21
ENGAGE/CIP/HPCl	0.17
ENGAGE/CIP/BMIMCl	0.39
ENGAGE/CIP/HMIMCl	0.47
ENGAGE/CIP/BMIM Otf	0.35
ENGAGE/CIP/BMIMPF$_6$	0.68
ENGAGE/CIP/EMIMDEP	0.29

the addition of HMIMCl improved the MR effect of ENGAGE/CIP systems two times and the addition of $BMIMPF_6$ by more than 3 times. Moreover, the addition of the same ionic liquids also caused an increase in the value of $\Delta G'$ for the composites filled with gamma iron oxide. Furthermore, the addition of BMIM Otf or EMIMDEP also improved the magnetoreheological effect. It appears that the improvement in the magnetorheological properties of cured samples could affect the positive effect of ionic liquids as carbonyl iron and γ-Fe_2O_3 dispersing agents. Probably, better carbonyl iron powder dispersion led to an increased amount of characteristic columnar structures that can be observed in the SEM image of the composites, which manifested itself in improved MR characteristics. It can also be clearly seen from Fig. 19 that the addition of HMIMCl, as a representative of the selected ionic liquids for isotropic ENGAGE/γ-Fe_2O_3 systems, improves the dispersion of the filler.

Morphology and microstructure of MRE

It is well known that the microstructure anisotropy has a significant effect on the properties of magnetorheological elastomers. Moreover, the dispersion of magnetoactive filler particles in the elastomer matrix has a significant effect on the activity of carbonyl iron powder and gamma iron oxide and their influence on cured samples properties [22]. Scanning electron microscopy was used to observe and to describe magnetorheological elastomer microstructures (Figs. 17—19).

A magnetorheological fluid operates on the principle that the magnetic particles are randomly distributed in the liquid when no magnetic field is applied, but the particles acquire a magnetic polarization and form chains in the presence of a magnetic field of sufficient strength. If the elastomer, with suspended ferromagnetic particles, is cured in the presence of a magnetic field, the magnetisable particles will form chains along the direction of the magnetic field prior to the elastomer cross linking process (curing), and anisotropic MRE is started. The addition of selected ionic liquids improve the dispersion of the applied magnetic filler particles in elastomer, which resulted in higher tensile strengths, crosslink densities and MR effects of the composites.

CONCLUSIONS

MRE composites were prepared according to the commonly used methods. It was found that micro- and nanosized iron oxides, carbonyl iron oxide, and gamma iron oxide were active fillers improving the mechanical properties of new, non-polar, ethylene-octane elastomer (the

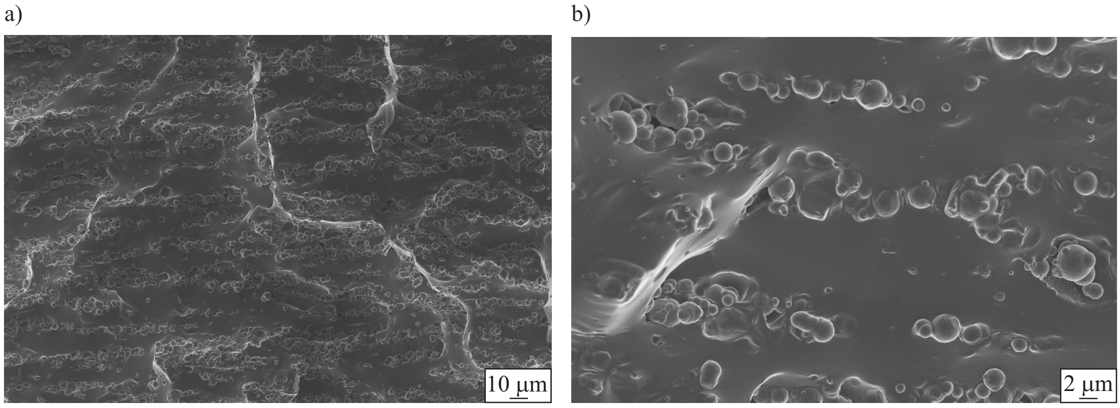

Fig. 17. SEM images of composites ENGAGE/CIP (60 phr)/EMIMDEP: a) magnification 1000×, b) magnification 5000×

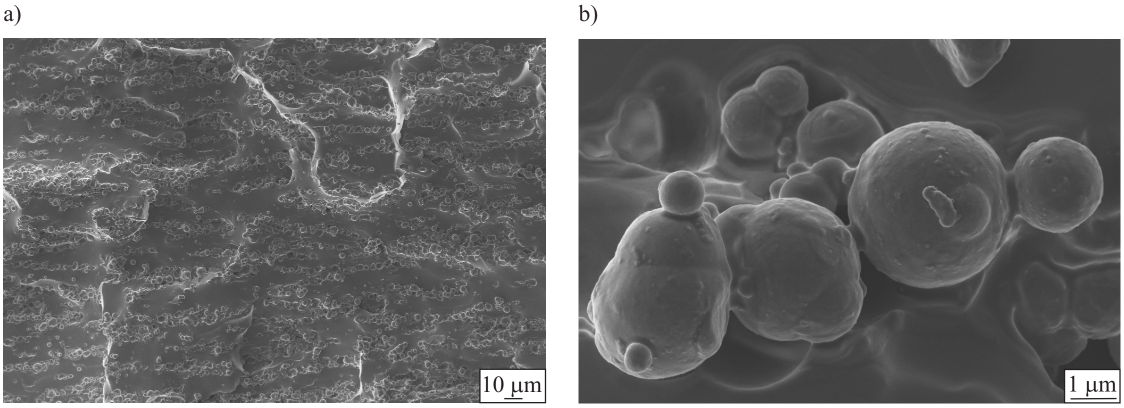

Fig. 18. SEM images of composites ENGAGE/CIP (60 phr)/BMIM Otf: a) magnification 1000×, b) magnification 25000×

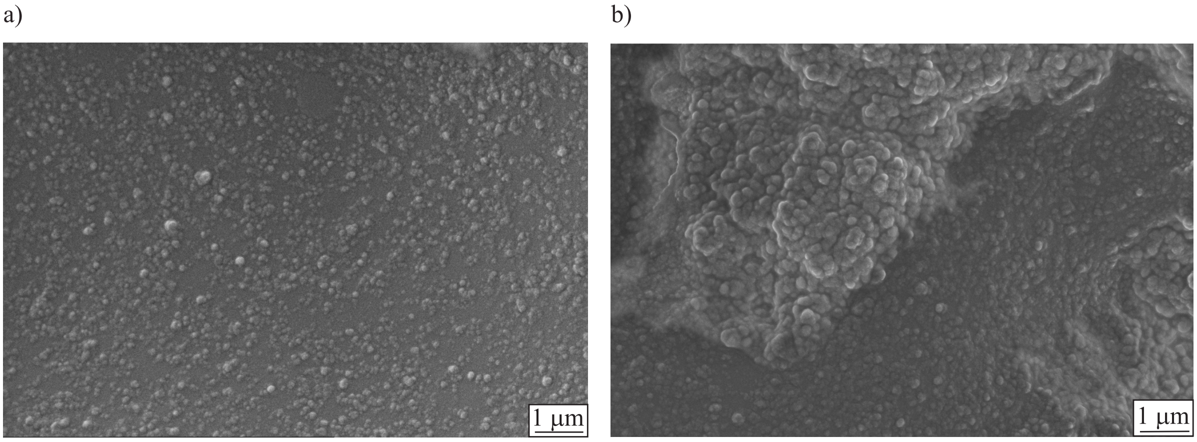

Fig. 19. SEM images of composites: a) ENGAGE/γ-Fe_2O_3 (60 phr), magnification 25000×, b) ENGAGE/γ-Fe_2O_3 (60 phr)/HMIMHCl, magnification 25000×

highest values of tensile strength characteristics being cured samples with 60 phr of microsized magnetite). They also changed their magnetic properties and reinforced the magnetorheological effects of the ENGAGE composites. Examinations of ENGAGE/CIP/ILs systems confirmed that all cured samples were anisotropic, in contrast to ENGAGE/γ-Fe_2O_3/ILs composites, which present isotropic characteristics.

The dispersion of carbonyl iron powder and gamma iron powder in the elastomer matrix can be improved by using selective ionic liquids as dispersing agents. Scanning electron microscopy images used to observe magnetorheological elastomer microstructures proved that the improvement in dispersion had a significant effect on the composite properties, especially magnetorheological. Moreover, it confirmed the anisotropic character of ENGAGE/CIP/ILs cured samples. The application of ionic liquids with γ-Fe_2O_3 and CIP particles increased the tensile strength of all prepared composites compared to those produced without ionic liquids as dispersing agents. Applying ILs also favorably affected the network density and magnetorheological effect of the MREs.

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