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Magnetorheological Elastomers Containing Ionic Liquids

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1. Introduction

The term ionic liquid (IL) refers to a class of liquids that are composed solely of ions¹. It is a synonym for molten salt. IL in a narrow sense often indicates room-temperature ionic liquid (RIL) that exists as a liquid at room temperature.

Ionic liquids (ILs), which have been widely promoted as “green solvents”, are attracting much attention for applications in many fields of chemistry and industry due to their chemical stability, thermal stability, low vapour pressure and high ionic conductivity properties². In recent years, ILs have been used in polymer science, mainly as polymerisation media in several types of polymerisation processes, including conventional free radical polymerisation³, living/controlling radical polymerisations (such as atom transfer radical polymerisations (ATRP), reversible addition-fragmentation transfer (RAFT))⁴, and ionic and coordination polymerisations⁵. When radical polymerizations are conducted in an IL, a significant increase of the k_p/k_t ratio is normally observed compared radical polymerizations conducted in other polar/coordinating solvents. As solvents for ATRP and RAFT, ILs facilitate the separation of the polymer from residual catalyst and reduce the extent of side-reactions. Applications of ILs as solvents for polymerisation processes have been reviewed by Kubisa⁶ and Shen and Deng⁷. However, application of ILs in polymer science are not limited to traditional polymerisation media. ILs have also been investigated as components of polymeric matrixes (such as polymer gels), as templates for porous polymers and as novel electrolytes for electrochemical polymerisations. This review focuses on recent developments and applications of ILs in the preparation of functional polymers.

There is much current interest in ionic liquids. The much lower melting points of ionic liquids compared to those of inorganic salts can be partially attributed to the bulky cationic groups, i.e., the low charge density and incompatibility of the Coulombic attraction forces with steric hindrance. Ionic liquids have very low vapour pressures, although it was recently shown that they are distillable⁸. Therefore, they do not produce hazardous vapors (in contrast to many conventional organic solvents). Most ionic liquids have high ignition points, and they do not generate explosive air-vapour mixtures. They can act as solvents for chemical reactions, including catalytic reactions⁹.

As a result of their interesting physical-chemical features ionic liquids have been extensively evaluated as environmentally friendly or “green” alternatives¹⁰ to conventional organic solvents for a broad range of organic synthetic applications. In addition, ionic liquids have

been used, *e.g.*, as catalysts¹¹ in organic synthesis, in compositions for stabilising and/or isolating nucleic acids in or from micro-organisms¹², as process aids for the synthesis of polynucleotides¹³, as lubricants¹⁴ in the preparation and stabilisation of nanoparticles¹⁵ and in the synthesis and stabilisation of metal¹⁶ and metal oxide nanoparticles¹⁷.

It is common practice to use dispersing agents to homogeneously stabilise fillers and pigments in liquid media and to obtain storage stable pigment pastes, paints and lacquers. According to the state of the art, dispersing agents have to fulfil the following requirements:

- Easy incorporation of fillers and pigments, which leads to shorter dispersing times and, allows for the use of simpler and cheaper dispersing aggregates (a dissolver instead of ball mills).
- Reduction of the pigment paste viscosity, which allows for high pigment loading and economical tinting systems.
- Development of optimal colour strength, *i.e.*, of the optimal hiding power when using opaque pigments.
- Avoidance of sedimentation in pigment pastes when stored over long periods of time or under extreme climatic conditions.
- Avoidance of flocculation for good reproducibility of colours, which is becoming particularly important when using mixing machines for the tinting of white base paints and lacquers.

These requirements have to be independently fulfilled regardless of the liquid medium into which a filler or a pigment must be dispersed. Hence, there has been no lack of attempts to develop polymeric dispersants¹⁸ with truly universal applicability. Additionally, a good dispersant wets and stabilises not only inorganic but also organic pigments exhibiting both hydrophilic and hydrophobic surfaces. Most modern polymeric dispersants are universal for pigments, but not for the surrounding medium. Generally, a pigment in a solvent-based liquid medium (hydrophobic) is only sterically stabilized, whereas a pigment in a water-based medium (hydrophilic) can be both sterically and electronically stabilized, depending on the presence of the appropriate functional groups in the polymeric dispersant (electrosteric stabilisation)¹⁹.

Magnetorheological fluids (MRFs) are dispersions of micrometre-sized (from 1 to 20 μm) magnetic particles in a carrier fluid, whose rheological behaviour can be controlled by means of a magnetic field²⁰. Thus, MRFs can change from a liquid to a solid-like state and vice versa almost instantaneously. MRFs have been used in various technological applications since their first preparation²¹. Current fundamental research on MRFs focuses mainly on the settling of dispersed magnetic particles (and redispersion phenomena), which may restrict their use in specific applications²². To overcome the problem of sedimentation, several strategies have been proposed (*e.g.*, the addition of thixotropic agents, surfactants, and nanoparticles; the use of viscoplastic media as carriers; and polymeric core/shell-structured magnetic particles)²³. The sedimentation problem in MRFs is of such importance that it has even been investigated (together with other properties) under microgravity conditions in outer space²⁴. A very recent study reports on the rheological behaviour of suspensions of hematite nanoparticles in an IL²⁵. On one hand, it was found that concentrated suspensions of nanoparticles show non-Newtonian characteristics, including shear thinning and shear thickening, which probably originate from particle-particle interactions. On the other hand, suspensions with a low content of nanoparticles show Newtonian behaviour similar to that shown by pure ILs. However, this study does not provide any information about the magnetorheological behaviour of the suspensions

and/or the influence of the structure of the ILs on the stability of the suspensions against sedimentation. It has also been reported recently that ILs can be used as stabilising agents in different heterogeneous systems²⁶. For these reasons, it is thought that the use of ILs as carriers of MRFs may lead to magnetic dispersions that are colloidally stable (against flocculation) and which offer an improved stability against sedimentation (in this report the term 'stability' is used in reference to sedimentation unless otherwise indicated).

Magnetorheological elastomers (MREs) are smart materials whose rheological properties can be changed by applying external magnetic field²⁷. They are solid analogues of magnetorheological fluids (MRFs). MRE and MRF consist of micro- or nano- sized particles of iron compounds dispersed in an elastomer matrix²⁸. The size of magnetically polarisable particles has a great influence on the stress of magnetorheological materials. It is well known from the literature²⁹ that the aggregation of magnetic particles results in local anisotropy and dispersion irregularity, which drastically diminishes the magnetic and magnetorheological effects of materials. Therefore, it is evident that the best magnetorheological effect can be achieved by improving the dispersion stability. As in the case of MR fluids, magnetoactive particles attempt to arrange themselves in the direction of an applied magnetic field³⁰. Ferromagnetic composites with an elastomer matrix are characterised by unique properties that are not characteristic of bulk magnetic materials. These properties, among others, are a high susceptibility to elastic strains in the magnetic field and the dependence of the magnetic permeability on stress. An interesting and useful property of the composites described is the change of their elasticity coefficients and other material parameters in a sufficiently high magnetic field. Due to their properties, ferromagnetic composites with an elastomer matrix have already found many applications, for example, in sensors, converters and controlled vibration dampers.

2. Materials and methods

2.1 Materials

Acrylonitrile-butadiene rubber ((NBR) - Europrene N3960, acrylonitrile unit content: 28 %) was purchased from Lanxess, and ethylene-propylene rubber ((EPM) Dutral CO 054, propylene unit content: 40 %) was obtained from Montedison Ferrara. Crosslinking agents: dicumyl peroxide DCP (Aldrich), triallyl-1,3,5-triazine-2,4,6(1H,3H,5H) TAC (Aldrich), zinc oxide ZnO (Huta Będzin), mercaptobenzothiazole MBT (Pneumax MBT) and sulphur S₈ (Z.P.S. Siarkopol).

Fillers: magnetite (Fe₃O₄), both micro- and nano- sized, were obtained from Sigma Aldrich, and carbonyl iron powder CIP was provided by BASF.

Ionic liquids: 1-ethyl-3-methylimidazolium diethylphosphate EMIMDEP, 1-butyl-3-methylimidazolium hexafluorophosphate BMIMPF₆, 1-hexyl-3-methylimidazolium chloride HMIMCl, 1-butyl-3-methylimidazolium trifluoromethanesulfonate BMIM OTf, 1-butyl-3-methylimidazolium tetrafluoroborate BMIMBF₄, trihexyltetradecylphosphonium chloride HPCL, and 1-butyl-3-methylimidazolium chloride BMIMCl were supplied by Aldrich.

Composition of a typical elastomer mixture: rubber - 100 phr, DCP - 2 phr, TAC - 0.5 phr, ZnO - 5 phr, MBT - 2 phr, S - 2 phr, Ionic liquids - 3 phr, filler 20-100 phr.

2.2 Methods

Elastomer mixtures, based on EPM or NBR filled with micro- and nano- sized iron oxides and carbonyl iron powder were prepared by common manufacturing procedures for rubber.

Magnetoactive particles were mixed with the rubber and vulcanisation system using two – roll mills at 30 °C. The injection and stirring of ionic liquids into the elastomer composites were performed in a Brabender measuring mixer N50 (temp. 50 °C, speed range 40 min⁻¹, time of the process 10 min). Then, the mixtures were vulcanised at 160 °C 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 particle size of the aggregates in water and paraffin oil and the zeta potential of the dispersions were measured with a Zetasizer nano S90 and Zetasizer nano 2000 respectively.

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/C-04216 standards. An ultraviolet ageing process was performed with UV2000 equipment (Atlas).

3. Influence of ionic liquids on the characteristic of magnetoactive fillers

3.1 Aggregate size of magnetoactive fillers

The particle size of ferromagnetic particles is a main parameter that has a great influence on the properties of magnetorheological composites. A reduction in the particle size results in an increase in the specific surface area of magnetoactive particles, providing better contact between the crosslinking agent particles and the elastomer chains. Moreover, the morphology of the filler particles determines the size of the interphase between the magnetoactive fillers and the elastomer. The sizes of the nanometric and micrometric Fe₃O₄ and carbonyl iron powder aggregates in water and in paraffin oil with and without the addition of ionic liquids are presented in Tab. 1-3. The morphologies of the magnetorheological elastomer composites are presented in Section 4.4 “Scanning Electron Microscopy Images”.

The sizes of the aggregates of the fillers were measured in water and in paraffin oil. Elastomers have a hydrophobic nature; therefore, the size of the magnetic particles was measured in a liquid hydrophobic medium-paraffin oil, which was chosen as the model for an elastomer matrix. The aim of this study was to estimate the tendency of particles to agglomerate in the elastomer. In all cases, the magnetoactive fillers particles exhibited a higher ability for aggregation or agglomeration in paraffin oil than in water. As expected nanometric Fe₃O₄ presented the smallest aggregate size (695 nm) measured in water in contrast to carbonyl iron powder, which showed the greatest aggregate size (3151 nm). Nearly the same situation was observed in paraffin oil. According to the assumptions of the work on the stabilisation of particles, ionic liquids were added together with ferroparticles to the water and oil dispersions, which led to decrease of the aggregate size no matter what type of the filler was used, *e.g.*, micrometric magnetite aggregates in water decreased from 695 nm (without IL) to 213 nm (with IL), nanometric magnetite aggregates from 1188 nm to 632 nm and CIP from 3151 nm to 429 nm. Magnetic filler aggregates size measured in paraffin oil were even more spectacular *e.g.*, for CIP, it decreased from 11210 nm to 3283 nm.

Ionic liquid	Aggregate size in water [nm]	
	Micrometric Fe ₃ O ₄	Nanometric Fe ₃ O ₄
-----	1188	695
BMIMBF ₄	940	812
BMIM OTf	1035	625
BMIMCl	632	552
EMIMDEP	790	543
HMIMCl	799	606
HPCl	690	213

Table 1. The micro and nanometric Fe₃O₄ aggregate sizes measured in water containing ionic liquids.

Ionic liquid	Aggregates size in paraffine oil [nm]	
	Micrometric Fe ₃ O ₄	Nanometric Fe ₃ O ₄
-----	4411	4916
BMIMBF ₄	1141	2247
BMIM OTf	5061	4249
BMIMCl	4080	2678
EMIMDEP	5438	5007
HMIMCl	2622	2453
HPCl	6744	7340

Table 2. The micro and nanometric Fe₃O₄ aggregate sizes measured in paraffin oil containing ionic liquids.

Ionic liquid	Aggregates size in water [nm]	Aggregates size in paraffine oil [nm]
	Carbonyl Iron Powder	
-----	3151	11210
BMIMBF ₄	1106	3283
BMIM OTf	4122	4907
BMIMCl	2695	10100
EMIMDEP	2801	8247
HMIMCl	3031	3432
HPCl	429	9615

Table 3. The carbonyl iron powder aggregate size measured in paraffin oil and water containing ionic liquids.

3.2 The electrokinetic potential (ζ - zeta) for water magnetoactive fillers suspensions

The zeta potential is an electrokinetic potential measured on the surface of a particle in solution. A charged surface results in the formation of an electric double layer, and the zeta potential is the potential between the charged surface and the electrolyte solution³¹. The zeta potentials of water-magnetoactive filler (nanometric Fe_3O_4 , micrometric Fe_3O_4 , carbonyl iron powder) suspensions containing ionic liquids were examined versus pH (Fig. 1-3). From the zeta potential measurements, the isoelectric points (IEP) of water dispersions were determined. The IEP is the pH value at which the zeta potential is zero. It is not a description of the absolute basicity or acidity of solid surface but a description of their relative strength. A high IEP value indicates that the surface shows more basic functionality compared with its acidic functionality. On the contrary, a low IEP surface reveals less basic functionality compared with its acidic functionality³². IEP is mainly related to the Brønsted acid and base definitions. The higher IEP corresponds to stronger affinity to protons. However, IEP is also a measure of the Lewis acidity or basicity because, when the oxide surface adsorbs a proton, the electron (or electron density) is transferred from the oxygen to the proton. Therefore, a strong proton acceptor is also a strong electron donor³².

The isoelectric point (IEP) of micrometric iron oxide (Fe_3O_4) was determined at pH 4.5, of nanometric iron oxide (Fe_3O_4) at pH 5.0 and of CIP at pH 3.8, whereas the IEP for ionic liquids and micrometric iron oxide (Fe_3O_4) dispersions was determined within a pH range from 4.0 (for BMIMBF₄) to 5.7 (for BMIMCl), and, for HPCl, there was no IEP. The IEP for ionic liquids and nanometric iron oxide (Fe_3O_4) dispersions was determined within the pH range from 5.0 (for EMIMDEP) to 6.0 (for HMIMCl and BMIMCl), and, for HPCl, there was no IEP. The IEP for ionic liquids and carbonyl iron powder dispersions was determined within the pH range from 3.2 (for BMIMBF₄) to 4.1 (for HMIMCl) and, at pH 8.3 for BMIMCl, and, for HPCl, there was no IEP. Thus, the properties of the surfaces of ionic liquids containing magnetic filler were determined to be acidic (in almost all dispersions), similar to pure micrometric and nanometric iron oxide and CIP (the isoelectric points are in the range of pH from 3.8 to 5.0; a negative zeta potential was determined over almost the whole range of measured pH), and the properties of micro- and nano- sized magnetite and CIP containing HPCl were basic (a positive zeta potential at the whole pH range).

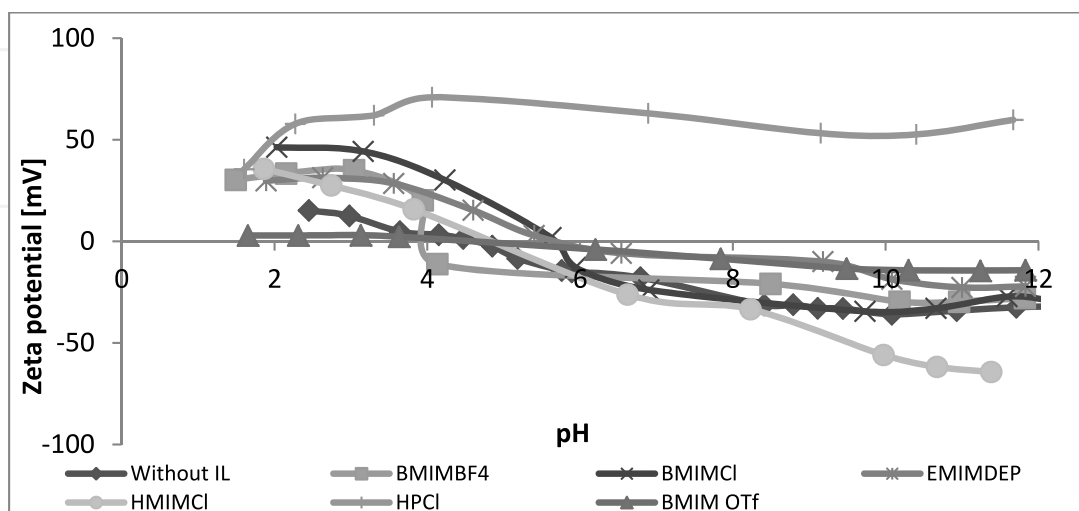


Fig. 1. The zeta potential of micrometric iron oxide (Fe_3O_4) dispersions containing ionic liquids.

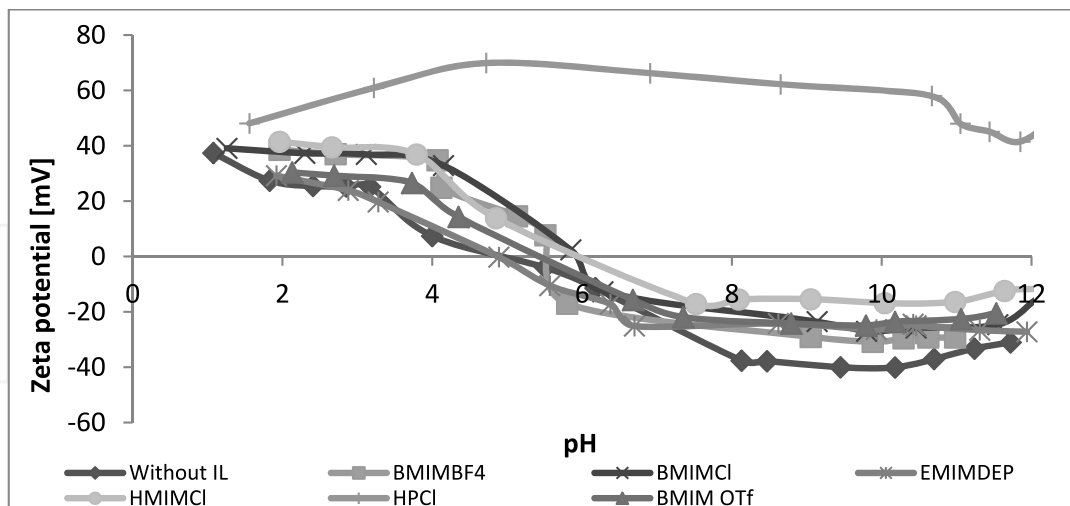


Fig. 2. The zeta potential of nanometric iron oxide (Fe_3O_4) dispersions containing ionic liquids.

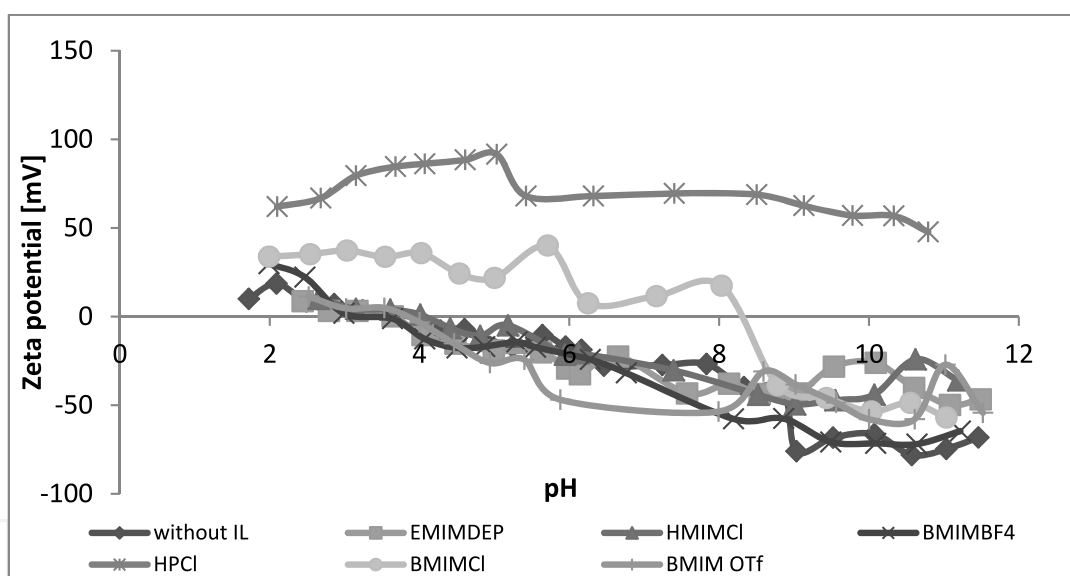


Fig. 3. The zeta potential of carbonyl iron powder (CIP) dispersions containing ionic liquids.

4. Specific properties of MRE containing ionic liquids

4.1 Mechanical properties, cross-linking density and ageing processes

The influence of ionic liquids on the ability of carbonyl iron powder particles in the crosslinking of EPM and NBR elastomers was estimated based on the tensile properties and crosslink density of the vulcanisates. The results are given in Tables 4 and 5. The application of ionic liquids into CIP particles increased the tensile strength of the composites significantly (especially in NBR vulcanisates) compared to those produced without ionic liquids as dispersing agents. Moreover, the stress at a relative elongation of 100% increased, and the elongation at break decreased, due to an increase in the crosslink density of

vulcanisates (Tab. 4 and 5). To increase the tensile strength of composites, the most effective ionic liquid appeared to be EMIMDEP apart from the type of used elastomer.

The crosslink density was determined by the equilibrium swelling of the vulcanisates in toluene. The influence of the addition of different ionic liquid on the crosslink density of NBR and EPM vulcanisates was analysed. Applying ILs as dispersing agents of carbonyl iron powder magnetic particles had a detrimental effect on the crosslink density. The calculated values confirmed that almost all of the applied ionic liquids increased in crosslinking density, and the most effective dispersing agent was HPCI, which did not depend on what type of vulcanisate was considered (EPM/NBR).

To determine the influence of ionic liquids on the mechanical properties of the magnetorheological elastomer composites, another inference occurred. Generally metals with variable oxidation state can influence the mechanical properties of materials after ageing. However, the conditions that were applied herein for ageing (thermal or UV), maintained the values of tensile strength and elongation at break of the NBR vulcanisates. Tables 6 and 7 show that, ageing factors measured for samples containing ionic liquids with micro or nanosized Fe_3O_4 were closer to unity than those of vulcanisates without dispersing agents. The application of selected ionic liquids in the elastomer matrix could effectively protect vulcanisates from thermal and UV ageing processes.

Ionic liquid	$v_e \cdot 10^{-5}$ [mol/cm ³]	SE_{100} [MPa]	T.S [MPa]	E.B [%]
-	5,37	1,01	2,43	537
BMIMBF ₄	6,11	1,16	2,31	384
BMIM OTf	6,93	1,55	3,14	233
BMIMCl	6,00	1,03	3,2	455
EMIMDEP	6,15	1,14	3,47	434
HMIMCl	6,48	1,12	3,08	321
HPCI	6,90	1,28	2,86	326

Table 4. Cross-link density (v_e), tensile strength - T.S, elongation at break - E.B and strength at elongation 100% - SE_{100} of NBR vulcanisates containing carbonyl iron powder and ionic liquids.

Ionic liquid	$v_e \cdot 10^{-5}$ [mol/cm ³]	SE_{100} [MPa]	T.S [MPa]	E.B [%]
-	5,53	0,72	2,01	632
BMIMBF ₄	6,48	0,75	1,96	558
BMIM OTf	3,56	0,74	2,08	866
BMIMCl	5,93	0,81	2,18	570
EMIMDEP	3,97	0,71	2,74	820
HMIMCl	4,09	0,72	2,63	738
HPCI	7,54	0,89	1,69	557

Table 5. Cross-link density (v_e), tensile strength - T.S, elongation at break - E.B and strength at elongation 100% - SE_{100} of EPM vulcanisates containing carbonyl iron powder and ionic liquids.

Ionic liquid	Heat ageing factors		UV ageing factors	
	T.S _{ag} /T.S	E.B _{ag} /E.B	T.S _{ag} /T.S	E.B _{ag} /E.B
-	0,78	0,82	0,73	0,83
BMIMBF ₄	0,87	0,93	0,83	0,86
BMIM OTf	0,80	1,02	0,64	0,87
BMIMCl	0,89	1,00	0,87	1,00
EMIMDEP	0,89	1,07	0,74	0,85
HMIMCl	0,52	0,87	0,59	0,91
HPCI	0,95	1,10	0,88	0,94

Table 6. Ageing factors (T.S – tensile strength, E.B – elongation at break, T.S_{ag} – tensile strength measured after ageing, and E.B_{ag} – elongation at break measured after ageing) of NBR vulcanisates containing micro-sized Fe₃O₄ and ionic liquids.

Ionic liquid	Heat ageing factors		UV ageing factors	
	T.S _{ag} /T.S	E.B _{ag} /E.B	T.S _{ag} /T.S	E.B _{ag} /E.B
-	0,78	0,82	0,73	0,83
BMIMBF ₄	0,87	0,93	0,83	0,86
BMIM OTf	0,80	1,02	0,64	0,87
BMIMCl	0,89	1,00	0,87	1,00
EMIMDEP	0,89	1,07	0,74	0,85
HMIMCl	0,52	0,87	0,59	0,91
HPCI	0,95	1,10	0,88	0,94

Table 7. Ageing factors (T.S – tensile strength, E.B – elongation at break, T.S_{ag} – tensile strength measured after ageing, and E.B_{ag} – elongation at break measured after ageing) of NBR vulcanisates containing nano-sized Fe₃O₄ and ionic liquids.

4.2 Magnetic properties

The orientation of particles and their arrangement were investigated by VSM. Studies of the magnetic properties of the MREs were conducted parallel to the sample long axis, corresponding to the magnetic field direction during curing. Four types of composites were investigated: NBR/microsized magnetite, EPM/micro-sized magnetite, NBR/CIP and EPM/CIP. Significant differences between the characteristic magnetic values recorded for vulcanisates containing different magnetoactive fillers can be seen in Tables 8-11. Higher values of coercivity and retentivity and lower values of magnetisation are characteristic of composites containing micrometre Fe₃O₄ in comparison to NBR/CIP and EPM/CIP compositions, which is certainly due to the specific magnetic properties of the different filler. Carbonyl iron powder presented a higher magnetisation saturation than micrometric magnetite. Coercivity values obtained for the MREs with micrometre Fe₃O₄ and CIP particles varying from 15 to 140 G indicate magnetically soft materials.

Additionally, to improve the dispersion of the applied filler properties, ionic liquids were added during preparation. No matter what kind of IL was admixed, all composites demonstrated magnetic properties regardless of the type of elastomer matrix, applied filler or ionic liquid. Moreover, an increase of magnetisation values was observed for magnetorheological NBR composites with micro-sized magnetite containing ionic liquids compared to vulcanisates where no ionic liquid was applied.

Ionic liquid	Coercivity (Hci) [G]	Magnetisation (Ms) [emu/g]	Retentivity (Mr) [emu/g]
-----	140,45	25,392	3,8768
BMIMBF ₄	137,71	27,179	3,4498
BMIM OTf	138,65	26,792	3,1009
BMIMCl	139,89	26,159	2,8098
EMIMDEP	140,13	28,336	3,2073
HMIMCl	135,39	27,509	2,798
HPCl	136,23	27,514	2,9412

Table 8. Magnetic properties of NBR vulcanisates containing micro- sized magnetite (60 phr) and ionic liquids.

Ionic liquid	Coercivity (Hci) [G]	Magnetisation (Ms) [emu/g]	Retentivity (Mr) [emu/g]
-----	144,64	29,132	4,38
BMIMBF ₄	145,06	29,160	4,294
BMIM OTf	140,44	29,054	4,5374
BMIMCl	143,18	28,715	4,4912
EMIMDEP	144,25	28,313	4,327
HMIMCl	142,92	28,755	4,4267
HPCl	144,14	28,535	4,1544

Table 9. Magnetic properties of EPM vulcanizates containing micro- sized magnetite (60 phr) and ionic liquids.

Ionic liquid	Coercivity (Hci) [G]	Magnetisation (Ms) [emu/g]	Retentivity (Mr) [emu/g]
-----	22,06	73,27	0,64
BMIMBF ₄	23,07	70,16	0,54
BMIM OTf	23,23	69,86	0,46
BMIMCl	22,92	70,18	0,51
EMIMDEP	22,51	70,16	0,53
HMIMCl	22,60	76,64	0,41
HPCl	22,47	70,28	0,47

Table 10. Magnetic properties of NBR vulcanisates containing carbonyl iron powder (60 phr) and ionic liquids.

Ionic liquid	Coercivity (Hci) [G]	Magnetisation (Ms) [emu/g]	Retentivity (Mr) [emu/g]
-----	22,11	75,27	0,75
BMIMBF ₄	15,77	72,81	0,56
BMIM OTf	22,45	72,87	0,71
BMIMCl	22,09	73,76	0,71
EMIMDEP	22,81	74,86	0,74
HMIMCl	22,66	72,43	0,72
HPCI	21,84	74,51	0,74

Table 11. Magnetic properties of EPM vulcanisates containing carbonyl iron powder (60 phr) and ionic liquids.

4.3 Magnetorheological properties

MR elastomers are normally operated with small deformations in the pre-yield regime of the linear viscoelastic region. MREs are intended to be used as structural materials in applications where the load is often of a dynamic type. In cyclic dynamic loading, the material deforms and returns to its original form over one cycle. The oscillating force is varied periodically, usually with a sinusoidal amplitude at the angular frequency ω . In viscoelastic materials, some of the deformation energy input is stored and recovered during each cycle, and some is dissipated as heat. 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 elastic (storage) modulus G' , loss modulus G'' and loss tangent ($\tan\delta$) of NBR composites containing different types of magnetic fillers were measured with an ARES rheometer (TA Instruments) as a function of angular frequency ω under different magnetic fields (Fig. 4-9). Experiments were conducted at 25 °C on samples with various particle contents. Thin slices were cut to a thickness of 2 mm and were 20 mm in diameter. The slope of the particle chains was equal to 45°.

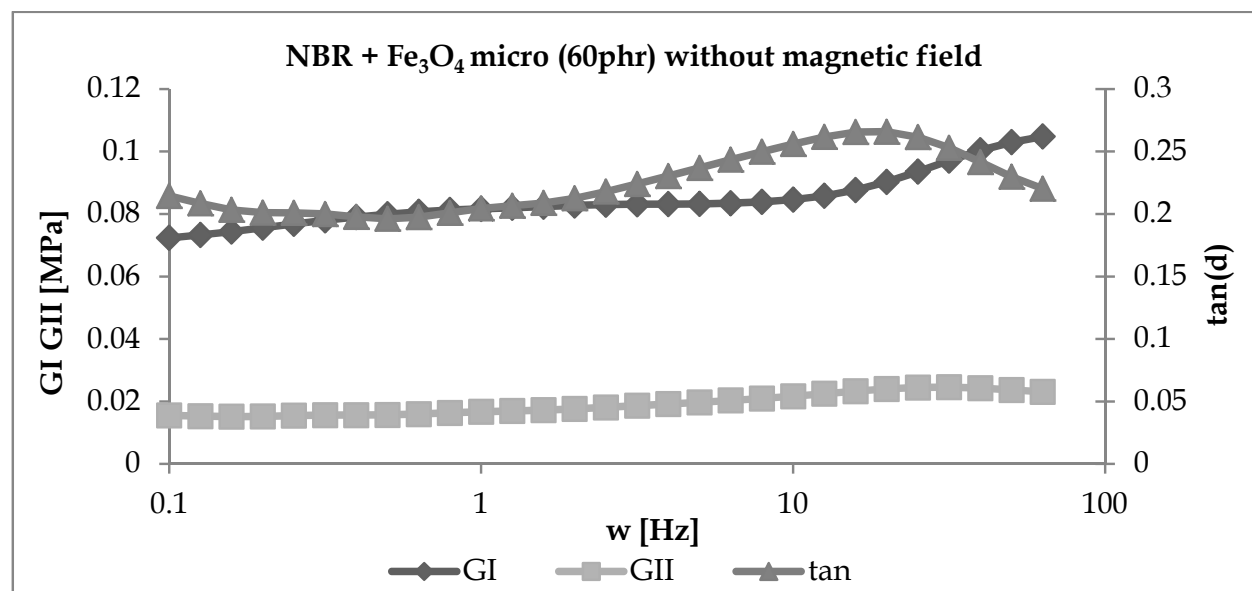


Fig. 4. Dependence of the elastic (storage) modulus ($G' = GI$), loss modulus ($G'' = GII$) and loss tangent ($\tan\delta$) of MRE samples containing micro Fe₃O₄ on the strain frequency.

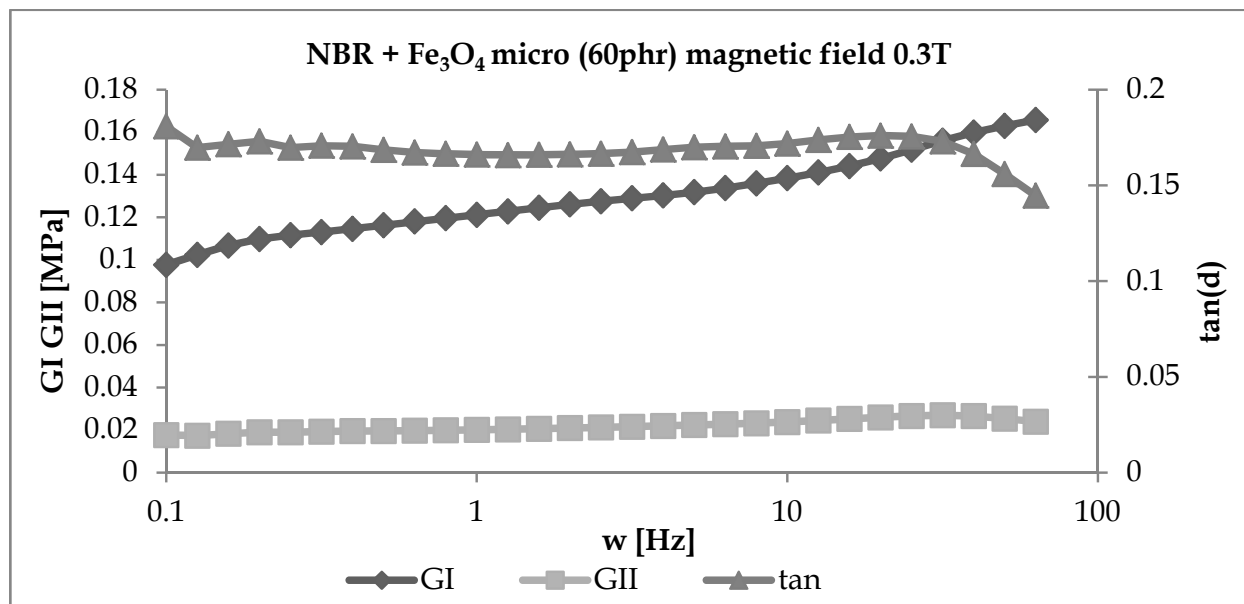


Fig. 5. Dependence of the elastic (storage) modulus ($G' = GI$), loss modulus ($G'' = GII$) and loss tangent ($\tan\delta$) of MRE samples containing micro Fe_3O_4 on the strain frequency.

The elastic modulus increased with the strain frequency for all filler types. In all cases, the application of an external magnetic field led to a significant increase in the elastic modulus (G') and loss modulus (G''). Higher initial values of the storage modulus for composites containing micrometre-sized Fe_3O_4 (Fig. 5) than nanometre-sized Fe_3O_4 or CIP (Fig. 7 and 9) show the appropriate alignment in the elastomer matrix and larger magnetic susceptibility.

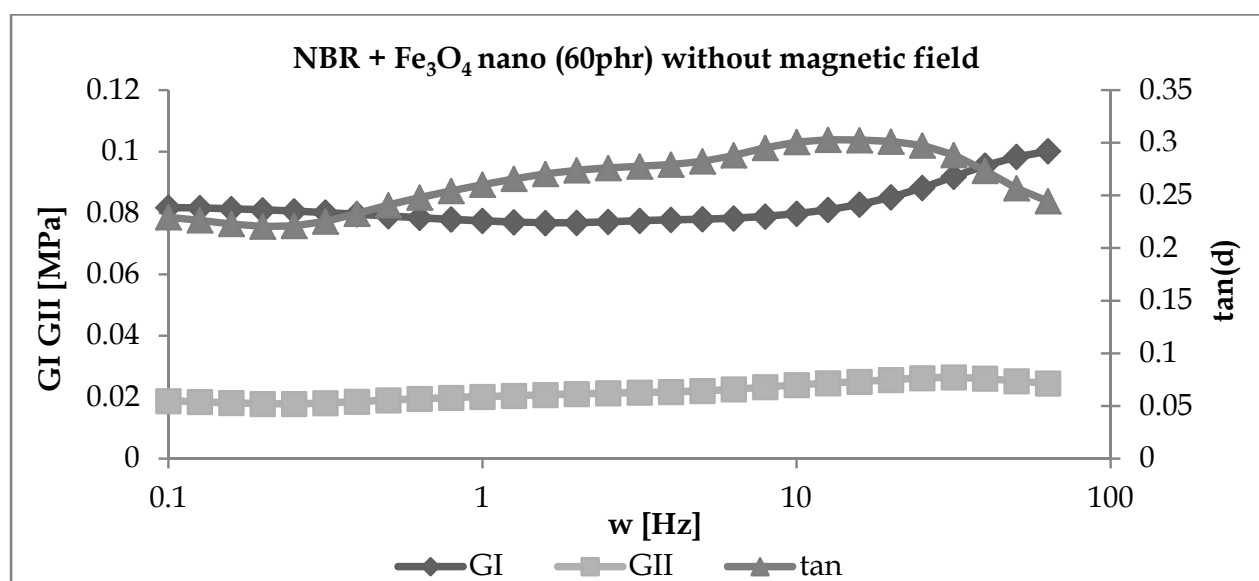


Fig. 6. Dependence of the elastic (storage) modulus ($G' = GI$), loss modulus ($G'' = GII$) and loss tangent ($\tan\delta$) of MRE samples containing nano Fe_3O_4 on the strain frequency.

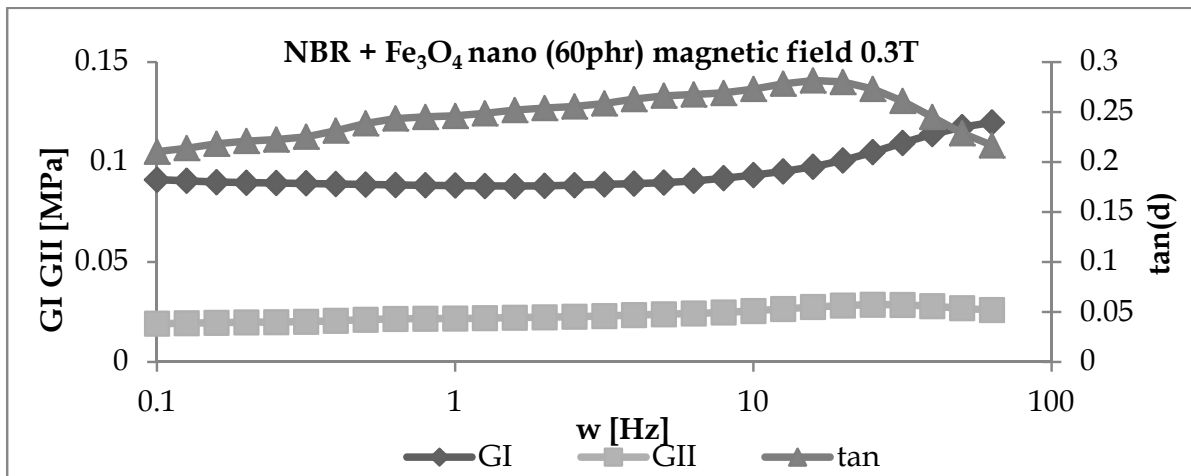


Fig. 7. Dependence of the elastic (storage) modulus ($G' = GI$), loss modulus ($G'' = GII$) and loss tangent ($\tan\delta$) of MRE samples containing nano Fe_3O_4 on the strain frequency.

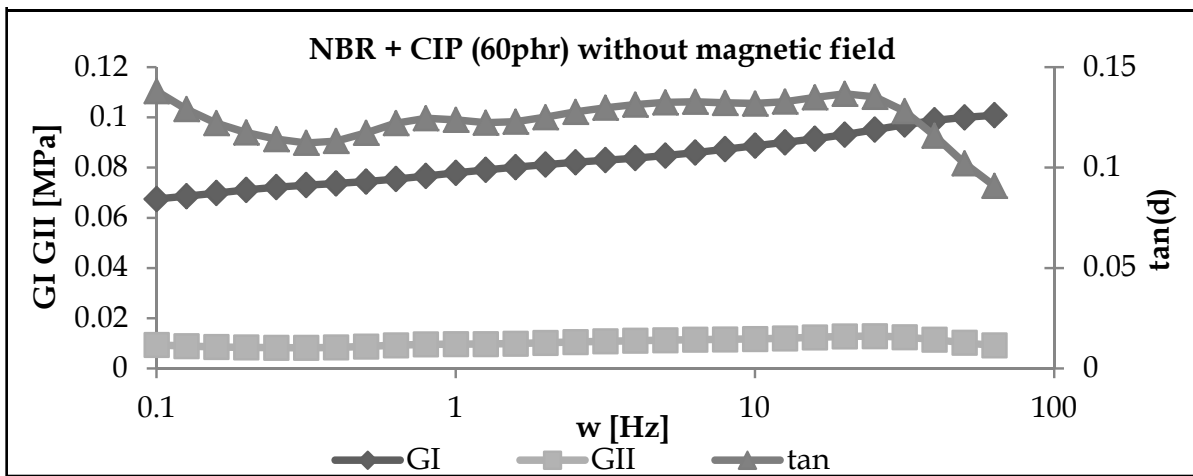


Fig. 8. Dependence of the elastic (storage) modulus ($G' = GI$), loss modulus ($G'' = GII$) and loss tangent ($\tan\delta$) of MRE samples containing CIP on the strain frequency.

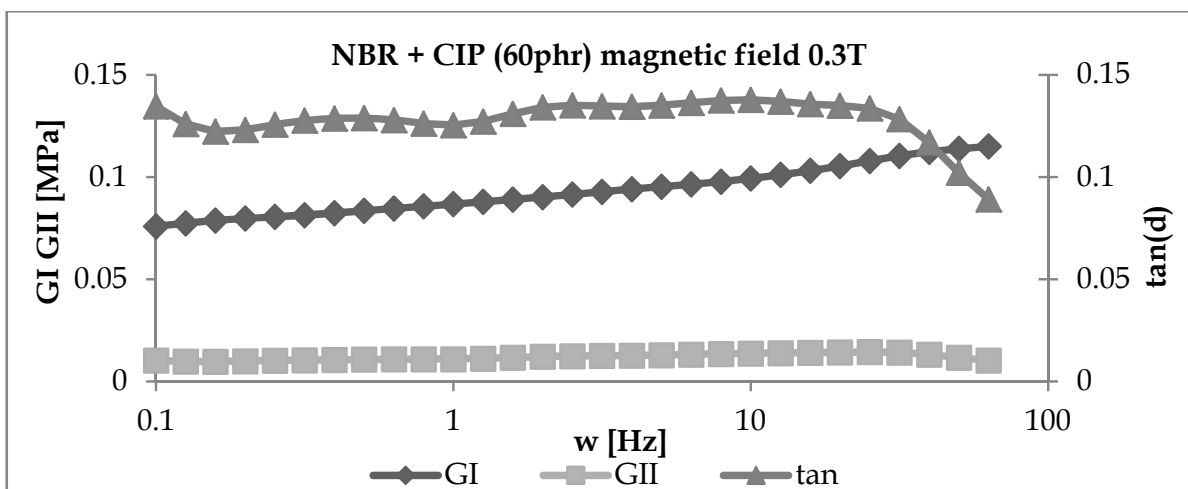


Fig. 9. Dependence of the elastic (storage) modulus ($G' = GI$), loss modulus ($G'' = GII$) and loss tangent ($\tan\delta$) of MRE samples containing CIP on the strain frequency.

4.4 Scanning Electron Microscopy Images – dispersion of magnetoactive filler particles in elastomer matrixes

The dispersion of magnetoactive filler particles in the elastomer has a significant effect on the activity of micrometre and nanometre iron oxides and carbonyl iron powder and their influence on vulcanisate properties. The dispersion of particles in the elastomers (EPM and NBR) was estimated based on the SEM images of the vulcanisate surfaces (Fig. 10-19). Micro-sized Fe_3O_4 (Fig. 10 and 12), nano-sized Fe_3O_4 (Fig. 12) and carbonyl iron powder (Fig. 16 and 18) particles were poorly dispersed in the elastomer matrix (EPM and NBR) and therefore were not homogeneously distributed. They created clusters of particles (agglomerates) with complex structures. The tendency of ferromagnetic particles to agglomerate in the elastomer matrix was confirmed by particle size measurement in water and paraffin oil (model of elastomer matrix), as presented in Section 3.1.

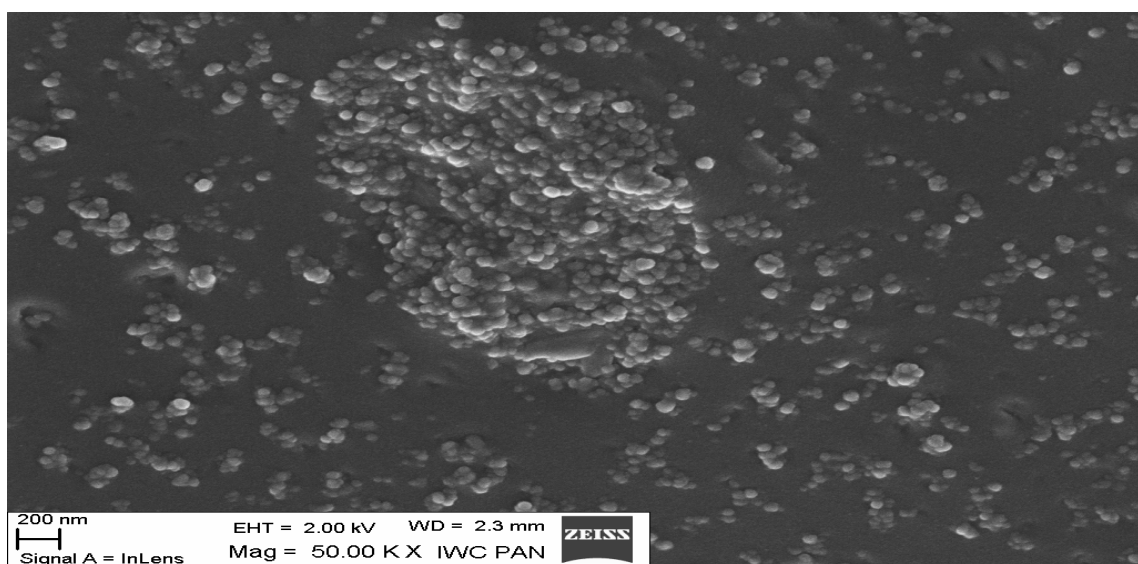


Fig. 10. SEM image of NBR vulcanisate filled with micro-sized 60 phr Fe_3O_4 .

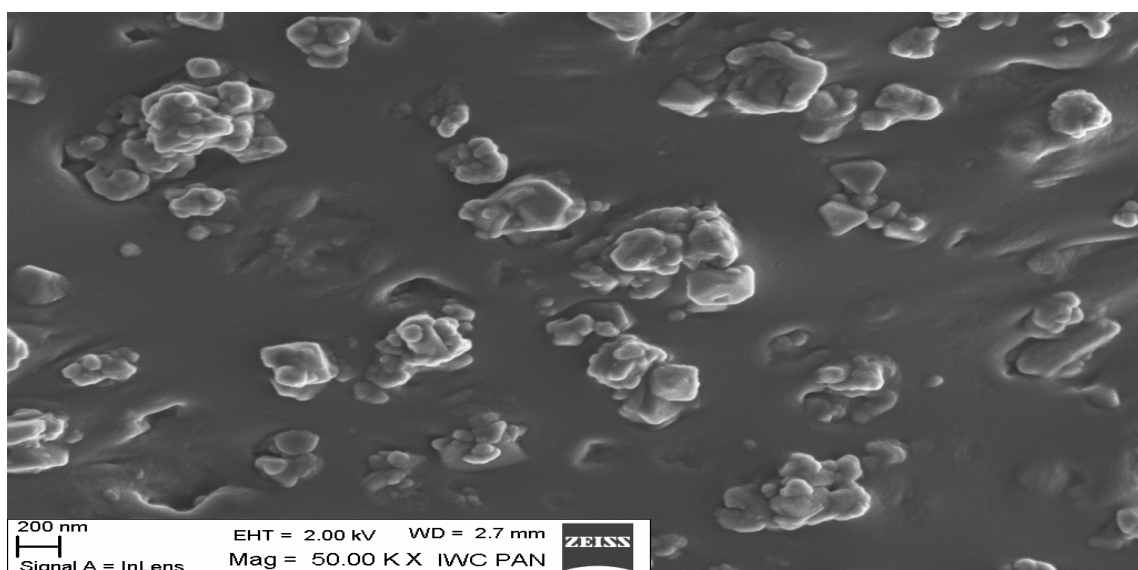


Fig. 11. SEM image of NBR vulcanisate filled with micro-sized 60 phr Fe_3O_4 and 1-butyl-3-methylimidazolium trifluoromethanesulphonate.

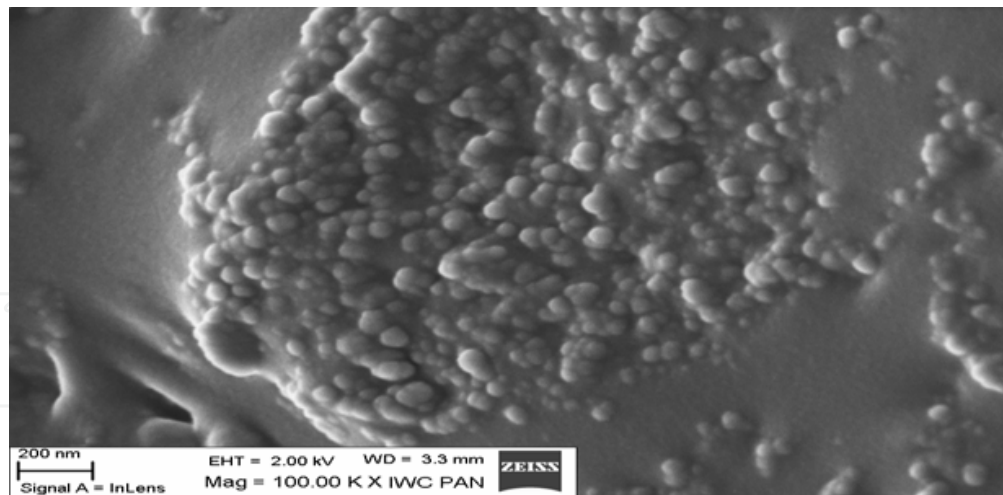


Fig. 12. SEM image of NBR vulcanisate filled with nano-sized 60 phr Fe₃O₄.

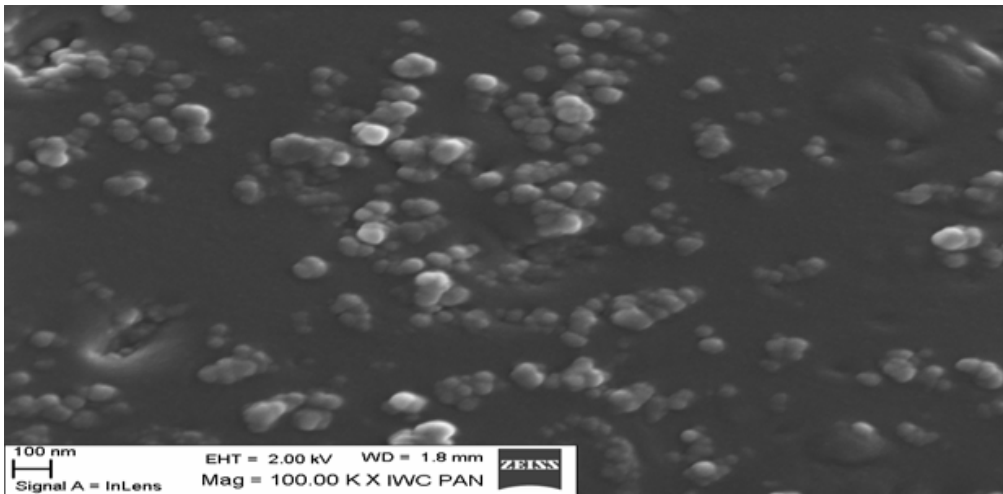


Fig. 13. SEM image of NBR vulcanisate filled with nano-sized 60 phr Fe₃O₄ and 1-butyl-3-methylimidazolium tetrafluoroborate.

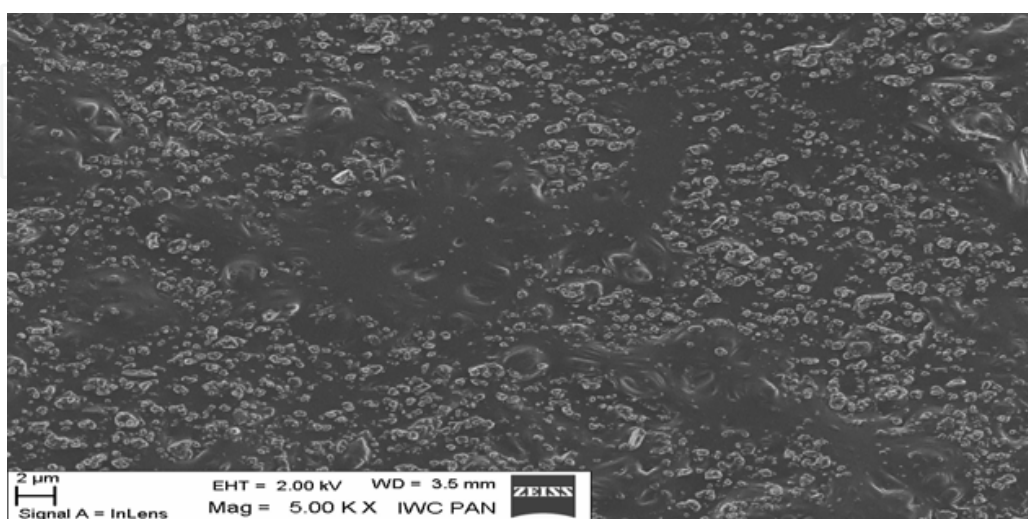


Fig. 14. SEM image of EPM vulcanisate filled with micro-sized 60 phr Fe₃O₄.

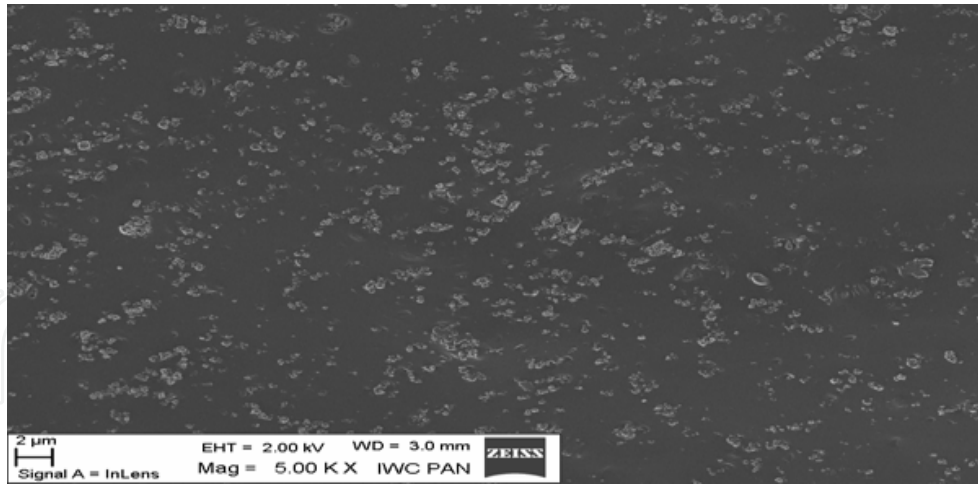


Fig. 15. SEM image of EPM vulcanisate filled with micro-sized 60 phr Fe₃O₄ and 1-butyl-3-methylimidazolium chloride.

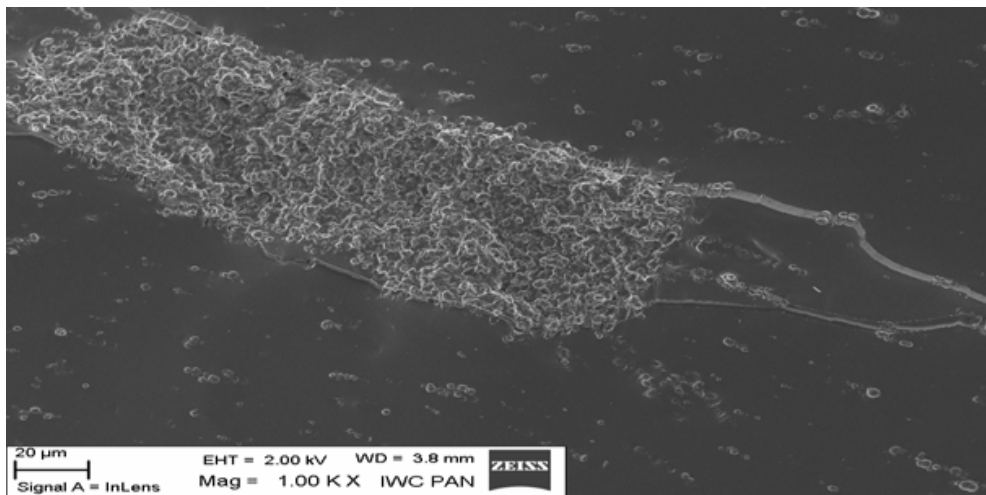


Fig. 16. SEM image of EPM vulcanisate filled with 60 phr CIP.

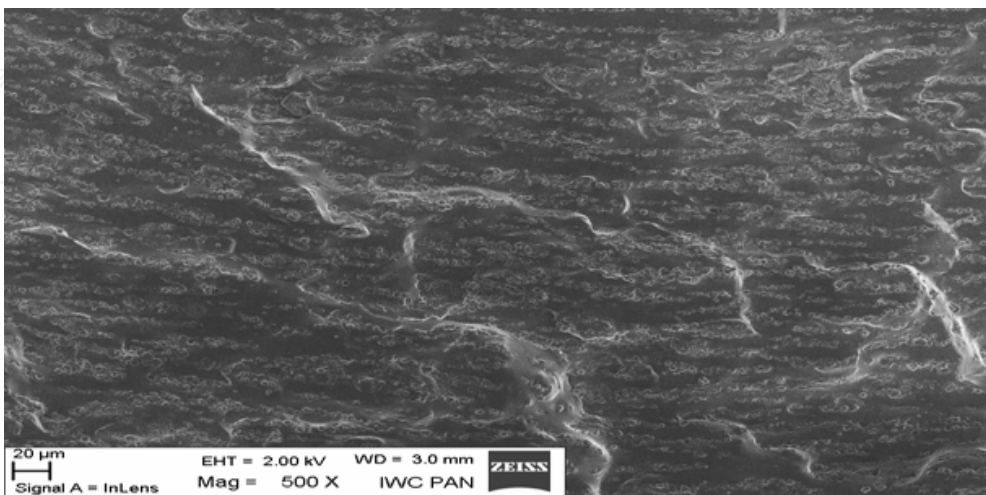


Fig. 17. SEM image of EPM vulcanisate filled with 60 phr CIP and 1-butyl-3-methylimidazolium tetrafluoroborate.

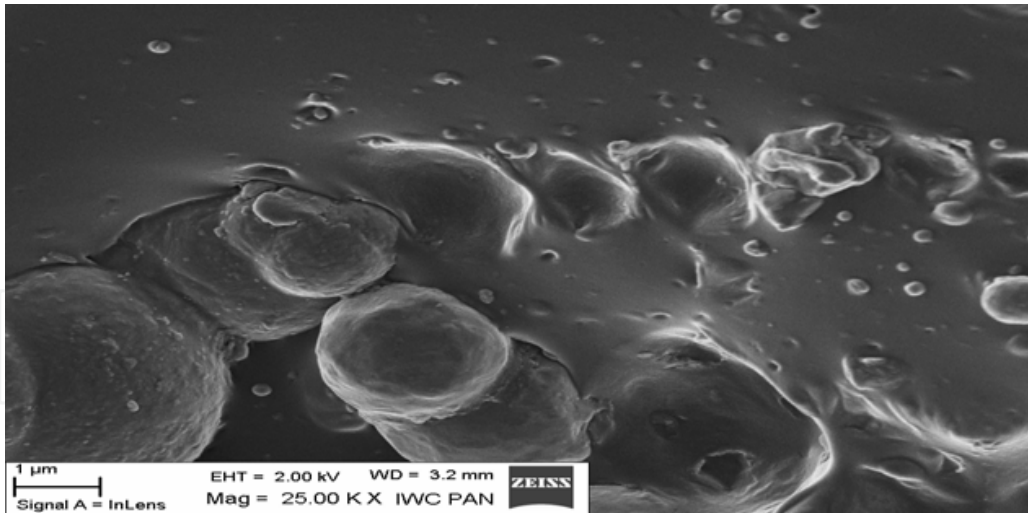


Fig. 18. SEM image of NBR vulcanisate filled with 60 phr CIP.

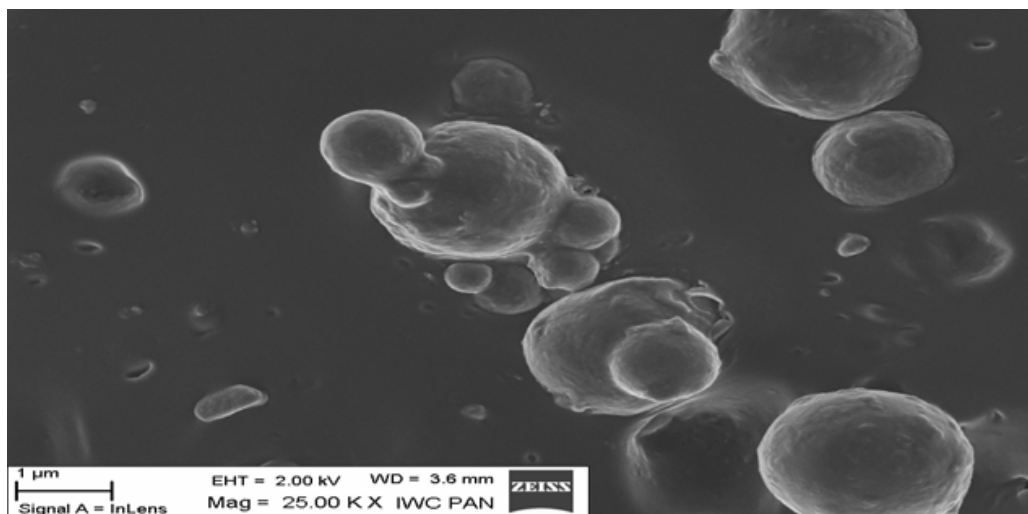


Fig. 19. SEM image of NBR vulcanisate filled with 60 phr CIP and trihexyltetradecylphosphonium chloride.

The addition of selected ionic liquids improved the dispersion of applied magnetic particle fillers for all types of elastomers (Fig. 11, 13, 15, 17, 19). The influence of ionic liquids as dispersing agents in magnetorheological composites included higher tensile strength and crosslink density in these vulcanisates, which was presented in Section 4.1.

Magnetorheological materials can be fluids, gels or even solids such as an elastomer. Magnetorheological materials have magnetically polarisable colloidal particles suspended in some functional suspension, *i.e.*, a viscous fluid (*e.g.*, silicone oil) or an elastomer matrix (*e.g.*, silicone rubber). 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 polarisation 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 a MRE is produced (Fig. 16-19). However, if the mixture is not cured in the presence of a

magnetic field and the particles are hence left randomly distributed, an elastomer ferromagnet composite (EFC) is produced (Fig. (10-15)).

5. Conclusion

MRE composites were prepared according to commonly used methods. Micro- and nano-sized iron oxides and carbonyl iron powder were the active fillers of acrylonitrile – butadiene and ethylene – propylene rubber. It was found that micro- and nano- sized iron oxides and carbonyl iron powder improved mechanical properties of elastomers. They also changed their magnetic properties and reinforced the magnetorheological effects of the composites.

The dispersion of nano- and micro- sized Fe₃O₄ or CIP in the elastomer matrix can be improved by using ionic liquids as dispersing agents. The addition of ionic liquids decreased the aggregates size independently of the type of magnetic filler used. Scanning electron microscopy images used to observe magnetorheological elastomer microstructures proved that the improvement in dispersion had a significant effect on the composites properties. The application of ionic liquids with magnetoactive particles increased the tensile strength of the composites significantly. Moreover, the stress at a relative elongation of 100% increased, and the elongation at break decreased, due to an increase in the crosslink density of the vulcanisates. Finally, the application of selected ionic liquids in the elastomer matrix could effectively protect the vulcanisates from thermal and UV aging processes.

6. Acknowledgment

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This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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