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Article

Electrical Conductivity, EMI Absorption Shielding Performance, Curing Process and Mechanical Properties of Rubber Composites

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Abstract: Three types of the composites were tested for electromagnetic interference (EMI) absorption shielding effectiveness, curing process and physical-mechanical properties. In the first type of composites, manganese-zinc ferrite, nickel-zinc ferrite, and both fillers in their mutual combinations were incorporated into acrylonitrile-butadiene rubber. The overall content of the filler, or fillers combinations was kept on 200 phr. Then, carbon black, or carbon fibres, respectively were incorporated into each rubber formulation in constant loading - 25 phr, while the content of magnetic fillers was unchanged - 200 phr. The work was focused on the understanding of correlation among electromagnetic shielding parameters and electrical conductivity of composites in relation to their EMI absorption shielding effectiveness. The absorption shielding ability of materials was evaluated within the frequency range from 1 MHz to 6 GHz. The study revealed good correlation among permittivity, conductivity, and EMI absorption effectiveness. Although, the absorption shielding efficiency of composites filled only with ferrites seems to be the highest, the absorption maxima of those composites were reached over 6 GHz. The application of carbon based fillers resulted in higher electrical conductivity and higher permittivity of composites, which was reflected in their lower absorption shielding performance. Though, the composites with filled with ferrites and carbon based fillers absorbed electromagnetic radiation within the desired frequency range. The presence of carbon based fillers caused the improvement in tensile behavior of composites. The study also demonstrated that the higher was the ratio of nickel-zinc ferrite in magnetic fillers combinations, the higher was the absorption shielding performance.

Keywords: rubber; manganese-zinc ferrite; nickel-zinc ferrite; carbon black; carbon fibers; electromagnetic absorption shielding

1. Introduction

Rapid development in radio and telecommunication devices has created new kind of environmental pollution, which is associated with accumulation of electromagnetic radiation in the environment. This radiation is often termed as electromagnetic smog or electromagnetic interference (EMI). The accumulation of EMI in the environment has raised a serious concern as electromagnetic radiation waves can not only disturb the normal operation of electronic equipment or cause their malfunction, but they can also pose a serious threat for physiological functions of humans [1–4]. Thus, the development of materials with the EMI shielding performance has become more and more desirable.

Rubber matrices are electrical insulators and thus they do not provide shielding effects. Though, the incorporation of suitable fillers (in form of particles, fibers, sheets, tubes, platelets, etc.) impart them EMI shielding performance. Different types of fillers based on carbon (carbon black, carbon fibers, carbon nanotubes graphite or graphene) as well as inorganic fillers (metals, metal oxides, MXenes, ferrites) have been potentially tested [5–12]. Although, the rubber matrix is the carrier of the main characteristics, the type and the content of the filler can have a significant influence on processability, physical-mechanical or dynamic properties as well as EMI shielding performance. Carbon based fillers reinforce the rubber matrix and provide good physical-mechanical properties to rubber composites. They also enhance thermal flow and electrical conductivity through composite materials. The drawback of conductive materials used for EMI shielding is that they have different impedance from that of the ambient, in which electromagnetic waves proliferate. This impedance mismatch at the interface between the shield and the ambient results in high proportion of the radiation to be reflected from the shielding material [13–15]. Reflection of EMI is unwanted, as the reflected radiation can interfere with other electronic sources, thus causing secondary EMI effect.

On the other hand, materials having magnetic dipoles as ferrites, reduce the difference between the impedance of the shield and the ambient, which results in attenuation of EMI by absorption [16–18]. The radiation absorbed by the shield is usually transferred into heat by joule effect. The absorption of the radiation by the shield is the most efficient way for EMI reduction. Though, the incorporation of solid ferrite powdery fillers into rubber matrices usually leads to the deterioration of physical-mechanical and utility properties.

Thus, the combination of carbon based fillers and materials having magnetic dipoles seems good way to fabricate rubber materials with good shielding efficiency and utility properties [19–22]. Rubber composites exhibit good elasticity, flexibility, dimensional stability, corrosion resistance, they are also lightweight or low cost.

Generally used electronic appliances emit electromagnetic radiation at frequencies below 4 - 5 GHz. Our previous experimental works have revealed that for low frequency absorption shielding, magnetic soft ferrites are good candidates for manufacturing of rubber composites. Manganese-zinc ferrite and nickel-zinc ferrite belong to well established group of ferrite family. Both ferrites were incorporated into rubber matrices in concentration scale ranging from 100 phr to 500 phr. It was shown that the best absorption shielding performance demonstrated the composites filled with 200 phr of ferrites. Thus, in this work, nickel-zinc ferrite, manganese-zinc ferrite and their mutual combinations were kept on constant loading – 200 phr. In the next two following series of rubber compounds, carbon based fillers – carbon black or carbon fibers, respectively were additionally added into each composite in constant amount – 25 phr. Acrylonitrile-butadiene rubber (NBR) was used as rubber matrix. NBR one of the most widely used specialty type rubber with good correlation between cost and properties. Due to its polar character, it has good resistance to oils and non-polar solvents. The work was focused on investigation of ferrites and combinations of ferrites with carbon-based fillers influence on absorption shielding efficiency of composites. Curing process and physical-mechanical properties were examined, too.

2. Experimental

2.1. Materials

In this work, manganese-zinc ferrite MnZn and nickel-zinc ferrite NiZn were used as magnetic soft ferrites. Both ferrites represent commercially available powdery fillers provided by Epcos Company, Czech Republic. They exhibit spinel-type structure and the particle size distribution of ferrites was very similar. It ranged within 0.2 – 70 μm for NiZn ferrite and within 0.7 – 50 μm for MnZn ferrite. The particle size distribution of both fillers with parameters D10 and D50 are summarized in Table 1. D10 and D50 demonstrate the ratio of particle size lower than the given value. D50 is the median showing that that 50 % of particles was lower than around 21 μm for NiZn ferrite and lower than roughly 16 μm for MnZn filler.

Table 1. Particle size distribution of magnetic fillers.

filler	Particle size distribution	<i>D10</i>	<i>D50</i>
MnZn ferrite	0.7-50 µm	4.7 µm	16.3 µm
NiZn ferrite	0.2-70 µm	3.0 µm	21.4 µm

As carbon based fillers, carbon black CB and carbon fibers CF were used. Specialty conductive type carbon black under the trade name VULCAN® XC 72 was supplied from Cabot Corporation, USA. Carbon fibers with commercial trademark Carbiso™G were provided from ELG Carbon Fibre Ltd., Great Britain. The length of fibers ranged between 80 – 100 µm with fibres diameter 7.5 µm. Acrylonitrile-butadiene rubber NBR (SKN 3345, content of acrylonitrile 31-35 %) provided by Sibur International, Russia served as rubber matrix. Sulfur in combination activators (stearic acid and zinc oxide) and accelerator (N-cyclohexyl-2-benzothiazole sulfenamide CBS) were used for cross-linking of rubber compounds. The chemicals for sulfur vulcanization process were provided by Vegum a.s., Dolné Vestenice, Slovak Republic.

2.2. *Methods*

2.2.1. Fabrication and Curing of Rubber Compounds

Three types of composites were fabricated and tested in the study. In the first type of composites, manganese-zinc ferrite, nickel-zinc ferrite and the mutual combinations of both fillers were incorporated into NBR-based rubber matrix. The total content of magnetic fillers was kept on constant level – 200 phr, only the mutual ratio of both fillers was uniformly changed. The composition of composites and their designation is mentioned in Table 2. In the second and third type of composites, carbon black or carbon fibers, respectively were added in constant loading – 25 phr, while the content of magnetic fillers was also kept on constant level. The composition of hybrid composites is summarized in Table 3. In graphical illustrations, the composites filled only with ferrites are designated as NBR, hybrid composites based on CB or CF and ferrites are marked as NBR/CB or NBR/CF, respectively.

Table 2. The composition of materials filled with ferrites in phr and their designation.

NBR	100	100	100	100	100
ZnO	3	3	3	3	3
stearic acid	2	2	2	2	2
CBS	1.5	1.5	1.5	1.5	1.5
sulfur	1.5	1.5	1.5	1.5	1.5
MnZn ferrite	200	150	100	50	0
NiZn ferrite	0	50	100	150	200
<i>designation</i>	<i>Mn200</i>	<i>Mn150</i>	<i>Mn100</i>	<i>Mn50</i>	<i>Ni200</i>
		<i>Ni50</i>	<i>Ni100</i>	<i>Ni150</i>	

Table 3. Composition of materials filled with carbon based fillers and ferrites in phr and their designation.

NBR	100	100	100	100	100
ZnO	3	3	3	3	3
stearic acid	2	2	2	2	2
CBS	1.5	1.5	1.5	1.5	1.5
sulfur	1.5	1.5	1.5	1.5	1.5
CB or CF	25	25	25	25	25
MnZn ferrite	200	150	100	50	0
NiZn ferrite	0	50	100	150	200
designation	CB, CF-Mn200	CB, CF-Mn150	CB, CF-Mn100	CB, CF-Mn50	CB, CF-
		Ni50	Ni100	Ni150	Ni200

The composites were fabricated in a laboratory kneading machine Bradender (Brabender GmbH & Co. KG, Duisburg, Germany) in two-step mixing process. The temperature of mixing was set up to 90°C with the rotor revolution 55 rpm. First, the rubber was put into the chamber and masticated for 2.5 min. Then, zinc oxide and stearic acid were added and after next 2 min, ferrite or ferrites in combination were applied. The mixing process continued for 4.5 min and after that the compounds were cooled down and sheeted in two-roll mill. Sulfur and accelerator were added in the second step and the mixing process proceeded 4 min at 90 °C and 55 rpm. In the final step, the compounds were additionally homogenized and sheeted in two-roll mill. To fabricate hybrid composites, that means the composites filled with carbon based fillers and ferrites, the rubber batches based on carbon black or carbon fibers were first pre-compounded in a large-volume kneading machine Buzuluk (Buzuluk Inc., Komárov, Czech Republic). Then, the compounding procedure with magnetic fillers and curing additives proceeded following the same procedure as mentioned above.

The rubber compounds were subsequently cured at 160 °C and pressure of 15 MPa into thin sheets with dimensions 15 x 15 cm and thickness 2 mm. Low platen hydraulic press Fontijne (Fontijne Presses, Turbineweg, The Netherlands) was used for vulcanization process and the time of heating corresponded to the optimum cure time of each rubber formulation.

2.2.2. Determination of Curing Characteristics

Curing characteristics of rubber compounds were determined from corresponding curing isotherms, which were investigated in oscillatory rheometer MDR 2000 (Alpha Technologies, Akron, Ohio, USA).

The investigated curing parameters were:

M_L (dN.m) - minimum torque

M_H (dN.m) - maximum torque

t_{c90} (min) – optimum cure time

t_{s1} (min) – scorch time

R_v (min⁻¹) – cure rate index, defined as:

$$R_v = \frac{100}{t_{c90} - t_{s1}}$$

(1)

2.2.3. Investigation of Mechanical Characteristics

Zwick Roell/Z 2.5 appliance (Zwick GmbH & Co. KG, Ulm, Germany) was used to evaluate tensile properties of vulcanizates. The tests were performed in accordance with the valid technical standards and the cross-head speed of the measuring device was set up to 500 mm.min⁻¹. Dumbbell-shaped test samples (width 6.4 mm, length 80 mm, thickness 2 mm) were used for measurements. The hardness was measured by using durometer and was expressed in Shore A.

2.2.4. Investigation of Shielding Characteristics

The frequency dependencies of complex (relative) permeability $\mu = \mu' - j\mu''$ for toroidal samples were measured using combined impedance/network analysis method by means of a vector analyser (Agilent E5071C) in the frequency range of 1 MHz – 6 GHz. During measurements, a toroidal sample was inserted into a magnetic holder (Agilent 16454A) and the complex permeability was evaluated from measured impedances (1):

$$\mu = \mu' - j\mu'' = 1 + (Z - Z_{air})/(j\mu_0 f \ln(b/c)) \quad (1)$$

where Z and Z_{air} are the input complex impedances of the 16454A holder with and without a toroidal sample, respectively, h is the height of the sample, $\mu_0 = 4\pi \cdot 10^{-7}$ H/m is the permeability of free space, f is the frequency, and b and c are the outer and inner diameters of the sample.

The frequency dependencies of complex (relative) permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ for disc samples were measured using combined impedance/network analysis method by means of a vector analyser (Agilent E5071C) in the frequency range of 1 MHz – 6 GHz. During measurements, a disc sample was inserted into a dielectric holder (Agilent 16453A) and the complex permittivity was computed from measured admittance (2):

$$\varepsilon = \varepsilon' - j\varepsilon'' = (Y \cdot h)/(j\omega\varepsilon_0 S) \quad (2)$$

where Y is the input complex admittance of the 16453A holder with a disc sample, h is the height of the sample, $\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m is the permittivity of free space, and S is the area of lower electrode. In case of electrically conductive material with dc electrical conductivity σ_{dc} , the imaginary part of ε should be replaced by $\varepsilon'' - \sigma_{dc}/2\pi\varepsilon_0$. The electrical dc conductivity of composite materials was evaluated using standard two-probe method.

High frequency single-layer electromagnetic wave absorption properties (return loss RL , matching thickness d_m , matching frequency f_m , bandwidth Δf for RL at -10 dB and RL at -20 dB, and the minimum of return loss RL_{min}) of composite materials were obtained by calculations of return loss (3):

$$RL = 20 \log |(Z_{in} - 1)/(Z_{in} + 1)| \quad (3)$$

where $Z_{in} = (\mu/\varepsilon)^{1/2} \tanh[(j\omega d/c)(\mu \cdot \varepsilon)]$ is the normalized value of input complex impedance of the absorber, d is the thickness of the single-layer absorber (backed by a metal sheet), c is the velocity of light in vacuum. The composite absorbs maximum of the electromagnetic plane wave energy when normalized value of impedance $Z_{in} \approx 1$. The maximum absorption is then reached at a matching frequency $f = f_m$, matching thickness $d = d_m$ and minimum return loss RL_{min} .

3. Results and Discussion

3.1. Curing Process

The influence of the tested fillers on vulcanization process of rubber compounds was evaluated by determination of curing characteristics, scorch time t_{s1} , optimum cure time t_{c90} , cure rate index R_v , minimum torque M_L and maximum torque M_H . It becomes apparent from Figure 1 that the longest scorch time exhibited rubber compounds filled only with ferrites. The application of carbon based fillers resulted in the decrease of scorch time. The lowest scorch time exhibited rubber compounds filled with ferrites and carbon fibers. As seen, almost no change in scorch time was recorded in dependence on the type of ferrite or ferrites combinations. The similar statement can be applied on

the optimum cure time (Figure 2). The longest optimum cure time exhibited rubber compounds filled only with ferrites, while the shortest time needed for optimal cross-linking required rubber compounds based on ferrites and carbon fibers. Although, the t_{c90} of rubber compounds filled with CF and ferrites seems to have decreasing trend with increasing content of nickel-zinc ferrite in magnetic fillers combinations, in general it can be stated that no significant influence of ferrites on optimum cure time was recorded. The shortest scorch time as well as optimum cure time of rubber compounds based on CF and ferrites were reflected in the highest cure rate index of the equivalent rubber compounds (Figure 3). That means the curing process of the compounds with incorporated carbon fibers proceeded the fastest. On the other hand, the lowest curing kinetics exhibited the rubber compounds filled only with magnetic fillers. Based on the achieved results it becomes apparent that the presence of carbon based fillers resulted in the acceleration of curing process. Carbon based materials are characterized by unique electrical as well as thermal conductivity. Their incorporation into rubber matrix enhanced thermal conductivity and thermal flow through the materials, which subsequently promoted faster vulcanization. From Figures 4 and 5 it is shown that the lowest minimum as well as maximum torque exhibited the rubber compounds filled only with ferrites. The application of carbon based fillers led to the increase of both, minimum and maximum torque. The highest values of both parameters exhibited rubber compounds based on ferrites and CF. Again, no significant influence of the type of ferrite or ferrites combinations on M_L and M_H was recorded. The minimum torque corresponds to the viscosity of rubber compounds before the curing process started, which clearly points out to the increase in viscosity of rubber compounds by incorporation of carbon based fillers. It is a logical reflection of the fact that the viscosity of the fillers is higher than that of the rubber matrix. Also, small nano-sized filler particles (like carbon black or carbon fibers) contribute to the viscosity much higher when compared micro-sized magnetic fillers. The maximum torque relates to the viscosity of cured rubber compounds, which is then closely connected with the cross-link density. It becomes apparent that carbon fibers contributed to the increase of viscosity and cross-link density of the tested materials.

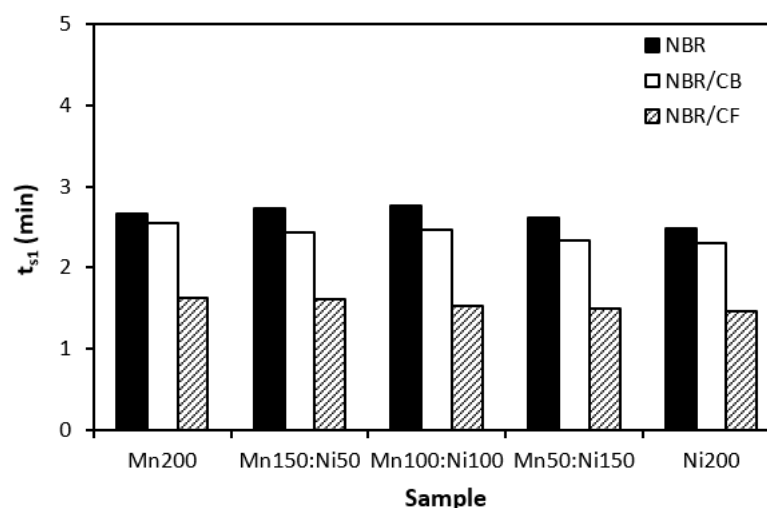


Figure 1. Influence of fillers on scorch time t_{s1} of rubber compounds.

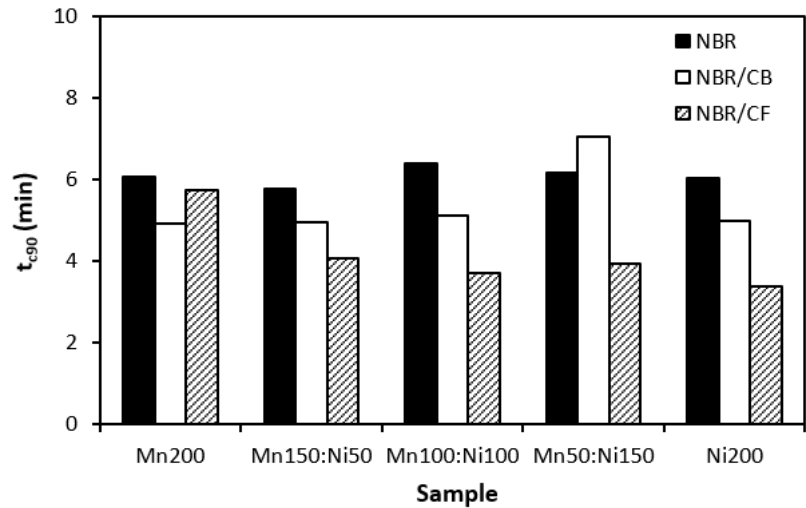


Figure 2. Influence of fillers on optimum cure time t_{c90} of rubber compounds.

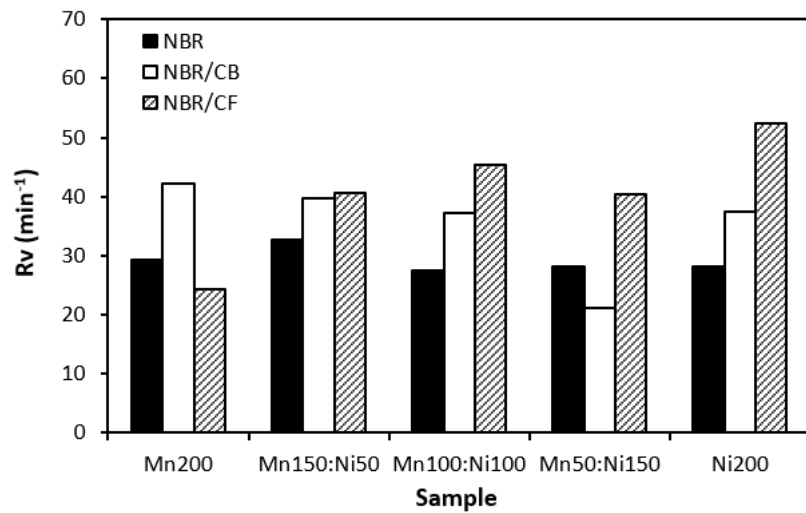


Figure 3. Influence of fillers on curing rate index R_v of rubber compounds.

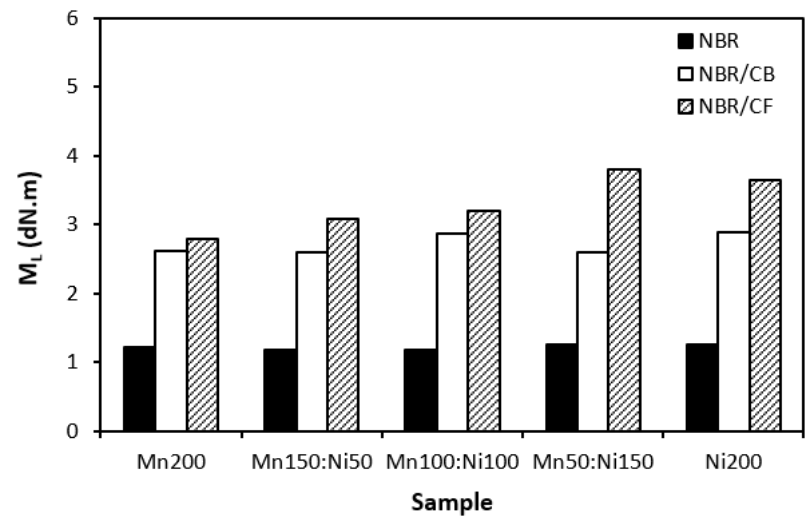


Figure 4. Influence of fillers on minimum torque M_L of rubber compounds.

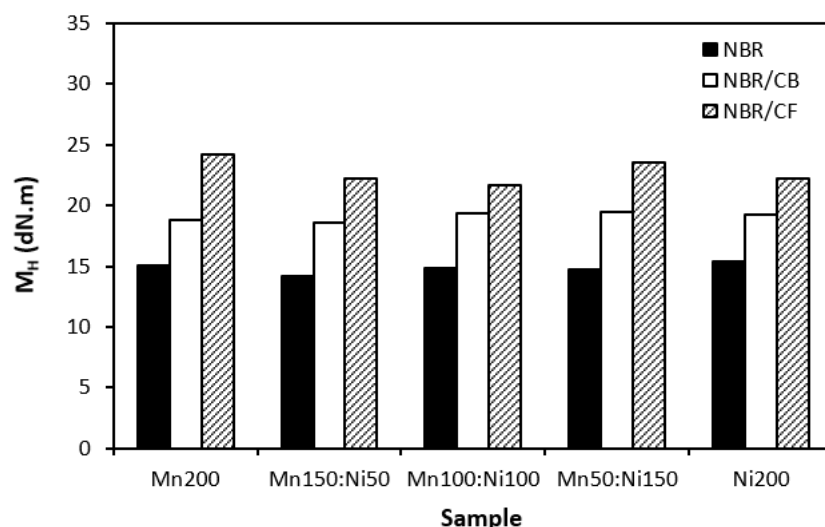


Figure 5. Influence of fillers on maximum torque M_H of rubber compounds.

3.1. Electromagnetic Absorption Parameters and Electrical Conductivity

Generally used electronic equipment like TV sets, laptops, mobile phones, etc. emit electromagnetic radiation within low frequency ranges, usually between 1 - 4 GHz. Thus, the shielding of EMI within this frequency range is of high importance. As already mentioned, shielding by reflection mechanism is often ineffective, as electromagnetic plane wave just reflects from the surface of the shield, but still propagates through the ambient. By contrast, absorption of electromagnetic radiation is the most promising way to protect the functionality of electronic devices, or human health. Therefore, the current work deals with the investigation of absorption shielding efficiency of composites, that means the ability of materials to absorb electromagnetic radiation. Absorption shielding efficiency of composites was investigated within the frequency range from 1 MHz to 6 GHz, which covers the operation frequency of commonly used electronic and electromagnetic instrumentation. To calculate the absorption shielding efficiency, electromagnetic parameters – complex permittivity and complex permeability were first evaluated. The complex permeability consists of two parts, real μ' and imaginary μ'' permeability. The real part corresponds to magnetic storage capacity, while imaginary permeability represents magnetic dissipation or losses. The complex permittivity is similarly composed of real ϵ' and imaginary ϵ'' part, representing electric charge storage, or dissipation, respectively.

The frequency dependences of complex permeability for tested composites are illustrated in Figures 6–8. From Figure 6 it is shown that the real permeability of composites filled only with ferrites does not change with frequency just up to roughly 500 MHz, then it significantly dropped down (under 1). The highest μ' seems to have the composite filled with 200 phr of MnZn ferrite, although it can be stated that no significant changes in real permeability were recorded in dependence on the type of ferrite or ferrites combinations. Very low influence of fillers composition was also recorded for imaginary permeability μ'' , which was frequency independent up to 100 MHz. Then, it passed over the maximum (between 1 - 2 GHz), which corresponds to maximum magnetic dissipation (resonance frequency).

The frequency dependences of complex permeability for composites filled with carbon fibers and ferrites (Figure 7) or carbon black and ferrites (Figure 8) were very similar. The real part showed slight decreasing trend with increase in frequency to 300 – 500 MHz. Then, sharp decrease occurred up to a maximum frequency. The imaginary permeability did not change very much with frequency up to roughly 100 – 200 MHz. It reached the maximum dissipation at a resonance frequency (1 – 2 GHz). The real and imaginary parts of hybrid composites seemed to be slightly higher when compared equivalent composites filled only with ferrites, mainly at very low frequencies. With increase in

frequency, differences between permeabilities became negligible and it can be stated that no significant influence of the tested fillers on complex permeability was observed.

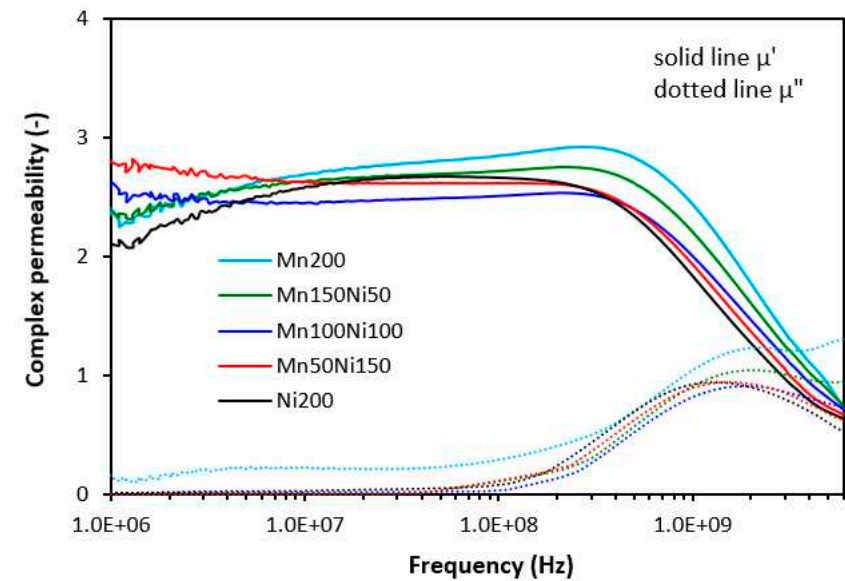


Figure 6. Frequency dependences of complex permeability for composites filled with ferrites.

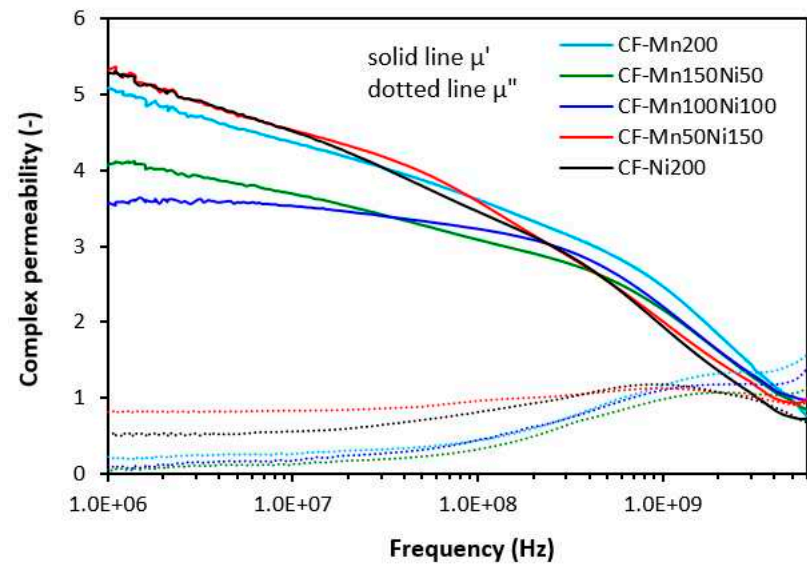


Figure 7. Frequency dependences of complex permeability for composites filled with ferrites and carbon fibers.

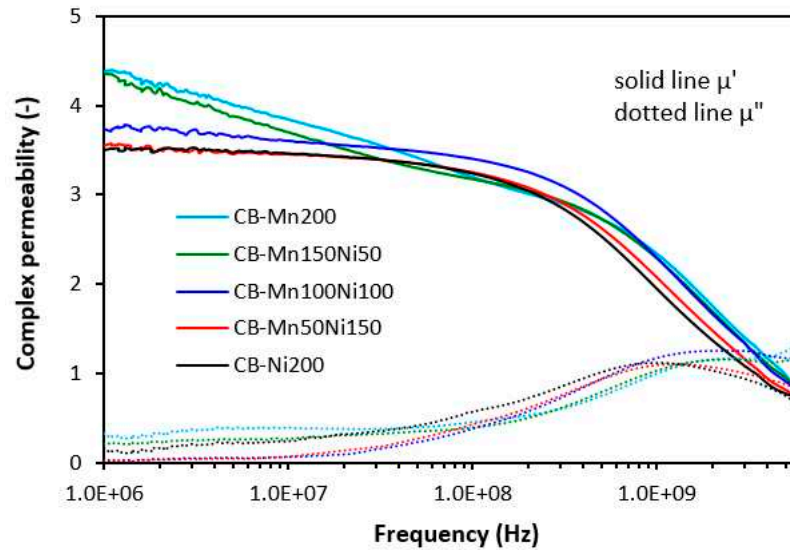


Figure 8. Frequency dependences of complex permeability for composites filled with ferrites and carbon black.

On the other side, as shown in Figure 9, there was recorded clear influence of complex permittivity of composites on the type of ferrite or ferrites combinations. The highest real part exhibited the composite filled with manganese-zinc ferrite (Mn200), while the lowest one was found to have the composite filled only with nickel-zinc ferrite (Ni200). It can be stated that the higher was the amount of nickel-zinc ferrite in magnetic fillers combinations, the lower was ϵ' . The highest differences among the real permittivity were observed at the initial frequency ($\epsilon' = 12$ for the composite Mn200, $\epsilon' = 5.2$ for the composite Ni200 at 1 MHz). With the increase in frequency, the differences in real part became smaller. From Figure 9 it also shown that upon first strong decline of ϵ' at low frequencies, the continual decreasing trend was recorded with next frequency rise. The recorded values were $\epsilon' = 3.6$ or $\epsilon' = 1.6$ at 6 GHz for the composites Mn200 or Ni200, respectively. The imaginary permittivity was lower than the real part and was also found to be dependent on the type of ferrite or magnetic fillers combinations, mainly at low frequencies. With increase in frequency, the ϵ'' declined to a very low values with almost no influence on the frequency or magnetic fillers.

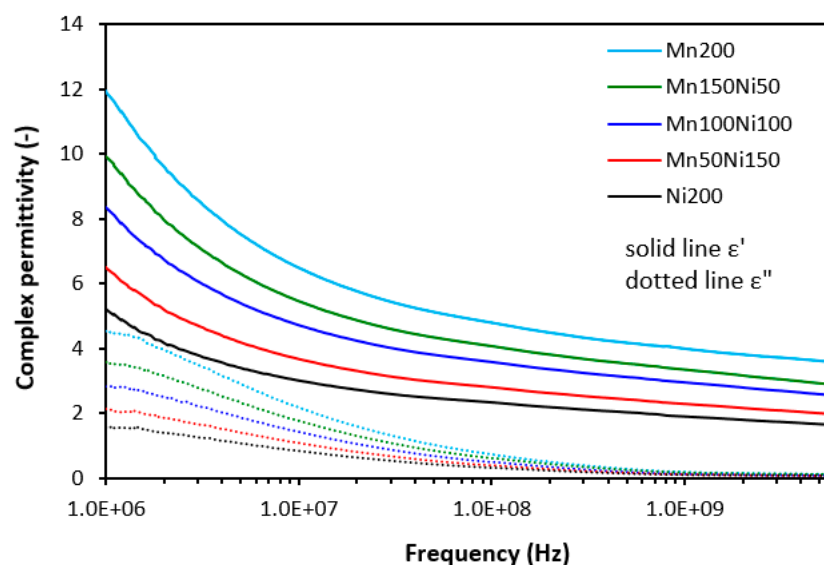


Figure 9. Frequency dependences of complex permittivity for composites filled with ferrites.

The complex permittivity of hybrid composites was also strongly dependent on ferrite or ferrites combinations, meaning that the higher was the amount of nickel-zinc ferrite in magnetic fillers combinations, the lower was the real and imaginary permittivity (Figures 10 and 11). The higher was the frequency, the lower were both, ϵ' and ϵ'' . When comparing the complex permittivity of composites, it becomes apparent that the application of carbon based fillers resulted in the enhancement of both, real as well as imaginary part. The calculated value ϵ' was 24.5 for the composite with designation CF-Mn200 at 1 MHz (Figure 10). Upon the increase in frequency up to maximum, the real part declined to 6.5. The real part of the composite CF-Ni200 decreased from 9.8 at 1 MHz to 3.2 at 6 GHz. The highest complex permittivity exhibited composites filled with combination of carbon black and ferrites (Figure 11). The real part of the composite CB-Mn200 reached almost 40 at 1 MHz, followed by the decrease to 10 at 6 GHz. The imaginary permittivity decreased from 18.7 down to 0.6 when the frequency increased from 1 MHz up to its maximum value. The composite CB-Ni200 exhibited the real and imaginary part of 16.2 and 7.2 at 1 MHz, respectively, which decreased down to $\epsilon' = 4.1$ and $\epsilon'' = 0.2$ at a maximum frequency.

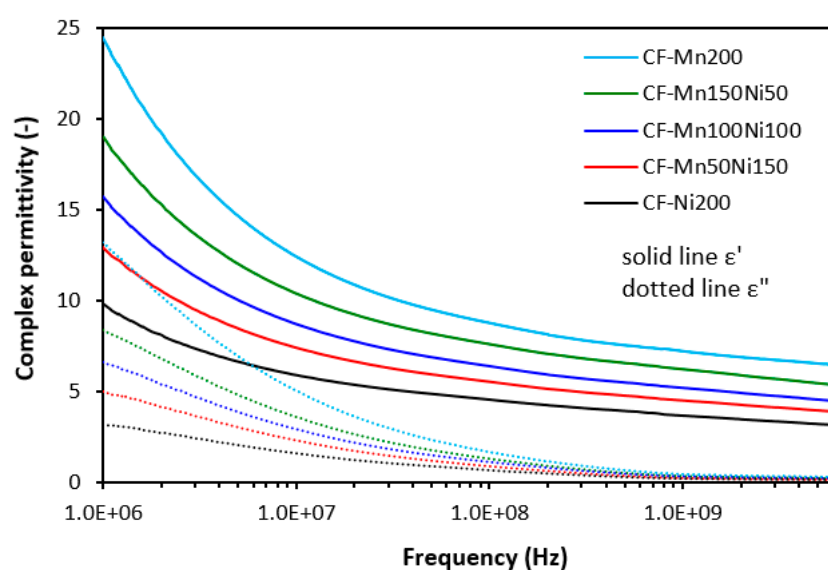


Figure 10. Frequency dependences of complex permittivity for composites filled with ferrites and carbon fibers.

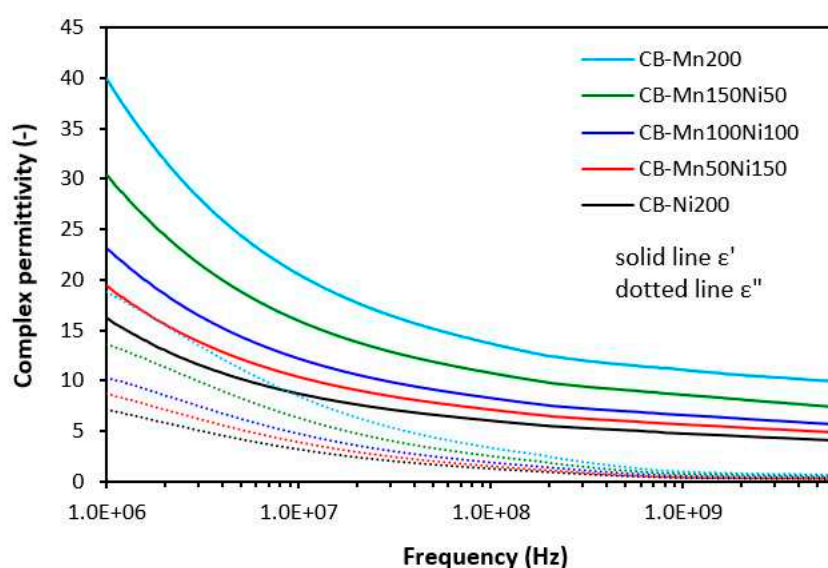


Figure 11. Frequency dependences of complex permittivity for composites filled with ferrites and carbon black.

Based on the calculated parameters, the absorption shielding efficiency of composites was investigated. Absorption shielding efficiency of composites was characterized through determination of return loss RL . Return loss provide information about the amount of EMI, which is absorbed by the composite shield. The materials exhibiting return loss at -10 dB can absorb about 90 – 95 % of incident radiation plane wave. Lower return loss is connected with higher EMI absorption. The material shields reaching return loss at -20 dB have been reported to absorb almost 99 % of harmful EMI and thus they are excellent radiation absorbers [23–25]. The efficiency of absorption shielding depends on the frequency bandwidths. That means the broader are the frequency bandwidths for absorption shielding, the higher is the absorption shielding ability of the materials.

The dependences of return loss RL on radiation frequency for composites filled only with ferrites or their mutual combinations are graphically illustrated in Figure 12. The calculated values of their electromagnetic absorption characteristics are summarized in Table 4. RL_{min} represents minimum value of return loss at a matching frequency or maximum absorption shielding efficiency, f_m is the matching frequency, Δf at -10 dB and -20 dB summarizes effective frequency absorption bandwidth of composites at the given return loss RL . It must be noted that composites with equivalent ratio of both ferrites (Mn100Ni100), composites with designations Mn50Ni150 and Ni200 reached absorption maxima over the tested frequency 6 GHz. The electromagnetic absorption parameters summarized in Table 4 represent only the results calculated to maximum frequency 6 GHz. The composite filled only with nickel-zinc ferrite did not reach return loss even at -10 dB within the tested frequency range and thus there are no data of electromagnetic absorption parameters for this composite. It can be inferred that the higher was the proportion of nickel-zinc ferrite in magnetic fillers combinations, the higher was the frequency at which the composites provided the absorption shielding efficiency. Within the tested frequency range, the evident absorption maxima were recorded only for the composite filled with 200 phr of manganese-zinc ferrite (Mn200) and for the composite Mn150Ni50. The absorption maximum of the sample Mn200 was -60 dB at a matching frequency 4670 MHz, while the composite Mn150Ni50 reached absorption maximum -51.4 dB at a matching frequency 5700 MHz. The effective absorption frequency bandwidth of the composite filled only with manganese-zinc ferrite ranged from 3050 MHz to 6 GHz at $RL = -10$ dB and from 4150 MHz to 5250 MHz at $RL = -20$ dB. The effective frequency bandwidth for the composite Mn150Ni50 moved from 3550 MHz at -10 dB, and from 5020 MHz at -20 dB to 6 GHz, respectively.

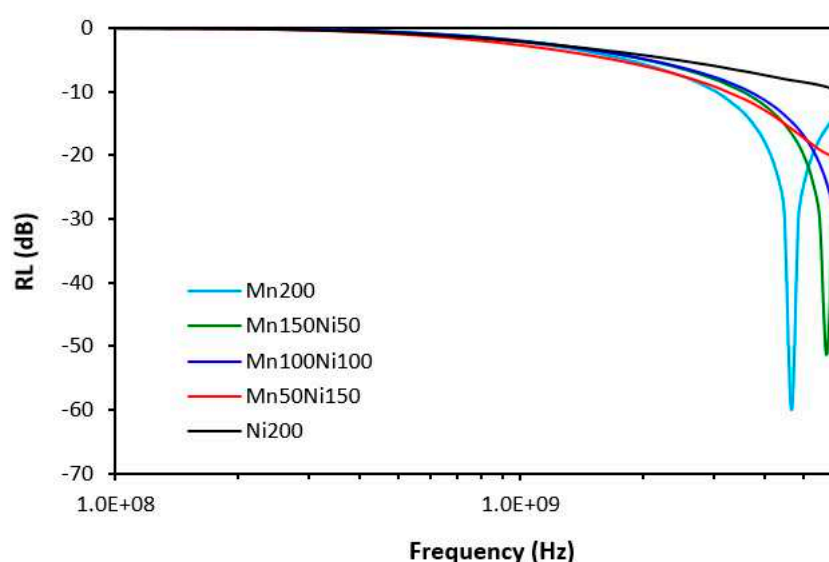


Figure 12. Frequency dependences of return loss for composites filled with ferrites.

Table 4. Absorption characteristics of materials filled with ferrites.

sample	$RL_{min} (dB)$	$f_m (MHz)$	$\Delta f (MHz) -10 dB$	$\Delta f (MHz) -20 dB$
Mn200	-60.1	4670	2950	1100
Mn150Ni50	-51.4	5700	2450	980
Mn100Ni100	-31.1	6000	2300	630
Mn50Ni150	20.3	6000	2800	200
Ni200	-9.7	6000	-	-

From Figure 13 it becomes apparent that the combination of magnetic fillers with carbon fibers resulted in shifting of EMI absorption shielding efficiency to lower frequencies and all composites exhibited clear absorption peaks within the tested frequency range. As also shown in Figure 13 and Table 5, the absorption shielding performance was clearly dependent on the type of ferrite or ferrites combinations. The composite filled with carbon fibers and manganese-zinc ferrite (CF-Mn200) demonstrated the absorption shielding performance at the lowest frequency (matching frequency was 2769 MHz with minimum value of return loss -58.3 dB). This composite exhibited the narrowest effective frequency bandwidth at $RL = -10$ and -20 dB (from 1920 MHz to 4050 MHz at -10 dB and from 2500 MHz to 3100 MHz at -20 dB). Thus, it can be stated that this composite is the worst absorber of electromagnetic radiation. With increasing amount of NiZn filler in ferrites combinations, the absorption shielding performance moved to higher frequencies. The composite filled with CF and 200 phr nickel-zinc ferrite (CF-Ni200) absorbed electromagnetic radiation at the highest frequency ($f_m = 4140$ MHz, $RL_{min} = -57$ dB). The effective frequency bandwidth ranged from 2.4 GHz to 6 GHz at -10 dB ($\Delta f = 3600$ MHz) and from 3500 MHz to 4880 MHz at -20 dB ($\Delta f = 1380$ MHz). The broadest absorption bandwidths suggest that this composite is the most effective absorber of electromagnetic radiation. When looking at Figure 13 and Table 5 one can see that effective frequency bandwidths of composites became broader with increasing proportion of NiZn ferrite. Thus, it can be concluded that nickel-zinc ferrite exhibits better absorption shielding performance.

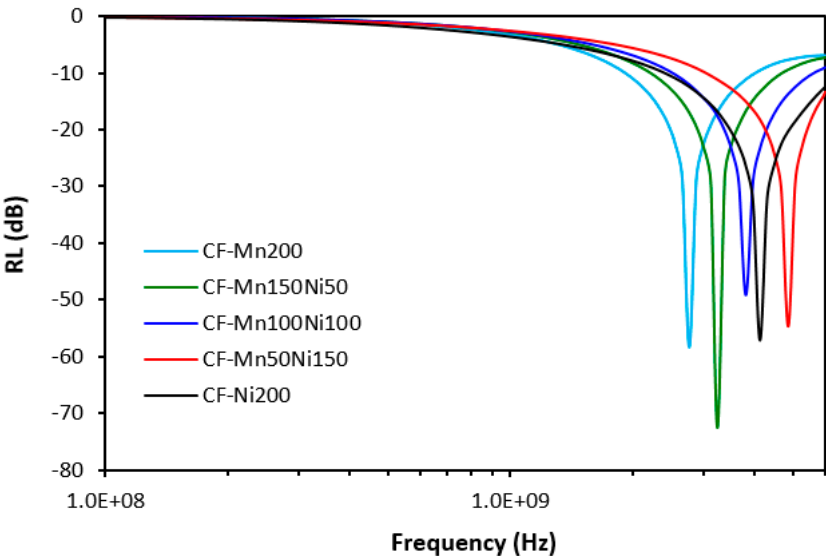


Figure 13. Frequency dependences of return loss for composites filled with ferrites and carbon fibers.

Table 5. Absorption parameters of materials filled with ferrites and carbon fibers.

sample	$RL_{min} (dB)$	$f_m (MHz)$	$\Delta f (MHz) -10\ dB$	$\Delta f (MHz) -20\ dB$
CF-Mn200	-58.3	2769	2130	600
CF-Mn150Ni50	-72.6	3250	2500	720
CF-Mn100Ni100	-49.2	3820	3140	900
CF-Mn50Ni150	-54.8	4860	2980	1130
CF-Ni200	-57.0	4140	3600	1380

From Figure 14 and Table 6 it shown that the frequency dependences of composites filled with carbon black and ferrites are also strongly influenced by the type of ferrite or ferrites combinations. Again, with increasing content of NiZn ferrite in magnetic fillers combinations, the absorption maxima shifted to higher frequencies and the effective frequency bandwidth at -10 and -20 dB became broader. The absorption maximum for the composite filled with CB and 200 phr of manganese-zinc ferrite (CB-Mn200) was -49 dB at 1780 MHz, while the composite with designation CB-Ni200 demonstrated absorption maximum -51 dB at 3250 MHz. The composite CB-Mn200 exhibited the narrowest absorption peak (RL ranged between 1340 MHz – 2400 MHz at -10 dB and from 1630 MHz to 1930 MHz at -20 dB). On the other hand, the widest effective frequency bandwidths of the composite CB-Ni200 set between 2020 MHz - 5120 MHz ($\Delta f = 3100$ MHz) and between 2840 MHz - 3720 MHz ($\Delta f = 880$ MHz) at -10 or -20 dB, respectively rank this composite as the best absorber of EMI.

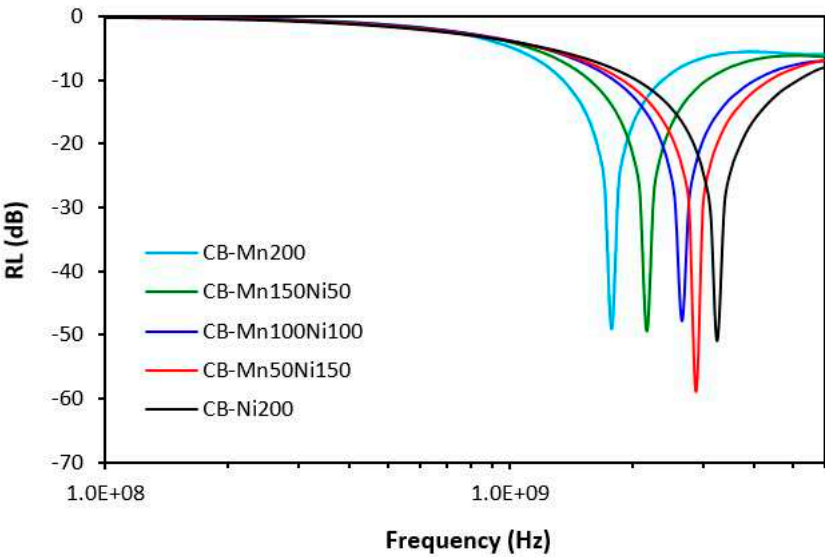


Figure 14. Frequency dependences of return loss for composites filled with ferrites and carbon black.

Table 6. Absorption parameters of materials filled with ferrites and carbon black.

sample	$RL_{min} (dB)$	$f_m (MHz)$	$\Delta f (MHz) -10\ dB$	$\Delta f (MHz) -20\ dB$
CB-Mn200	-49.0	1780	1060	300

CB-Mn150Ni50	-49.5	2180	1500	430
CB-Mn100Ni100	-47.8	2660	2240	600
CB-Mn50Ni150	-59.0	2880	2500	700
CB-Ni200	-51.0	3250	3100	880

When comparing electromagnetic absorption parameters of composites filled only with ferrites (considering only the composites with designations Mn200 and Mn150Ni50, which demonstrated absorption maxima within the tested frequency range) and hybrid CF-ferrites or CB-ferrites based composites one can see that composites filled only with ferrites exhibited the highest matching frequencies f_m and the broadest effective absorption frequency bandwidths Δf at -10 and -20 dB. Based upon that it can be concluded those composites are the best EMI absorber shields. Simultaneously, they can shield electromagnetic radiation at the highest frequencies. The incorporation of carbon based fillers resulted in the shifting of absorption shielding performance of composites to lower frequencies on one hand. On the other hand, their absorption shielding performance was lower as an evidence of lower effective frequency bandwidths. The lowest ability to absorb EMI demonstrated the composites filled with carbon black and ferrites showing the narrowest absorption peaks. They also provided the absorption shielding performance at the lowest frequencies. It can be stated that absorption maxima RL_{min} were not significantly influenced by the composition of composite materials.

To better understand the influence of tested fillers on absorption shielding performance, the electrical conductivity of composites was investigated. From Figure 15 it is obvious that the lowest conductivity were found to have the composites filled only with ferrites. Carbon based fillers demonstrate unique electrical properties and it becomes clearly apparent that their application into rubber compounds resulted in the increase of electrical conductivity. The highest electrical conductivity exhibited the composites filled CB and ferrites. The conductivity of hybrid composites was found to increase with increasing content of manganese-zinc ferrite, which could point out to higher conductivity of MnZn filler. Though, this was not experimentally confirmed for composites filled only with ferrites. As shown, their conductivity fluctuated only in a very low range of experimental values almost independently on the type of ferrite or ferrites combinations. It might be stated that some synergic effect between carbon based fillers and ferrites was observed when considering the conductivity. The highest conductivity manifested the composite CB-Mn200. This composite simultaneously showed the highest real and imaginary permittivity (Figure 11). With increasing proportion of NiZn ferrite, the conductivity of both types of hybrid composites showed decreasing trend and similar decrease was observed for their permittivity. Also, the highest conductivity of composites filled with CB and ferrites was reflected in their highest real and imaginary permittivity. On the other hand, the lowest permittivity demonstrated the composites filled only with ferrites with the lowest conductivity. Also, as their conductivity was not significantly influenced by the type of ferrite, there was also recorded the lowest difference between the real and imaginary permittivity for composites Mn200 and Ni200. Thus, the dependence between the conductivity and permittivity was established, meaning that higher conductivity was reflected in higher complex permittivity of composites. As outlined, real permittivity relates to the electrical charge storage capacity. It can be measured as the amount of accumulated charges, microcapacitors and polarization centers [18,26]. Polarization of the filler, rubber matrix and polarization at the interfacial region between the filler and the matrix can occur in dependence of radiation frequency [27,28]. The presence of carbon based fillers resulted in higher accumulation of electric charges within the composite materials. Simultaneously, the application of carbon based fillers caused the reduction of the distance between the filler particles, which are surrounded by the rubber matrix. Even, small content of carbon-based fillers significantly reduces space between particles due to tubular structure of carbon fibers or structural aggregates of carbon black. This led to higher polarization of the rubber

matrix as well as formation of localized charges at interfacial filler-rubber region (interfacial rubber-filler polarization). Imaginary permittivity is connected with the dissipation of electrical energy. The presence of carbon based fillers contributed to the formation of conductive networks within the composite matrix, which is beneficial for dielectric dissipation and thus higher imaginary permittivity [29,30].

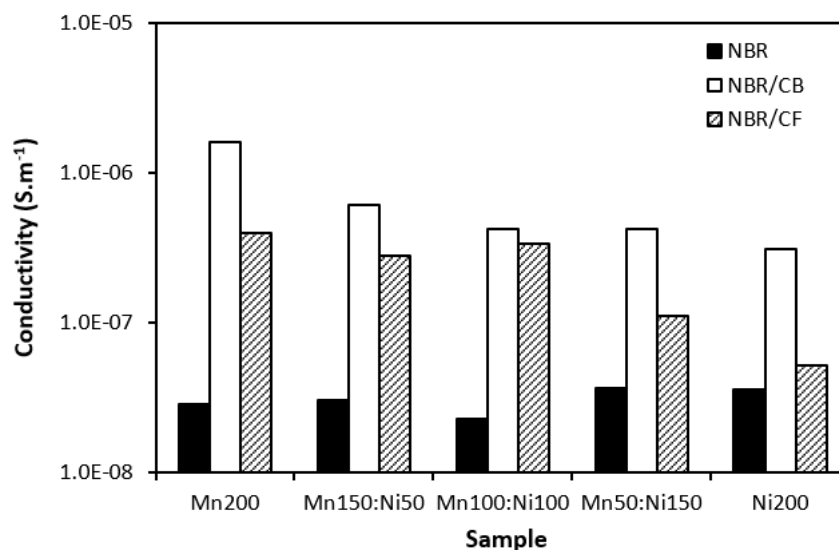


Figure 15. Influence of fillers on conductivity of composites.

Although, at lower frequencies (below 1 GHz), slightly higher real and imaginary permeability exhibited hybrid composites, in overall it be stated that the permeability of composites was found not to be significantly influenced by the fillers composition. Real and imaginary permeability corresponds to magnetic storage and dissipation, respectively. As shown, the complex permeability is influenced only by the presence of magnetic fillers with magnetic dipoles with almost no influence of highly conductive carbon based fillers. Materials having magnetic dipoles and thus high permeability have been reported to be good EMI absorber shields [31–33]. Although, all tested composites exhibited very similar values of permeability, higher permittivity and conductivity of composites containing carbon based fillers are believed to be the crucial parameters, which diminished their absorption shielding performance. It has been revealed that highly conductive materials are good candidates for low frequency reflection shielding [34–36]. The results also demonstrated that the higher is the conductivity, the lower is the frequency for absorption shielding.

3.1. Physical-Mechanical Characteristics

Physical-mechanical properties were investigated to determine the utilization of tested materials in practical applications. Looking at Figures 16 and 17, one can see very similar dependences of modulus M_{300} and tensile strength on the tested fillers. The lowest modulus (Figure 16) and tensile strength (Figure 17) demonstrated the composites filled only with magnetic fillers. It is a logical reflection of the fact that ferrites as stiff powdery fillers do not act as reinforcing fillers when they are incorporated into rubber matrix. By incorporation of carbon based fillers, both modulus and tensile strength increased. The highest values of both characteristics manifested the composites filled with combination of ferrites and carbon black. CB is the most widely used nano-filler in rubber technology with aggregated structure providing enhanced tensile behavior to rubber materials. As shown in Figure 17, the tensile strength increased from about 2.5 – 3 MPa for composites filled only with ferrites to roughly 8 MPa for composites with incorporated carbon black. The application of carbon based fillers led to the increase of elongation at break and hardness of composites (Figures 18 and 19). In this case, the highest values of both properties exhibited composites filled with ferrites and carbon fibers. Though, it seems that modulus and tensile strength of hybrid CF and ferrites filled composites

showed increasing trend with increasing proportion of NiZn ferrite in magnetic fillers combinations, in general it can be stated that no significant changes in physical-mechanical properties were recorded in dependence on the type of ferrite or ferrites combinations.

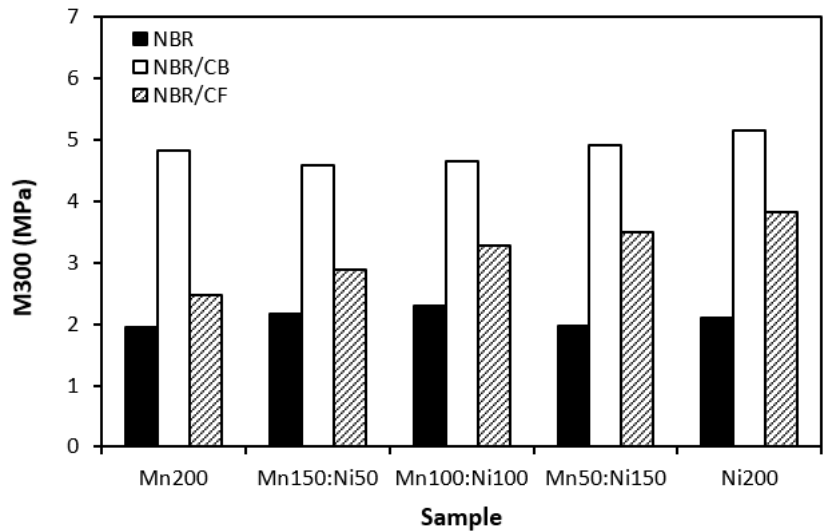


Figure 16. Influence of fillers on modulus M300 of composites.

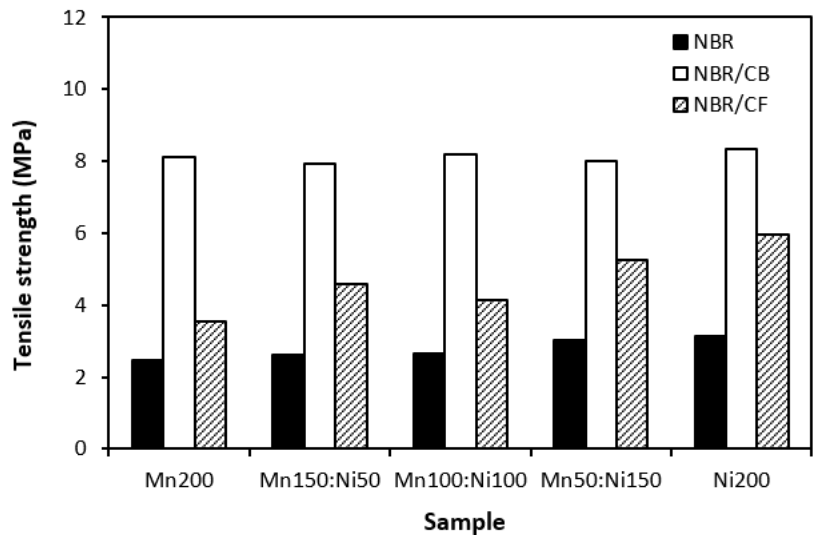


Figure 17. Influence of fillers on tensile strength of composites.

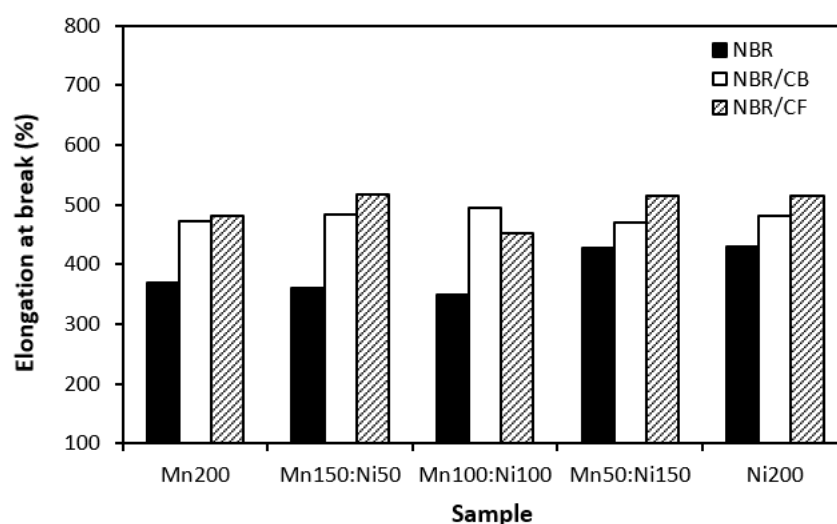


Figure 18. Influence of fillers on elongation at break of composites.

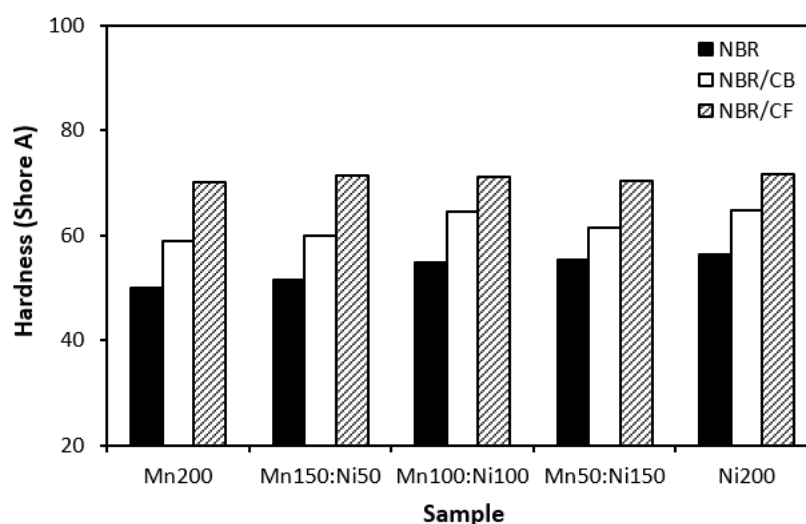


Figure 19. Influence of fillers on hardness of composites.

4. Conclusions

Rubber composites based on magnetic fillers, and combination of magnetic fillers with carbon based fillers were examined for their curing process, physical-mechanical properties and EMI absorption shielding performance. The results showed that curing characteristics were not dependent on the type of ferrite, or ferrites combinations. The application of carbon black and carbon fibers resulted in the acceleration of the curing kinetics, as carbon based fillers enhanced thermal flow through the materials and enabled them to be heated faster up to the curing temperature. Similarly, no influence of the type of ferrite or magnetic fillers combinations on physical-mechanical characteristics was recorded. The incorporation of carbon based fillers caused the enhancement of physical-mechanical properties. The highest modulus and tensile strength exhibited composites filled with ferrites and carbon black, while the highest hardness and elongation at break manifested composites with ferrites and carbon fibers. The presence of carbon based fillers in rubber compounds led to the increase of their conductivity and permittivity. The conductivity and permittivity of composites increased in order: ferrites < CF/ferrites < CB/ferrites. The higher was the conductivity and permittivity, the lower was the absorption shielding performance. The absorption shielding efficiency of composites increased as follow: CB/ferrites < CF/ferrites < ferrites. The frequency for absorption shielding increased in the same order. The higher was proportion on nickel-zinc ferrite in

magnetic fillers combination, the lower was the conductivity and permittivity, suggesting that nickel-zinc ferrite provided better absorption shielding performance.

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