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PhD THESIS

ABSTRACT

A STUDY REGARDING THE PROPERTIES OF NANOFERRITE-MODIFIED EPOXY SYSTEM

PhD student,
Eng. MUNTENIŢĂ Cristian

Scientific Coordinator,
Professor PhD. Eng. BÎRSAN Iulian-Gabriel

ROMÂNIA
MINISTERUL EDUCAȚIEI NAȚIONALE ȘI CERCETĂRII ȘTIINȚIFICE
UNIVERSITATEA „DUNĂREA DE JOS” DIN GALAȚI

DECIZIA

nr. 3543/27.12.2016

Conform modificărilor aduse Codului studiilor universitare de doctorat prin Hotărârea Guvernului României nr. 134/2016 şi de Regulamentul de organizare şi funcţionare al CNATDCU aprobat prin Ordinul Ministrului Educaţiei Naţionale şi Cercetării Ştiinţifice nr. 3482/24.03.2016;

având în vedere referatul conducătorului ştiinţific Prof.dr.ing. Iulian-Gabriel BÎRSAN nr. 41917/21.12.2016, privind propunerea comisiei de susţinere publică a tezei de doctorat;

conform aprobării Consiliului pentru studiile universitare de doctorat în data de 27.12.2016

în baza Ordinului Ministrului Educaţiei Naţionale şi Cercetarii Ştiinţifice nr. 3174/18.02.2016 privind numirea rectorului;

Rectorul universităţii decide:

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Art. 2. Şcoala doctorală de Inginerie, Secretariatul doctorat, Compartimentul salarizare şi Serviciul financiar vor duce la îndeplinire prevederile prezentei decizii.

RECTOR,
Prof. dr. ing. Iulian Gabriel BÎRSAN

CHAPTER 5. ANALYSIS OF THE THERMAL AND HYDRO-THERMAL PROPERTIES OF NANOFERRITE-MODIFIED COMPOSITE MATERIALS

INTRODUCTION

Composite materials are the first materials with internal structural layout conceived by man, both through of their molecular structure and through preferential directions, thus giving them increased resistance, superior to those of their constituents.

The use of polymeric materials represent a number of advantages compared to traditional materials. The properties of these materials are: low energy consumption for during production, minimize the impact on the environment, corrosion resistance, tensile strength, wear resistance, resistance to high temperatures, the hardness of the surface, dimensional stability, resistance to the environment, the thermal conductivity or thermal insulation, electrical conductivity; and large usage spectrum: medicine, by making dental implants and bone; aerospace industry by developing various components of the vehicle; automotive industry by developing various structural components; the sports industry through the development of various vehicles: bicycles, boats and sport equipment; energy industry through by applications in the field of wind energy (the wind turbines whose blades are made of composite).

The developing of the composite materials was based both on economic and technical considerations. Among them we can remember: the need to make materials with special properties, impossible to attain by traditional materials, the need to increase the safety and reliability in operation, the need to reduce the consumption of materials deficient, expensive or precious, with the possibility to reduce the time for the technological manufacturing and manhours and last but not least the extend of the lifetime of the materials.

The polymer engineering offers a variety of the array of properties can be controlled or modified by techniques and specific mechanisms. Epoxy resin is widely used for wide applications having, however, reduced performance regarding the dumping of the vibrations. This is due to its mechanical properties and limitations of the contraction-acclimatization report. In order to overcome these problems organic nano-particles are used incorporated in epoxy resin. Such resins have a number of advantages: tape relatively simple at room temperature, lowst risk of toxicity, mechanical and thermal properties. However, the resins presents a major disadvantage, are impossible to recycle. A similar situation is meets at silicone rubbers.

Because composites properties depends largely on their formation techniques, in order to exploit them fully, engineers and designers in this area should inform themselves very well in terms of the characteristics of each component involved in the formation of a composite so that in the intended material not to appear unfavorable changes.

As per this study the target was to obtain a uniform dispersion of ferrites nano-particles. This was solved by mechanical mixing of the main component of each epoxy system with the necessary quantities of nano-ferrites (for a ferrite material with5% mass fraction development and for a mixture of ferrites with 10% mass fraction development). There were thus colloid obtained (because of low size and weight of the dispersant, and due to the dispersing medium properties – viscosity) with epoxy resin as a main component of dispersion medium that proved to be stable over the time (no precipitation of solid material are registered).Thus formed colloids have been mechanically mixed with necessary quantities of hardener (different hardeners and different amounts of hardener for each epoxy system) as a condition to obtain the pre-polymer mixture.

The initial approach was prompted by previous studies were micrometric baric ferrites were used. Studies have shown that the concentrations up to 10% ferrites materials with uniform dispersion of the modifying agent could be obtained, without producing structural changes to the polymer and moreover, for high concentrations, mechanical properties of formed materials decreases (causing defects for the polymeric matrix).

This work goal is to analyze the composite materials modified with nano-ferrites (barium and strontium ferrites) with matrix made from three different epoxy resins. In this case, because of particles small size, ferrites particle alignment is desired by applying an external magnetic field during the polymerization. The possible alignment of the ferrite particles should have an effect on the formed materials properties (in particular electromagnetic properties).

Inorganic nano-particles are very attractive for their use as modifying agents, due to their specific properties: low density, high temperature resistance, corrosion resistance, surface area extremely high (compared to other particle sizes).Using different kind of nano-metric powders on to the matrix leads to nano-composites materials. Nano-structure effects can however be obtained by methods that do not require powders dispersion but through direct involvement (chemical or physical) on the precursors dispersed in the matrix.

According to the literature, the formation of polymeric composites, does not allow discussing interest issues from a single point of view, more than that, polymers properties can be controlled by synthesis and adapted to applications. Starting from the idea that the composite materials have good mechanical properties and affordable forming techniques, these are increasingly used in elements repairing or even replace them. Here we can mention the current trend of replacing traditional structures with composite materials, which have a higher life expectancy, high corrosion resistance, good elastic properties than traditional materials (pipelines for transportation - gas, water etc).

Current trends in technology led to the need to coat the surfaces with various thin layers to improve the material quality. This method leads to a development of coating by laser ablation techniques, by chemical deposition, on the surface of the polymer or modified polymers. This field of composite materials is a very expensive one (in terms of costs) but effective in terms of investment (in terms of volume of production and consumption volume).Thanks to the enlargement opportunities and advantages, composite materials will continue to capture the attention of researchers and specialists.

In these studies several issues have been pursued: determining the formation method and design of composite materials, modifying agents choosing methods and required quantities, the mold establishing, mechanical, electromagnetic, thermal and hydro-thermal methods for testing and morphology of formed composite materials.

SEM analyses showed that devised method allowed to obtain materials with no massive clusters of ferrite nano-particles, a fact proven by mechanical tests which showed a very good repeatability of the results for specimens for different samples. To achieve the effect of the presence of external magnetic field on the properties of formed materials, for boards molds, magneto static fields were applied by placing permanent magnets on the two parallel sides of the molds.

The study of such materials is justified by the fact that such a matrix - modified with nano-ferrites - can be used to form carbon fiber reinforced material that will produce high efficiency electromagnetic shielding structures.

One of the major issues concerning the composite materials is the production of raw materials, the use period in finished products and their degradation, because composites materials are highly resistant to degradation, making it difficult to eliminate from nature. Recent research in order to minimize the negative impact of composite materials have demonstrated that they should be replaced with other biodegradable materials.

For this reason there are increasingly more legal restrictions of production and use of these materials with high impact on the environment. As a solving method introducing a new material is required, accompanied by neutralize techniques that affects waste from the composites formation.

CHAPTER 1.

COMPOSITE MATERIALS: CURRENT TRENDS

1.1. Defining the composite materials

The literature reports that composite materials do not have a definition generally valid and employed. For this reason, composite materials can be defined as being: materials made up of at least two constituents, possibly arranged geometrically, which maintain their properties and among which are established links at the level of interphase [1], [2], [3]. A composite material consists of two elements: *a matrix* playing the part of support for the second component, *reinforcement and/or additive* chosen depending on the field of using the formed composite material and the properties intended for these [29], [30].

The two constituents (phases of the composite), have different roles: one – *the matrix* - confers shape and dimensions of the material or structure, the other - *immersion phase* - ensures special properties of the material formed and it is the one that may be arranged orderly (geometrically) or randomly so that the composite material may have higher properties [4], 5], [6], [7].

The term of *composite* emerged in the engineering when it has been discovered that two or more combined materials can rectify a number of shortcomings compared to the use of stand-alone materials [5], [6]. A composite may be defined as a heterogeneous mixture of two or more homogeneous phases that have been bonded each other [5],[7],[8]. These phases may be: metallic, polymeric, ceramic, solid or even fluid [9], [10], [11], [12].

1.2. Classification of the composite materials

The composite materials can be classified as follows [31], [32], [33]:

– fiber-reinforced composite materials - long fibers placed in a preset arrangement or short fibers placed randomly;

– hybrid composite materials - made from several types of fibers;

– layered composite materials - made up of several layers, bound together;

– additivated composite materials.

Depending on the type of admixture material, we can distinguish two classes of composite materials [35]:

– additivated composite materials – where the additive is in the form of powder, with smaller sizes compared to those of the structure;

– fiber-reinforced composite materials – where the size of the reinforcing component has the same order of size as the structure dimensions.

From the geometrical point of view (Figure 1.2.), we can distinguish several types of phase arrangements in the volume of a material:

a) random dispersion of the spheres;
b) regular dispersion of filaments (oriented fibers);
c) regular arrangement of plates;
d) irregular geometry.

1.3. Ferrite modified composite materials

The type and form of nano-particles used for the enriching of polymer matrices have a significant effect on the mechanical properties of the composite material formed [37],[38]. The incorporation of inorganic particles into a matrix has been proven to be an effective way of improving the mechanical properties, especially the properties of material hardness. However, the content of additive necessary for improving the performance of a composite material must be maximum 20% of the volume [39], [40], [41], [42], [43], [44].

The additives have been used in the process of forming composite materials with a view to reducing the costs of materials achieved. It has been subsequently observed that entering an additive into a polymeric matrix leads also to improvements in the properties of the material concerned, such as increased rigidity, the ability to use the material at high temperatures, good thermal conductivity, etc. [39], [40], [41], [45], [46].

We can differentiate three basic shapes of nano-metric size additives used in the process of enriching composite materials (Figure 1.4.): A) regular, b) rod, c) flat.

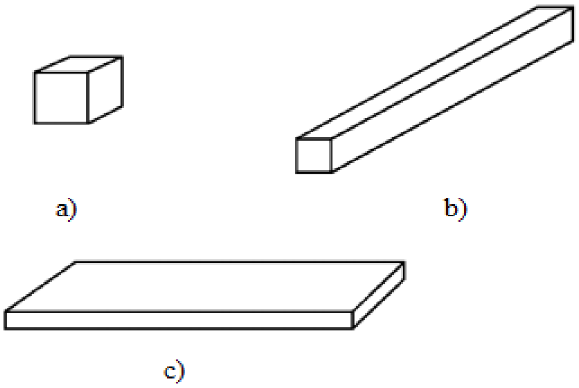


Figure 1.4. Shapes of nanoparticles: a) regular; b) rod, and c) flat. [177]

All three shapes of additives have a certain interest in the process of forming composite materials [40], [41], [42]. For example flat-shaped nanoparticles (mainly silicates and titanium) get a special attention since they are achieved through processes of controlled precipitation, exactly for preventing agglomeration. The particles with a regular shape and the rod-shaped ones (mainly from carbon or metal) are used with a view to forming materials intended for electrical applications [166], [177].

1.3.1. Barium ferrite

Barium ferrite ($BaFe_{12}O_{19}$) is a magnetic material, in the form of nanoparticles, having a hexagonal crystal structure, shown in Figure 1.5., resistance to high temperature, resistance to corrosive and oxidative environments.

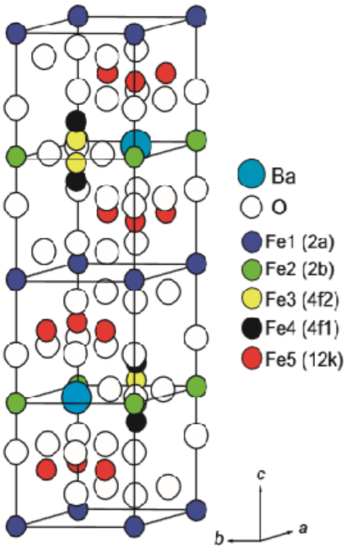


Figure 1.5. Crystal structure of barium ferrite – $BaFe_{12}O_{19}$. [56]

1.3.2. Strontium ferrite

Strontium ferrite belongs to a class of magneto-lead materials having a mixed spinel (S = $Fe_6O_8^{-2}$ and S* blocks) and a hexagonal one (strontium contains $SrFe_6O_8^{-2}$ and R* blocks), with nearly compact structure with an atom of Sr^{2+} type substituting for an oxygen atom and Fe ions that occupy the interstices [63], [64]. The Z-type hexa-ferrite cell units are made up of 44 atomic layers, which are grouped on the C axis. This structure can be described as a set of six types of blocks: R, S, T, R*, S* and T*. Where R, S, T are independent blocks, the asterisk shows the characteristics of the same package, rotated 180° around the C axis. [184].

1.4. Polymer matrix

The polymer matrix is a continuous phase, which should have the ability to incorporate the disperse component without changing or destroying it. In most cases represents the matrix is the plastic part of composite materials, having a strength lower than that of the complementary (additive) material which is included [174].

Generally the matrix should fulfill certain basic conditions [38], [46], [47], [48], [66].

– to be ductile, plastic and deformable;
– to have a high elasticity modulus;
– to perform a good connection to the complementary material interface;
– to ensure a better distribution of the embedded material.

1.4.1. Epoxy resins

The polymer composite materials use as matrix an epoxy resin. Epoxy resins have been discovered in 1909 [57], [126]. Over the years they have become synonymous with performance. They fall in the category of materials of interest in practice, thanks to their properties (used as stand-alone material) and also for improving the properties of formed materials (used as additive: structural adhesives, polymeric matrix or coatings). In the literature these resins are presented as having advantages in use, such as: [75], [76], [77], [78], [79], [80], [81], [82], [83], [84].

– they form in a relatively low temperature range of 50-130°C;
– show resistance to acids, solvents and alkaline substances;
– are thermally stable up to a temperature of about 250°C;
– have an increased hardness;
– are easy to handle;
– adhere easily to other materials.

Table 1.1. Comparative characteristics of the polymers

Thermoplastic Polymers	Thermoset Polymers
- flexible and elastic	- hard and unsound
- can be stretched in wires and sheets	- cannot be stretched in wires and sheets
- gets dissolved in solvents	- does not dissolve in solvents
- low mechanical properties	- good mechanical properties
- low water absorption	- higher water absorption
- good electrical properties	- low electrical properties
Ex: acrylonitrile butadiene styrene (ABS) Polyvinyl Chloride (PVC) polyester ether ketone (PEEK) fluoropolymers polyethylenes polypropylenes polysulfonates	**Ex**: epoxy resins polyesteric vinyl ester polyurethanic acrylic phenolic melamines

1.5. Mechanical properties of the modified composite materials

The behavior of materials during mechanical loadings (caused by external forces), depends on the specific characteristics of the material of which are formed the components and which are hereinafter called mechanical properties [167], [171].

Knowing the mechanical properties of polymer materials is necessary in all areas where these are applicable. Thus, the rigidity and mechanical strength are key properties for most applications where composite materials are used with polymer matrix [92], [174].

Due to this fact it is required a differential treatment of structures and properties of the additivated and/or reinforced composite materials. Within this differentiated approach are also taken into account the properties of added material that goes into the composite materials [93], [94], [95],[96].

The behavior of materials during mechanical loadings depends on the chemical structure and/or the morphological structure, some of them having a stronger influence than others and being called properties-generating structures. Nevertheless, it is not the morphological and structural details that influence the mechanical properties of composite materials [167], [171], [174].

1.5.1. Compression Tests

A compression test is the plastic deformation of a material under the action of a force, called compression force. Compression behavior depends on the matrix nature and the presence of additive material, the latter being the one that causes cracks in the material.

1.5.2. Bending Tests

A bending test can be defined as the mechanical testing of materials during which the effort is distributed linearly in the material, which leads simultaneously to stretching an area and compressing the other area. In the case of composite materials with additives, the rigidity is higher due to additives. The reverse consists in the influence of particles concentration, which when is high, can cause a decrease of bending resistance [102].

1.5.3. Tribological Tests

Tribology is the science that studies the wear of surfaces in motion and contact among them(friction). The tribological properties of materials depend both on the nature of surfaces that come in contact and on the following factors [106], [107], [108]:

- contact pressure and surface loading;
- relative speed in the rotation movement of the two surfaces;
- values of surface temperatures;
- nature of movement (continuous, intermittent)
- Surface roughness.

1.6. Electromagnetic Properties

The researchers' interest in the field of polymer materials is to achieve composites with polymer matrix having higher electrical properties [14], [115]. The research purpose is to increase the value of electrical conductivity through various methods, starting from carrying out polymer composite materials (by additivation or reinforcement with various powders and/or fibers that have better electrical properties), up to metal coating on the exposed surfaces of composite structures [91], [164], [165], [173].

Making composite materials that would have higher electrical properties is actually a real interest for researchers, but at the same time it has also a huge inconvenience as the improvement of electrical properties restricts the use of composite polymer structures in applications exposed to the risk of electrostatic charge [116], [117], [118], [164].

1.7. Thermal Properties

The thermal properties are a current interest as concerns the process of forming a composite material (with epoxy matrix), since both polymerization temperature and melting temperature of the material are high. These aspects do not refer to the materials formed under laboratory conditions, but the commercial materials, coming from outside, having the most various destinations and extreme conditions of operating (high temperature, aggressive chemical environments, etc.). Actually, analyzing a material from the thermal point of view, it is nothing but studying the state changes of a material [127].

1.8. Hydro-Thermal Properties

Water is known as a compound with adverse effects on the material structural properties. According to the literature it is recognized that water absorption occurs only in the amorphous phase.

1.9. Objectives of the Research

Polymer nano-structured composite materials are more and more often used in industry, a reason for which the development of a polymer composite material is a process that has to take into account all possible situations with a view to reaching the proposed goals.

The main purpose of this study was to emphasize the effect of modifying a polymer matrix (epoxy resin) with ferrite nano-powders (two types of nano-ferrites have been purchased) and to compare the effects of this type of approach on three different polymers belonging to the same class. Introducing nano-ferrites in the polymer matrix leads, obviously, to a change in all the polymer properties, the most targeted by this approach being, however, the electromagnetic properties. Despite the relatively high price of nano-metric powders of the two ferrites, this method of modifying the polymers properties remains a cheap one since forming materials does not involve sophisticated equipment or last generation technology.

Nevertheless, entering nano-ferrites in the polymer matrix does not have only the expected effects (change in the electromagnetic properties) but also effects on the mechanical properties - as we have shown above, the presence of a particle in the polymer matrix means an interruption in the polymer network, with effects regarding the transmission of charges. Therefore, it is necessary to analyze all properties of the formed materials the more so as this type of polymer could be used in the future to form more complex composites (reinforced with fibers or fabrics, modified at the same time with other agents).

In this context, this study could be considered a success if the following objectives are attained:

- determining the manufacturing characteristics of the three epoxy resins chosen;
- analysis of strategies for the dispersion of nano-powders in the pre-polymer mixtures;
- establishing the dispersion strategy based on the manufacturing properties analysis of the three polymers;
- analysis of the requirement of specimens for testing in order to determine the number and type of samples that will be formed;
- establishing the type of mold and mold release strategy;
- forming the materials and strengthening them by heat treatments recommended by the manufacturers of polymers;
- setting the testing strategy, given for some test are required large-sized specimens;
- extracting the specimens necessary for tests;
- testing the materials electromagnetically, through the electro-technical method;
- testing the electrical conductivity of materials by direct method;
- thermal testing the formed materials in order to determine the specific heat of the formed materials;
- structural analysis of the materials by electron microscopy techniques;
- structural analysis of materials through the Raman spectroscopy;
- tribological testing of formed materials;
- studying the mechanical properties on compression of the materials formed;
- study of the mechanical properties during bending of the materials formed;
- analysis of water absorption in the materials formed;
- statistical analysis of experimental data;
- analysis of results achieved and data interpretation.

CHAPTER 2.

NANO-FERRITE MODIFIED EPOXY MATRIX

2.1. Materials Used

For achieving this study three types of epoxy resins have been used: Epoxy RESIN C, produced by Bostik – (that will be hereinafter referred to as C-type resin), Epyphen RE 4020, produced by R&G Gmb Waldenbuch – (hereinafter referred to as E-type resin) și Epoxy RESIN HT2, produced by R&G Gmb Waldenbuch – (hereinafter referred to as HT-type resin). These resins have been selected and used as epoxy matrix as they have a molding shrinkage factor very low, unlike other types of resins. Each resin type corresponds to a specific hardener: Härter C, Epoxi HARDENER DE 4020 and HARDENER HT.

The objective of this study was to form composite materials with special electromagnetic properties, by modifying a polymer matrix with ferrite nano-powders (Barium ferrite and strontium ferrite, respectively). On the other hand, the presence of ferrite nanoparticles causes changes in the mechanical and thermal properties of the matrix, so that it is also necessary to analyze these properties.

2.2. Forming Materials

Forming composite materials with ferrite nanoparticles-modified epoxy matrix was carried out in laboratory conditions and observed the steps shown in Figure 2.3.

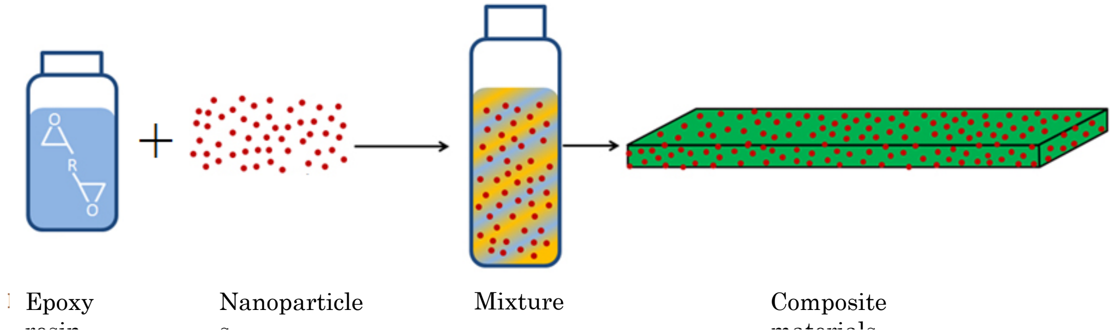


Figure 2.3. Steps of forming the composite nano-powder formed

There are multiple methods of forming composite materials with thermosetting matrix, these being determined, on the one hand, by the intended properties of the materials formed and, on the other hand, by the pre-polymer maneuverability.

There have been established protocols for preparing the molds (polypropylene tubes and flat glass molds with a rubber gasket), so as to be possible an intact extraction of materials (without damaging the edges or surfaces). In the process of casting the materials the following steps have been covered:

1. Preparing the mold;
2. Changing the epoxy systems;
3. Casting mixture in the mold;
4. Closing the mold;
5. Applying thermal treatment;
6. Extracting the specimens.

2.3. Conclusions

Designing and forming the polymer nanocomposites should be carried out mostly based on certain tests. The empirical use of parameters relating to the selection of components and forming technique is successful in most cases.

The key point for parameters optimization in order to get the best quality materials consists in knowing and understanding the nature of nanoparticles, studying the physical and chemical properties of the polymer, composite material performance, as well as the manners to subsequently process them, etc.

The use of modification agents in order to modify epoxy matrix constitutes a reliable technique for forming a polymer composite material, taking into account the agent characteristics, its dispersion into the matrix volume and method of forming.

Thanks to the characteristics of the specific surface of nanoparticles, ther is a possibility of wide variety as concerns the development of new techniques for the production of modified composite materials.

About the purpose of forming ferrite-modified materials, it can be said that it is closely related to:

- choosing the elements in order to achieve the casting mold and the method of forming the materials;
- dispersion mode of the modifying agent in the epoxy matrix, which results in a change of the final properties of the materials formed;
- if the concentrations, combinations and types of additives used are not studied, there may occur interactions among components, leading to: preferential orientations of the modifying agent and, implicitly, the occurrence of non-uniformities in the formed material volume;
- the epoxy resins properties do not change significantly in the presence of only one type of modifying agent because the amount is very small.

CHAPTER 3.

STRUCTURAL ANALYSIS OF COMPOSITE MATERIALS MODIFIED WITH NANO-FERRITES

3.1. Overview

Spectroscopy is the interaction study of the electromagnetic radiation with the matter. Spectroscopic methods may be based on phenomena of emission, absorption, fluorescence or scattering. This method is used in order to determine the qualitative (establishing the sample identity) and quantitative (determining the concentration of analytic) analysis [155],[156],[163].

3.2. Raman Analysis

3.3. Results and Discussions

The Raman spectral analysis was carried out for epoxy resins and epoxy composite material modified with ferrites. The spectra obtained have been processed for rendering in the comparative graphical form (Figure 3.1., Figure 3.2. and Figure 3.3.) and aimed to emphasize the possible chemical changes occurred in the structure of composite materials formed.

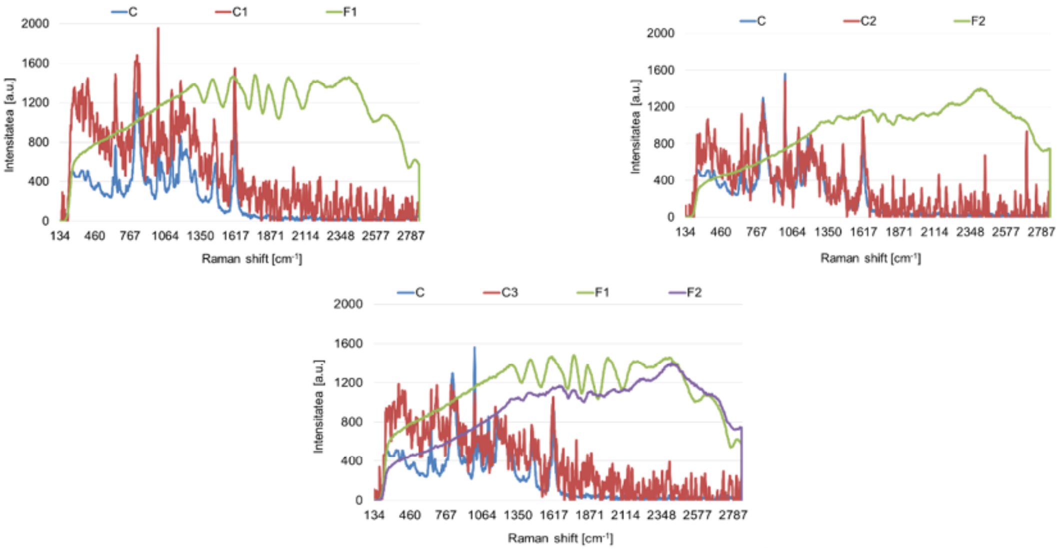


Figure 3.1. Raman spectra for composite materials with C-type epoxy matrix.

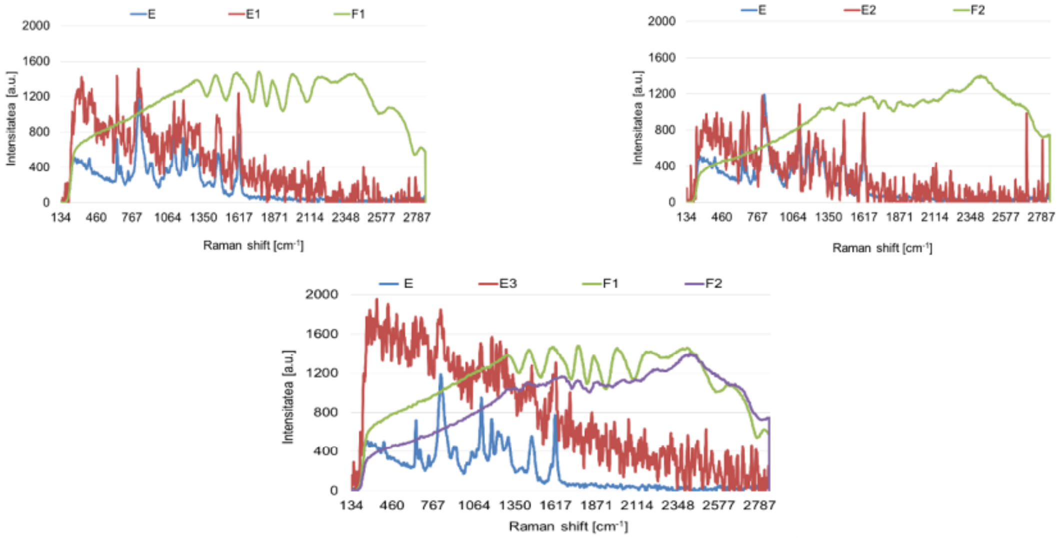


Figure 3.2. Raman spectra for composite materials with E-type epoxy matrix.

Materials analysis was possible to be made by means of a laser emitting 780 nm, the laser power being > 500 mW. The acquisition of spectra ranging from 0 - 30000a.u. in the case of unmodified epoxy resins (control) and from 9 - 2000a.u. in the case of epoxy resins modified with nanoferrites. Background and fluorescence corrections were applied to all spectra.

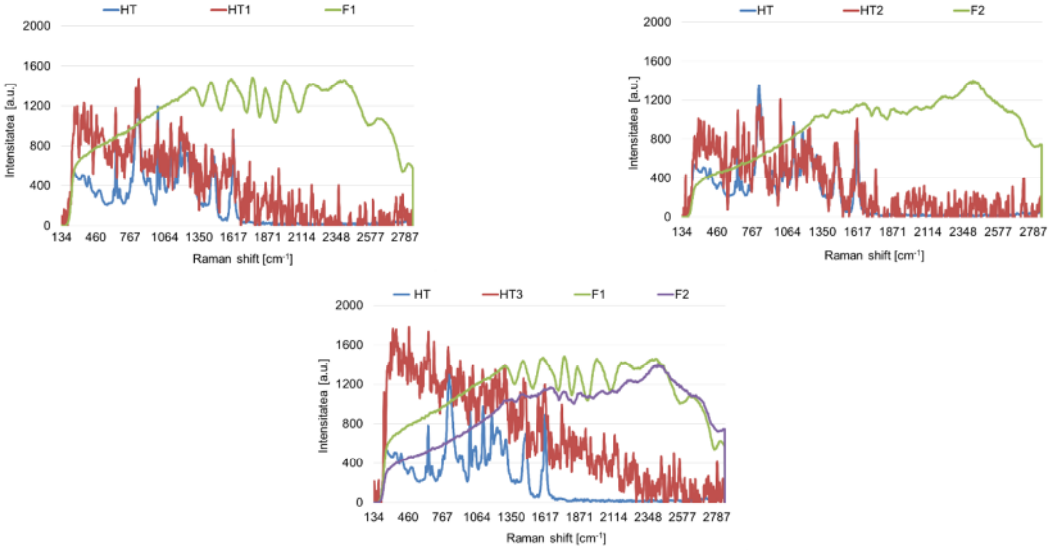


Figure 3.3. Raman spectra for materials with HT-type epoxy matrix.

3.4. SEM Analysis

3.5. Results and Discussions

In Figure 3.5., Figure 3.6. and Figure 3.7. are shown the SEM images and X-ray emission spectrum for materials with C-type epoxy matrix modified with nano-ferrites.

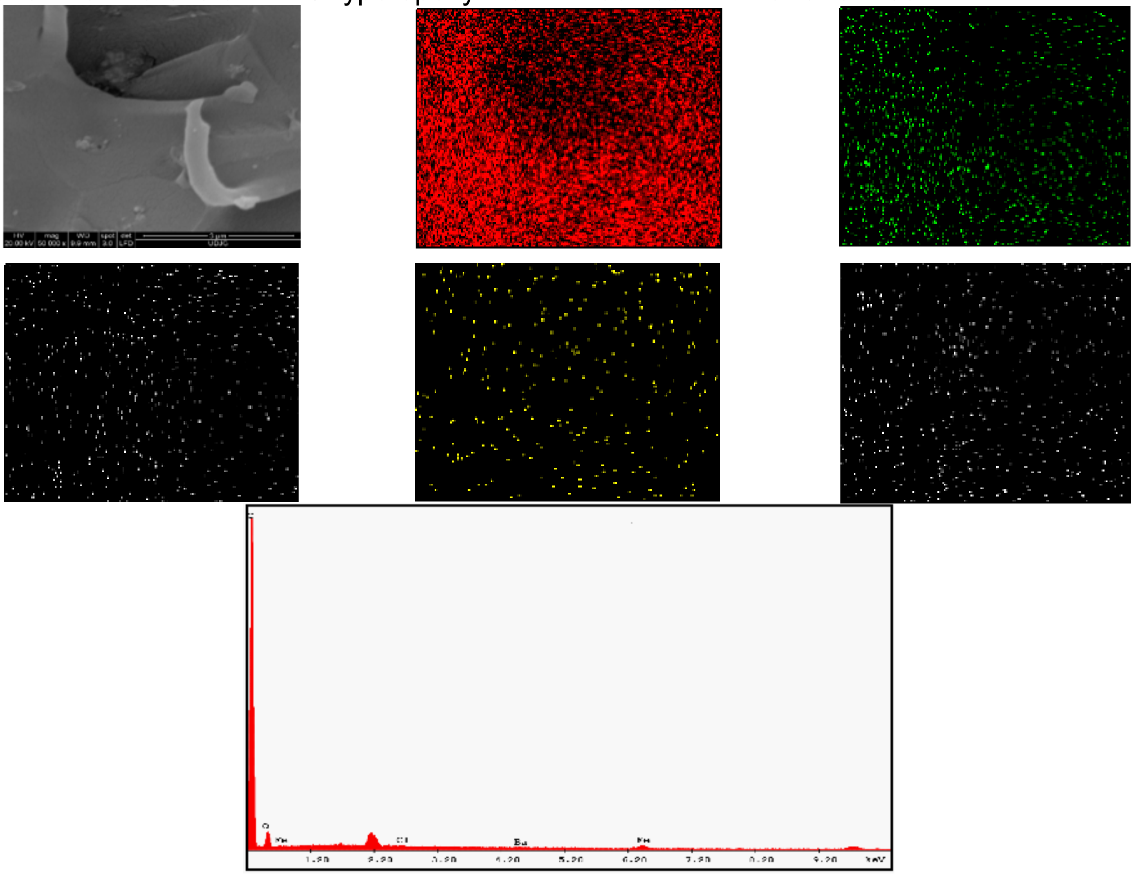


Figure 3.5. EDAX-SEM spectral analysis for C1 material (X50000).

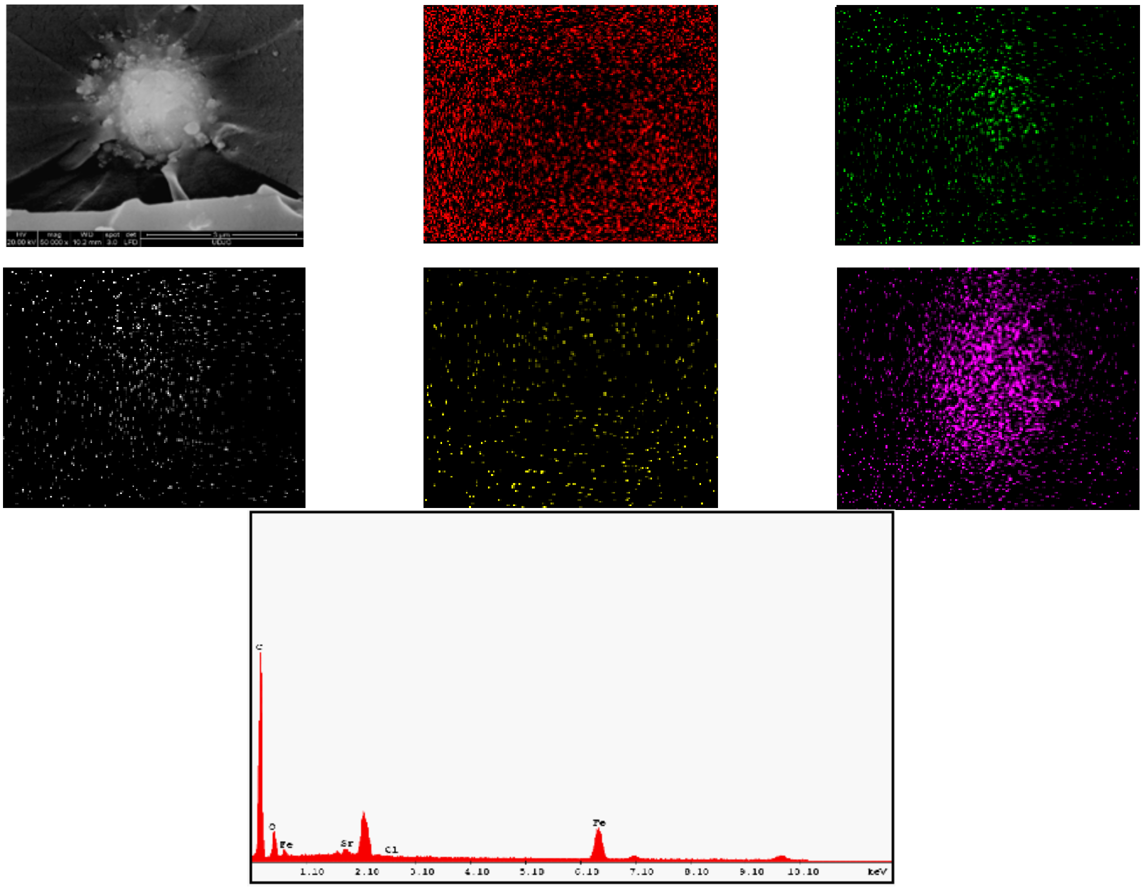


Figure 3.6. EDAX-SEM spectral analysis for C2 material (X50000).

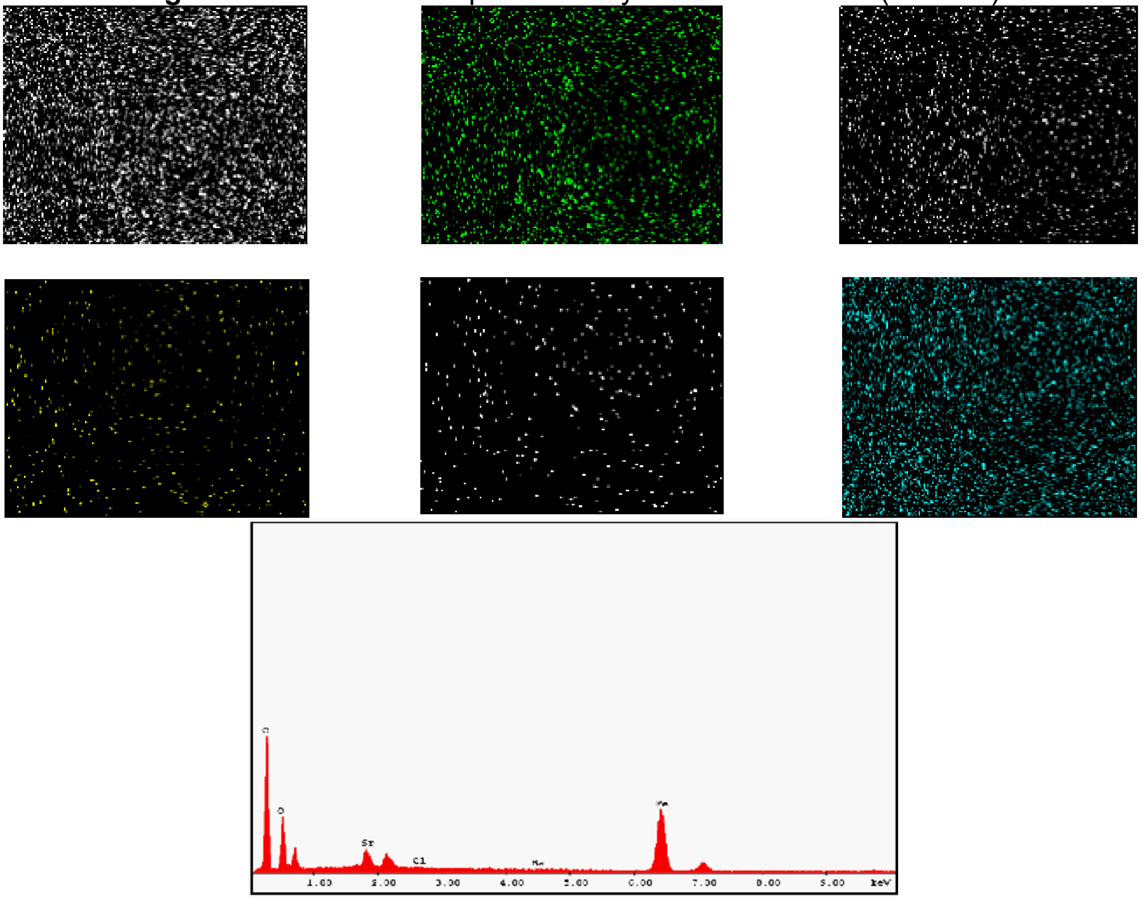


Figure 3.7. EDAX-SEM spectral analysis for C3 material (X50000).

As it can be observed, the most significant is the presence of carbon followed by oxygen (present both in the polymer structure and in the ferrite composition).

In general, the SEM images were centered on the brightest points on the surface (areas with high metal concentrations) .

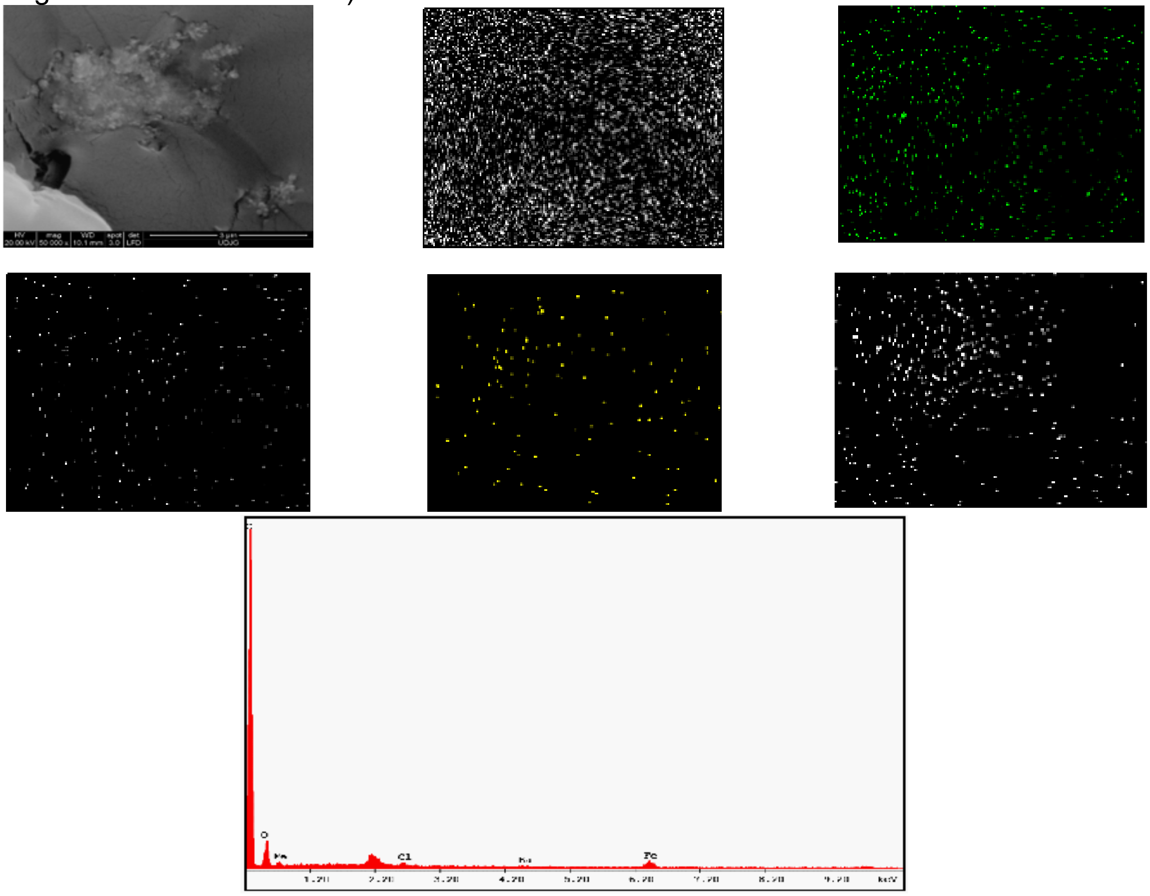


Figure 3.9. EDAX-SEM spectral analysis for E1 material (X50000).

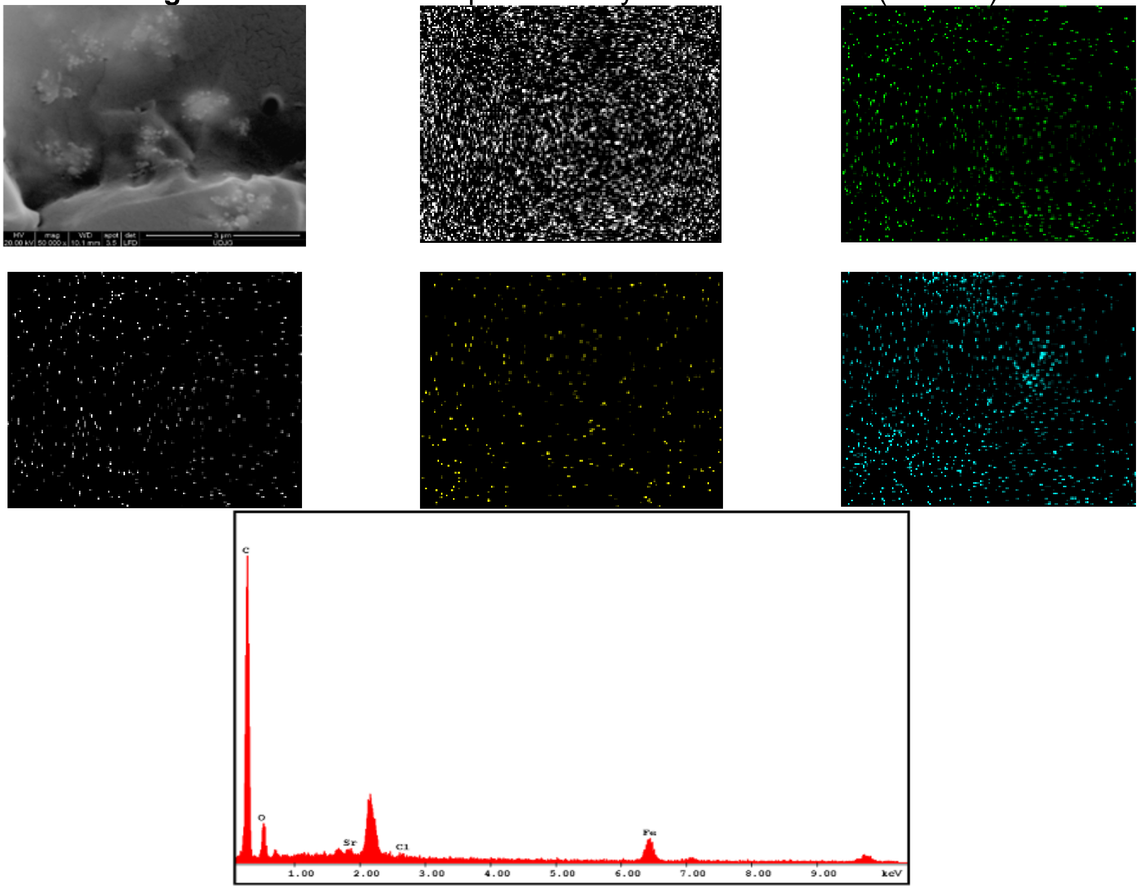


Figure 3.10. EDAX-SEM spectral analysis for E2 material (X50000).

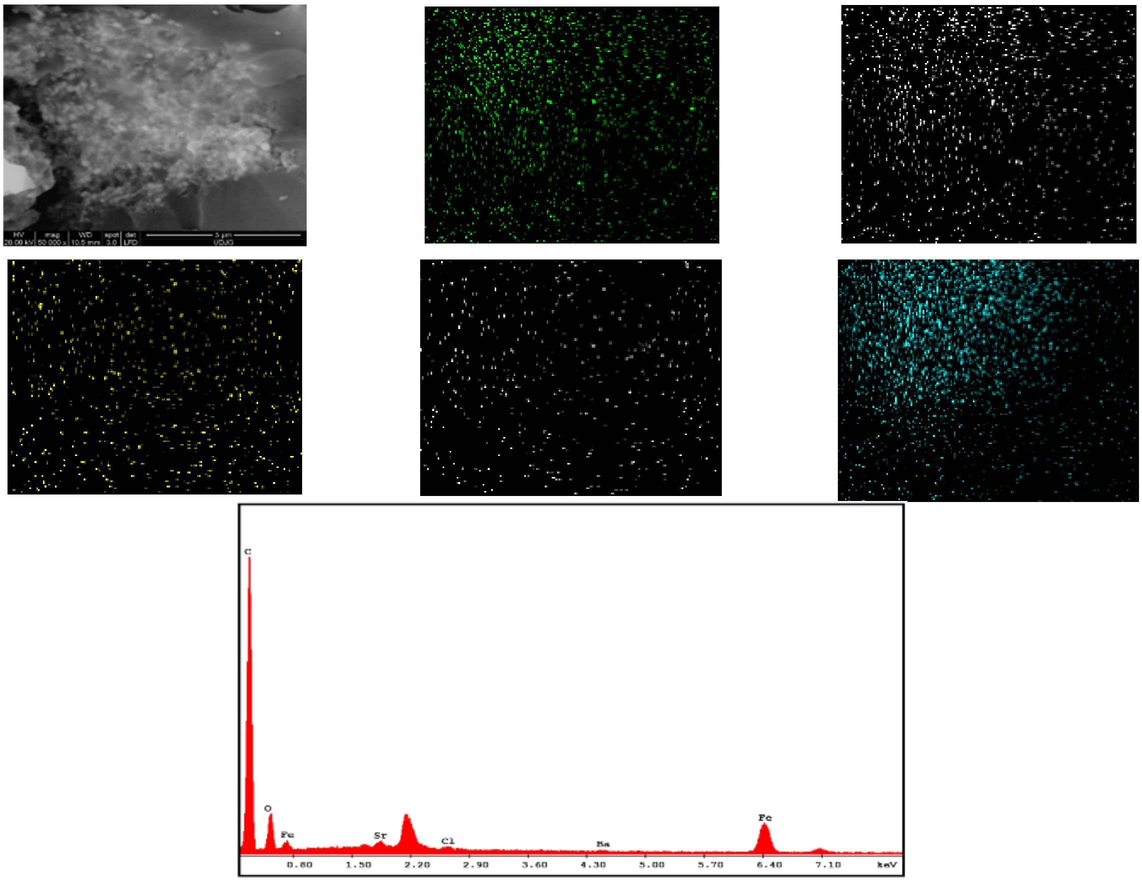


Figure 3.11. EDAX-SEM spectral analysis for E3 material (X50000).

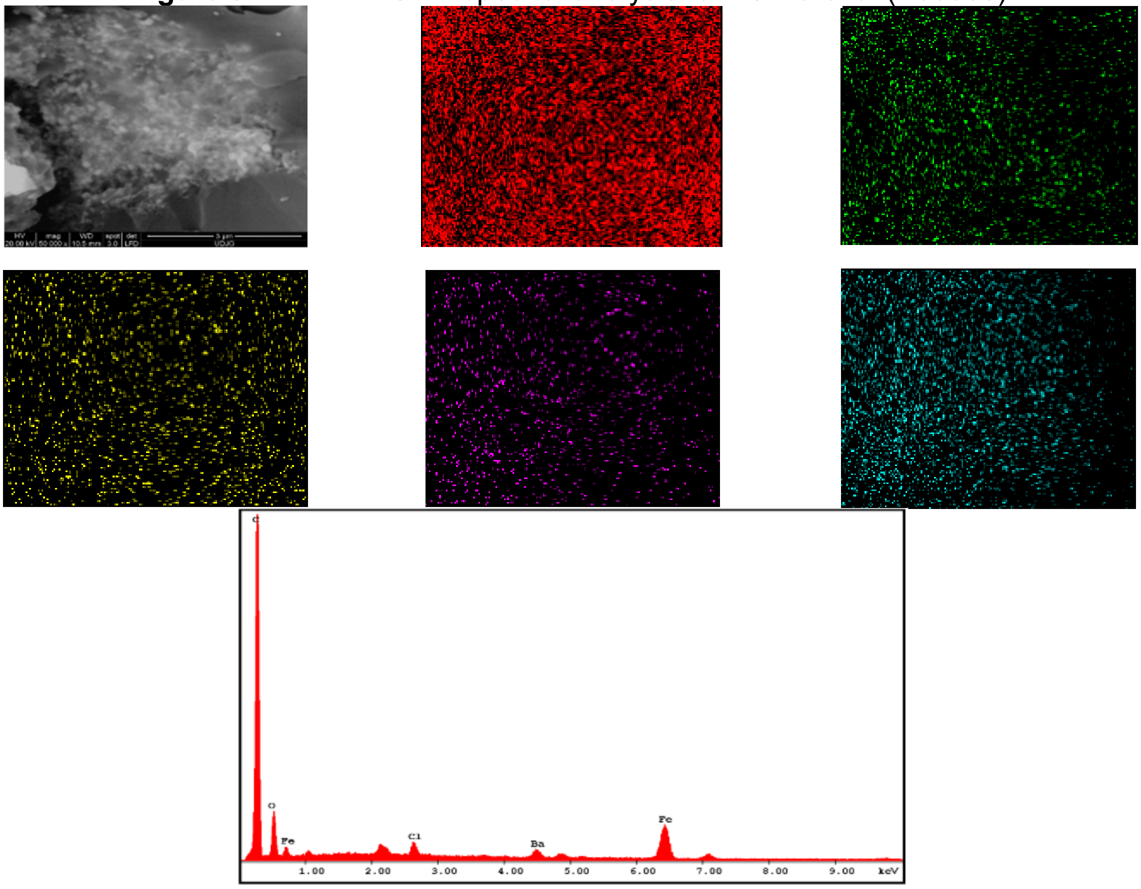


Figure 3.13. EDAX-SEM spectral analysis for HT1 material (X50000).

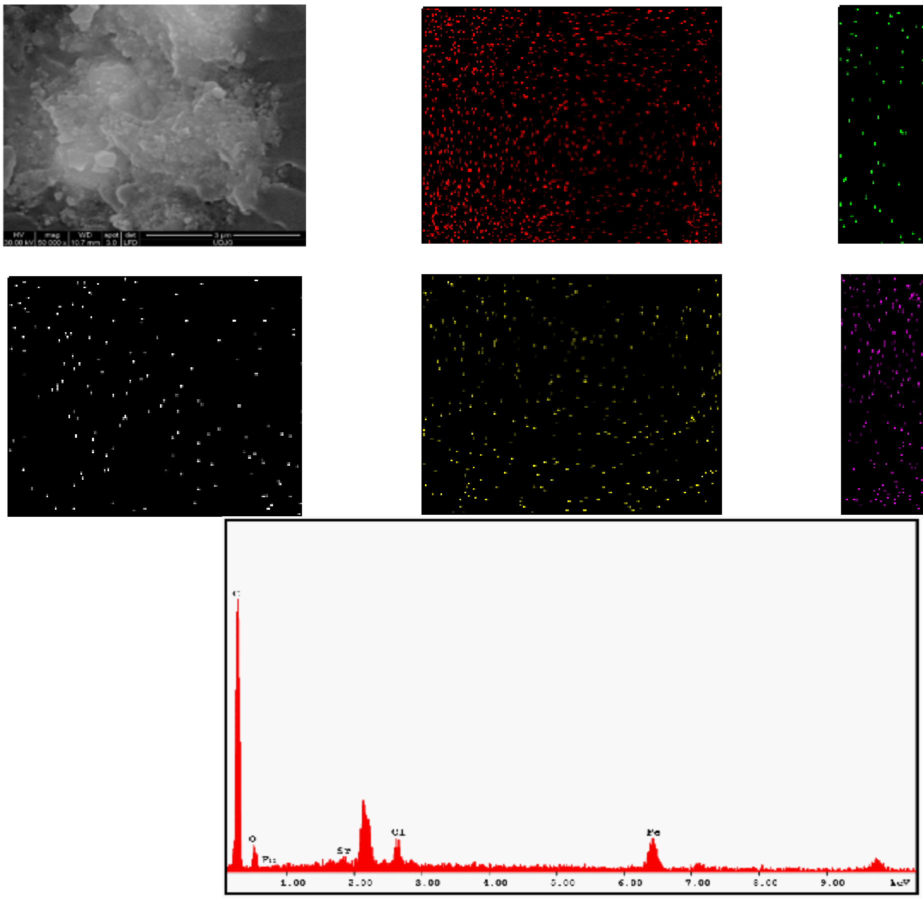


Figure 3.14. EDAX-SEM spectral analysis for HT2 material (X50000).

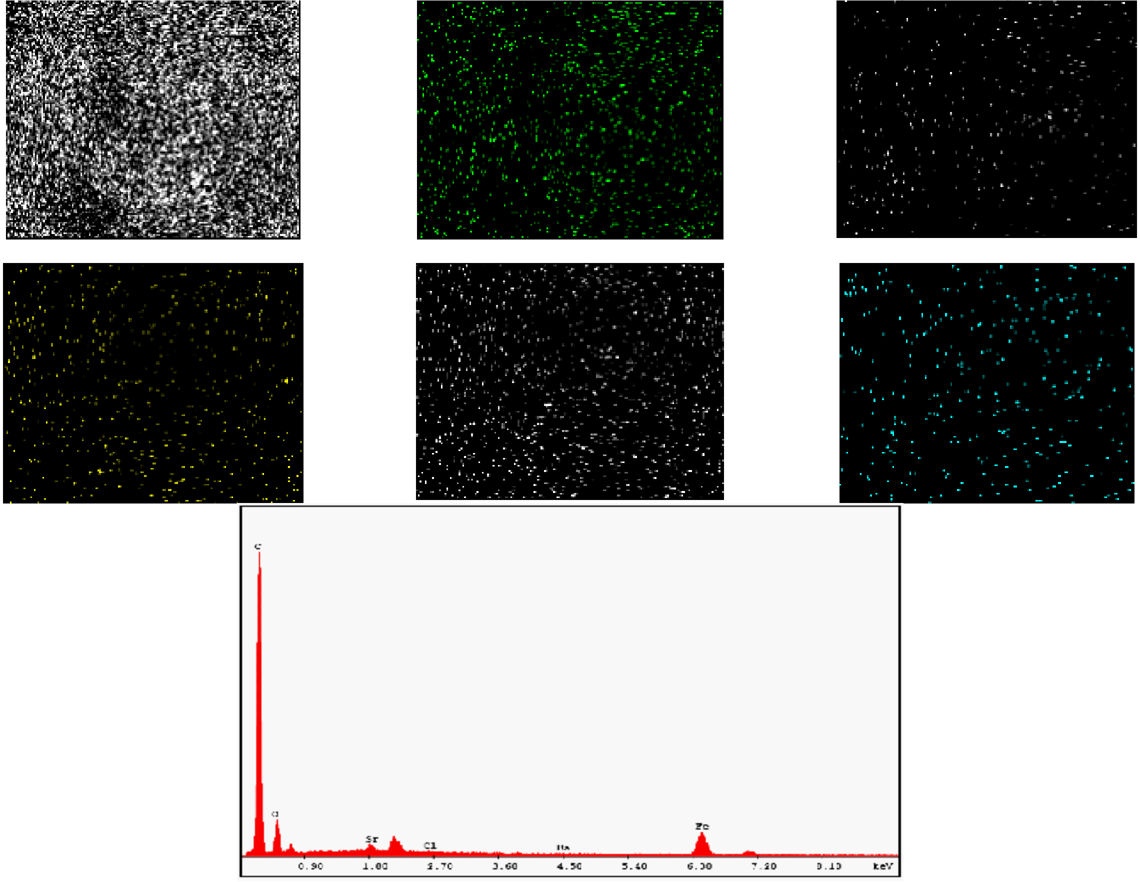


Figure 3.15. EDAX-SEM spectral analysis for HT2 material (X50000).

An analysis of fracture surfaces images of the three polymers outlines morphological differences depending on the nature of each of them. Given that the fractures have been carried out in the same way, the different appearance of fractures shows differences between their chemistries and, as a consequence, differences concerning their mechanical properties.

After analyzing a few areas of formed materials, it can be observed that the ferrite nanoparticles introduced so as to modify the epoxy system properties had a different dispersion. This is due, on the one hand, to the type of modifying agent and, on the other hand, to its concentration in the volume of formed material.

3.6. Conclusions

Raman microscopy is an analysis tool non-destructive and sensitive at the same time, able to provide a rapid identification of chemical species present in the analyzed material.

The microscopic Raman mapping has proven to be a method effective and efficient at the same time with a view to characterizing the composition of formed material. The Raman analysis enables the access to information related to wavelengths ranging from 2-100 μm, which caused this kind of analysis to be an ideal technique for studying the formed materials.

The materials have been analyzed by means of the scanning electron microscopy (SEM) and presented morphologically.

By using the dispersed X-ray (EDAX) analyzes, could be possible the deceleration of barium and strontium ferrite nanoparticles in the volume of materials, as well as material characterization in terms of quality and quantity.

The inclusion degree of nanoparticles both from the qualitative and quantitative point of view is relatively small.

CHAPTER 4.

ANALYSIS OF THE MECHANICAL PROPERTIES OF NANOFERRITE-MODIFIED COMPOSITE MATERIALS

4.1. Overview

4.2. Compression Tests

The mechanical tests on compression of the composite materials formed have been carried out on the mechanical tests machine, INSTRON 8030 model. Determining the characteristics of composite materials tested was possible using the Bluehill 3 software.

The compression tests have been run with the speed of 1.3 mm/min. There have been carried out five tests for each of the studied materials and the numerical results presented represent the average values of those obtained for each specimen in part.

4.3. Results and Discussions

Below are presented the contact force curves - degree of compression for the materials with epoxy matrix modified with ferrite nanoparticles so as to determine the influence of two types of ferrites (barium and strontium) on the compression behavior in three points. For each material have been made on average five tests (Figure 4.1., Figure 4.2. and Figure 4.3.).

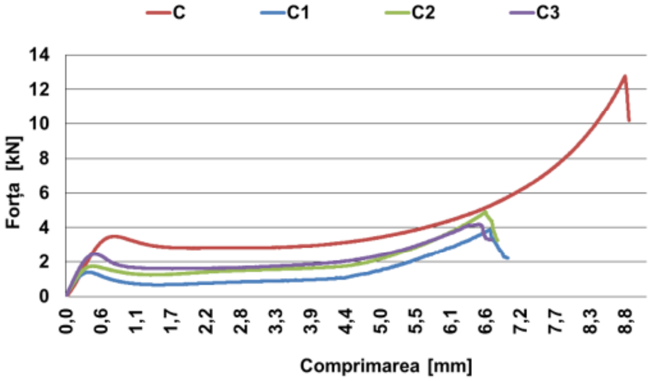


Figure 4.1. Compression behavior of C-type epoxy matrix materials.

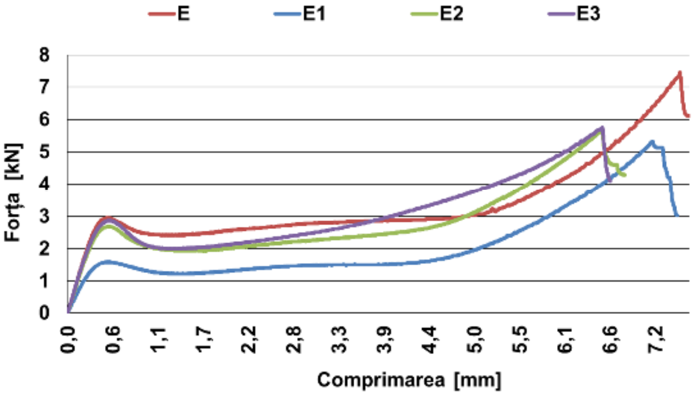


Figure 4.2. Compression behavior of E-type epoxy matrix materials.

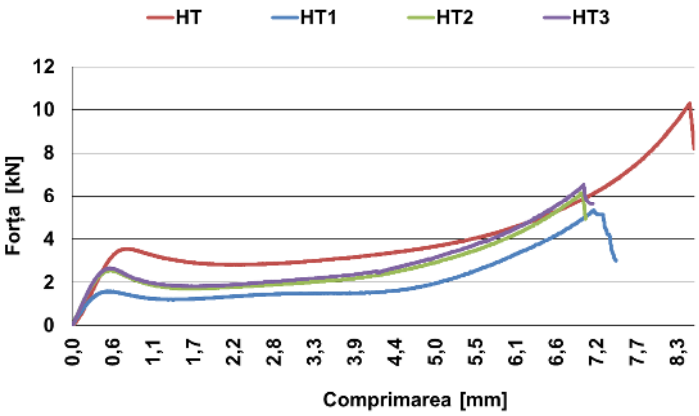


Figure 4.3. Compression behavior of HT-type epoxy matrix materials.

In Figure 4.4. and Figure 4.5. are plotted the most significant parameters that can give information concerning the behavior of materials modified with C-type epoxy matrix compared to the unmodified system, during the mechanical tests of compression. These parameters have been obtained based on the curves shown in Figure 4.3.

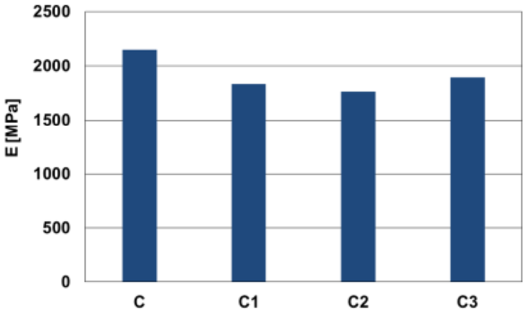


Figure 4.4. Elasticity modulus on compression of the materials with C-type epoxy matrix.

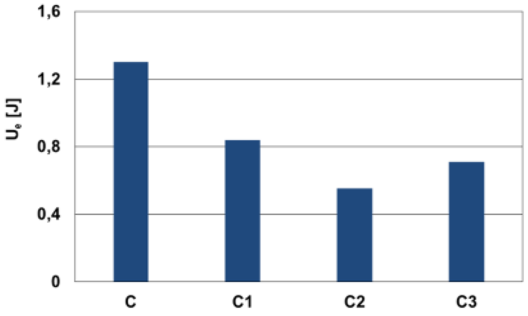


Figure 4.5. Energy at the elasticity limit of materials with C-type epoxy matrix.

In Figure 4.6. and Figure 4.7. are plotted the values of elasticity modulus and of compression charging, depending on the behavior of materials with E-type epoxy matrix, presented in Figure 4.4. In both cases the values of parameters determined for unmodified materials (E) show the highest values compared with the unmodified materials. If materials E2 and E3 are studied, it can be seen a value approximately equal to the elasticity modulus, despite the concentration differences of the modifying agent. This type of behavior could be explained by assuming that there is a high quality of the polymer interphase - strontium ferrite. This leads to the idea that E-type epoxy resin modified with two types of modifying agent gives the composite material formed (E3) possibilities for use in environments that may include mechanical loading.

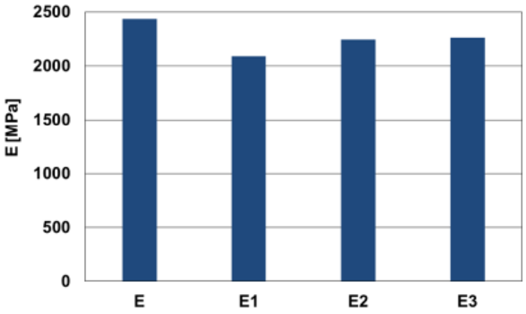


Figure 4.6. Elasticity modulus on compression of the materials with E-type epoxy matrix.

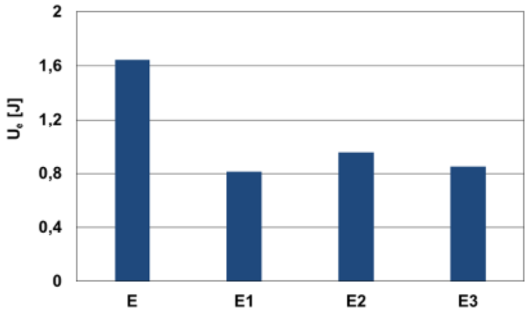


Figure 4.7. Energy at the elasticity limit of materials with E-type epoxy matrix.

In Figure 4.8. and Figure 4.9. are highlighted two parameters resulting on the curves analyzed in Figure 4.3., which outlines the behavior of materials with HT-type epoxy matrix and the effect of modifying agent on the compression properties.

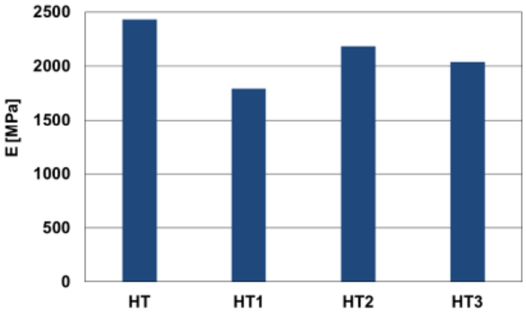


Figure 4.8. Elasticity modulus on compression of the materials with HT-type epoxy matrix.

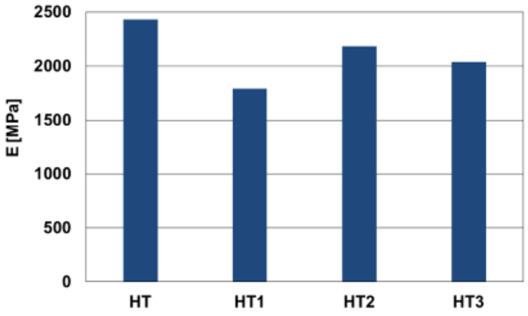


Figure 4.9. Energy at the elasticity limit of materials with HT-type epoxy matrix.

For materials with HT-type modified epoxy matrix, the strontium ferrite modifying agent from the composition of HT2 material confers a good mechanical behavior to compression, while the barium ferrite modifying agent from the composition of HT1 material reduces the elastic properties on compression, fact evidenced by the values of elasticity modulus in compression (Figure 4.8.) and the energy at the elasticity limit (Figure 4.9.).

In the case of materials with E-type epoxy matrix, the strontium ferrite presence neutralizes the effects of barium ferrite while in the case of materials with HT-type epoxy matrix, the effect is reversed. If we take into account that all materials have been formed in the same conditions and with the compliance same proportions of the agents of change, it can be concluded that strontium ferrite is proposed for use in order to form composite materials with special properties.

4.4. Bending Tests

The mechanical tests on compression of the composite materials formed have been carried out on the mechanical tests machine, INSTRON 8030 model. Determining the characteristics of composite materials tested was possible using the Bluehill 3 software.

The three-point bending tests have been carried out according to standard SR EN ISO 14125, on cylindrical specimens (110x8 mm) as shown in Figure 4.13. The travel speed of the die was 5 mm/s. There have been made a number of five bending tests for each of the materials formed.

4.5. Results and Discussions

From plotting the curves of loading - elongation of the materials with C-type epoxy matrix, it can be noticed that depending on the type of modifying agent used, the behavior of materials is different. Thus if comparison is made between the unmodified epoxy system and modified materials is observed that the presence of the modifying agent led to a worsening of the inhomogeneity type in the material structure, so the mechanical bending results being weak. If comparisons are made between the modified materials, it can be seen that the best answers following the three-point bending have been provided by the C3 material modified with two types of modifying agent (barium ferrite and strontium ferrite).

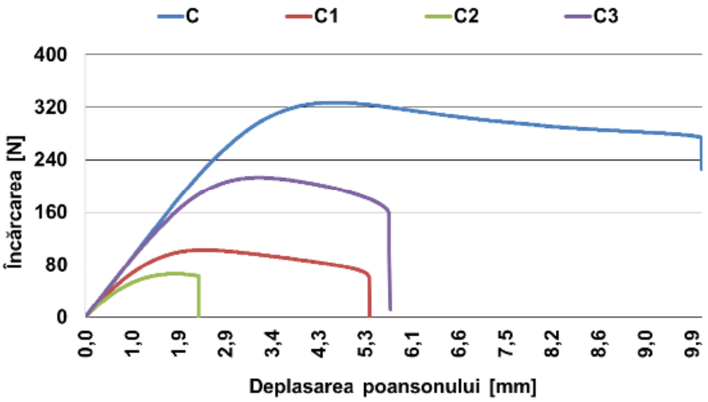
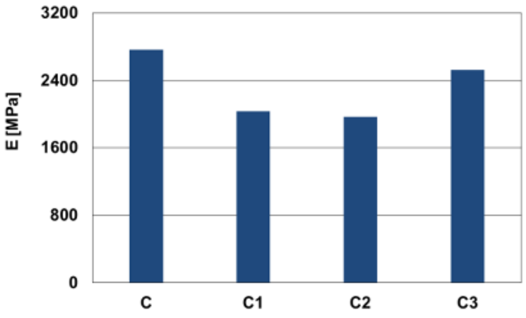


Figure 4.14. Bending behaviour of materials with C-type epoxy matrix.

This aspect that can lead to the idea of forming the interphase modifying agent - epoxy system, a phenomenon not met in the case of C1 and C2 materials. The latters contain the same modifying agent in a proportion of 5%, used separately.



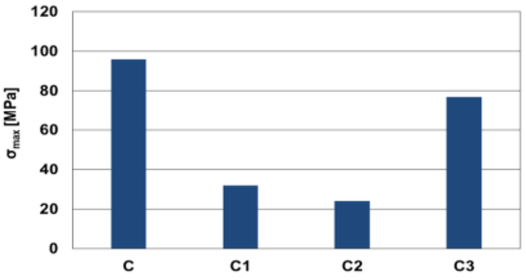


Figure 4.15. Apparent module of bending elasticity for materials with C-type epoxy matrices.

Figure 4.16. Maximum loading on bending of materials with C-type epoxy matrix.

In Figure 4.17. are shown the loading - elongation curves after running the mechanical bending tests for the materials with *E*-type epoxy matrix.

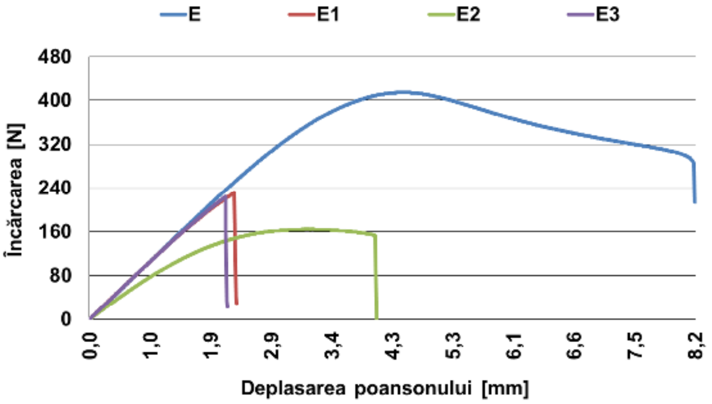
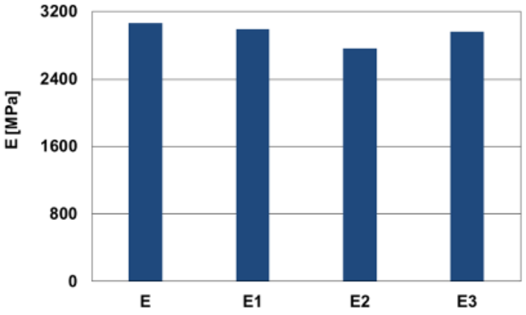


Figure 4.17. Bending behaviour of materials with E-type epoxy matrix.

From plotting the loading - elongation curve for materials with *E*-type epoxy matrix, (Figure 4.17.), it can be observed a completely different behavior of the modified materials compared to the unmodified epoxy system. If the comparison is made strictly on the modified materials, then we can say that the E1 and E3 materials show resistance to good loading, an elastic behavior closed to that of the unmodified epoxy system, while the E2 material shows weak properties in the elastic area, but compared to the two other modified materials it has a better plastic behavior.

In Figure 4.18. and Figure 4.19. are presented two important parameters that can provide information regarding the behavior of materials with E-type epoxy matrix modified with nano-ferrites: apparent elasticity modulus and maximum loading on bending.



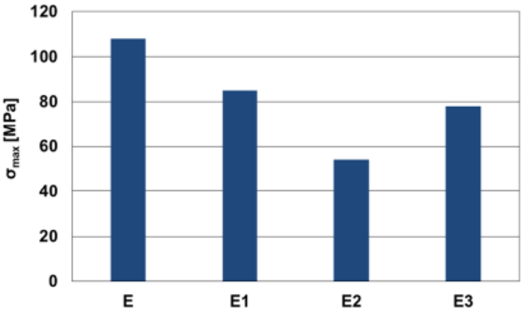


Figure 4.18. Apparent elasticity modulus on bending of the materials with E-type epoxy matrix.

Figure 4.19. Maximum loading on bending of the materials with E-type epoxy matrix.

Through a comparison of the behavior of these materials studied, are seen very similar values of the apparent elasticity modulus. The best values have been recorded in the case of E1 material (where the modifying agent interacted very well with polymer) and of E2 material, respectively (where barium ferrite has succeeded in substituting to a large extent the properties of strontium ferrite), thus conferring the formed material remarkable elastic properties, (Figure 4.18.)

In Figure 4.17. are shown the loading - elongation curves after running the mechanical tests of bending for the materials with HT-type epoxy matrix.

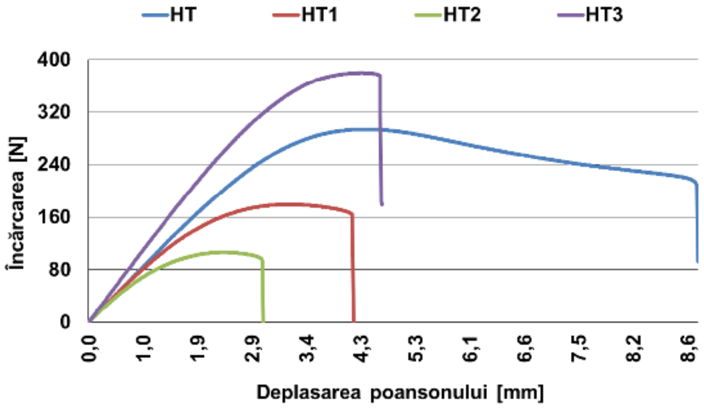


Figure 4.20. Bending behaviour of materials with HT-type epoxy matrix.

For the HT material representing the unmodified epoxy system and the HT3material containing combinations of the two types of modifying agent, the elastic modulus values are roughly the same (Figure 4.21.). If we refer to the mechanical properties of these two types of materials, we will observe that the HT3 material has also a good bending resistance (Figure 4.22.), a fact that is due to the amount of modifying agent and their mechanical properties.

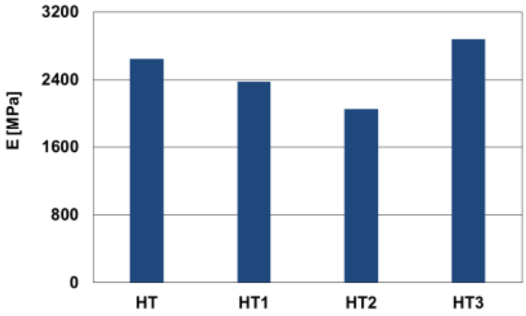


Figure 4.21. Apparent elasticity modulus on bending of the materials with HT-type epoxy matrix.

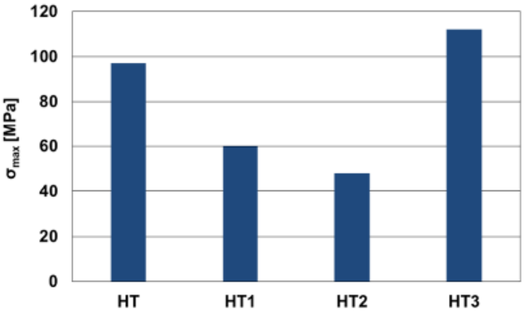


Figure 4.22. Maximum loading on bending of the materials with E-type epoxy matrix.

Following the analysis of charts resulted after running the tests for bending in three points, it appears that the presence of the modifying agent can influence the material polymerization by improving or worsening the quality of interphase matrix - modifying agent.

4.6. Tribological Tests

The tribological characterization of materials with ferrite nanoparticles-modified epoxy matrix, whose forming process is shown in Chapter 2 – Nanoferrite-Modified Epoxy Matrix), has been made using the WAZAU Tribometer TRM 1000.

The tribological tests have been run on the pin-on disk modulus type. This tribometer enables viewing and setting both of the control parameters, and of the parameters measured (in real-time): speed of rotation, testing time, loading force, friction force and wear factor.

4.7. Results and Discussions

In Figure 4.25. it is noticed that, during the initiation stage of the tribological process, the friction coefficient values recorded are different for the three regimens studied. The lowest values of the friction coefficient for the initiation stage of the process (running-in period) are observed in the case of the R1 regimen. This value of the friction coefficient increases along with the decrease of the applied force, expected behavior, as the friction coefficient values are inversely proportional to the amount of normal force applied.

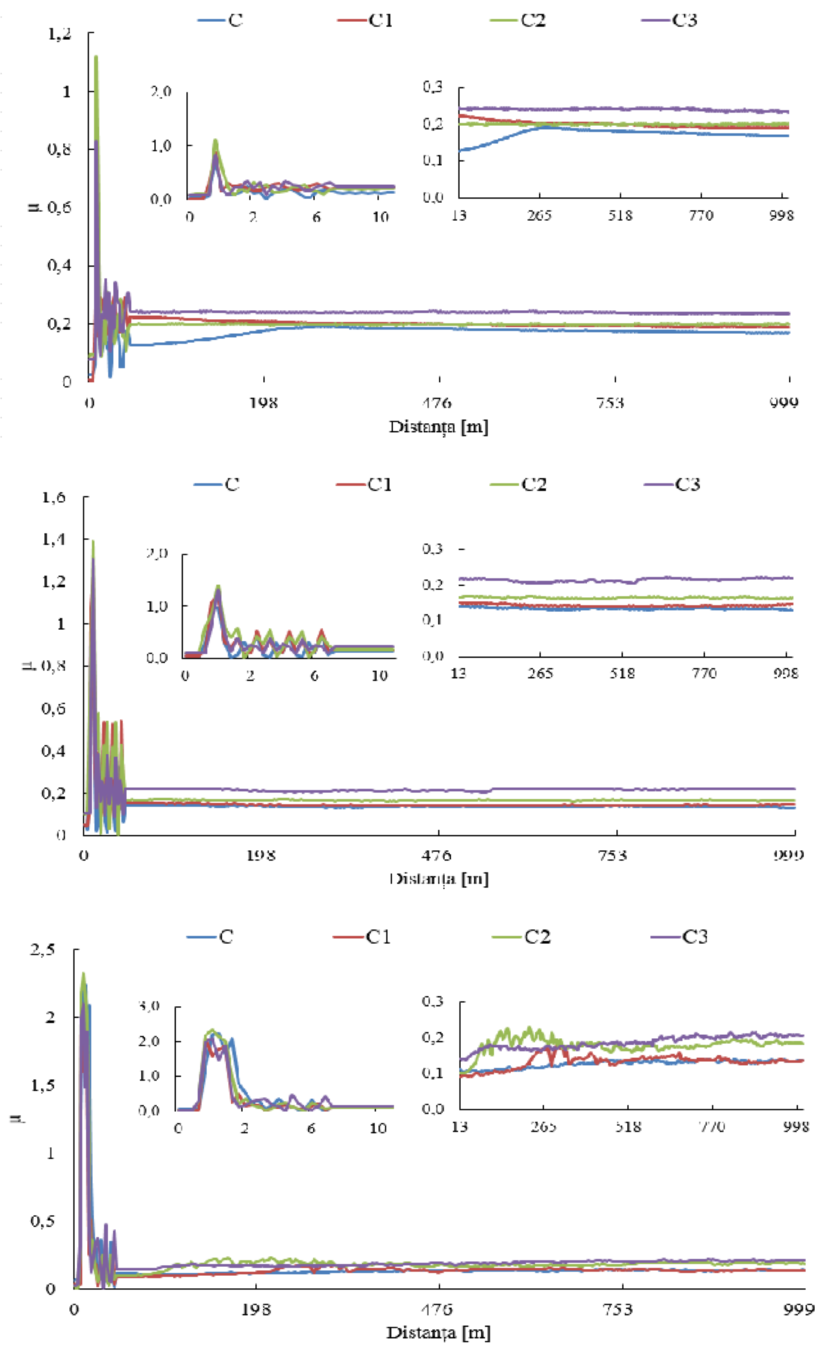


Figure 4.25. Tribological behavior of C-type materials (above: R1, middle: R2 and down: R3).

Evolution of the friction coefficient, depending on the sliding distance for three regimens studied in the case of materials with C-type epoxy matrix, shown in Figure 4.25, has a slight decrease together with the decrease in values of normal force applied, from 0.1 (15N) to 0.18 (5N).

The friction coefficient fluctuations occur throughout the entire test duration and, in the case of these materials with E-type epoxy matrix, being less obvious in materials containing small amounts of modifying agent (E1 and E2). The fluctuations occur due to the modifying agent properties which lead to its removal from the contact surface.

The variation of friction coefficients with sliding distance for materials with E-type epoxy matrix is plotted in Figure 4.28.

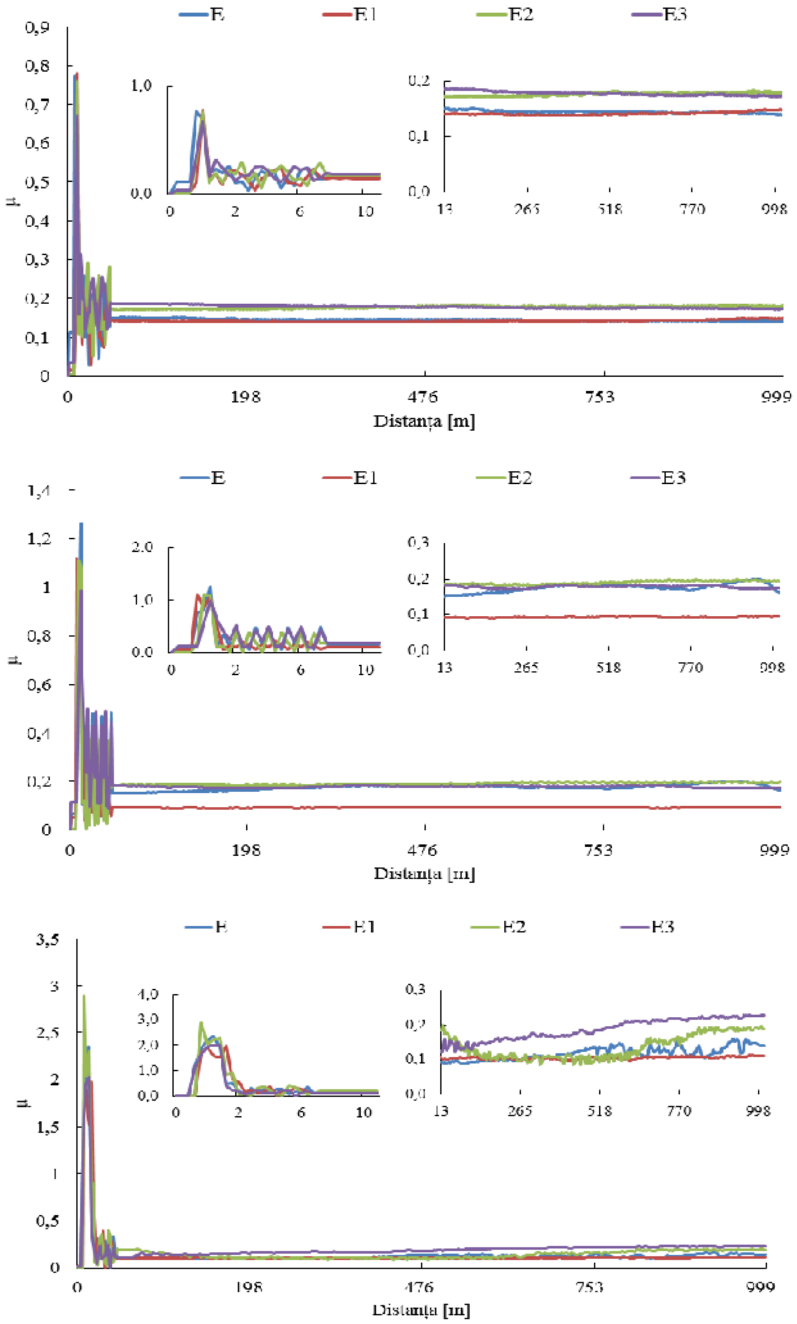


Figure 4.28. Tribological behavior of E-type materials (above: R1, middle: R2 and down: R3).

In Figure 4.28. is seen that the friction coefficient value increases along with the decrease of the applied force. If a comparison is made between the unmodified system and modified materials it can be observed that the highest value of the friction coefficient is recorded for the R2 regimen. To some extent, the friction coefficient evolution throughout the sliding distance is relatively stable, except for the E3 material for R1 regimen, where it is seen a visible decrease in the friction coefficient value over a sufficiently large distance. This is due to the phenomenon of pulling out from the contact surface a quantity of material, which occurs due to the interaction of the two hard surfaces pin – disk being in contact.

The behavior of materials with HT-type epoxy matrix, characterized depending on the friction coefficient evolution on the sliding length can be seen in Figure 4.31.

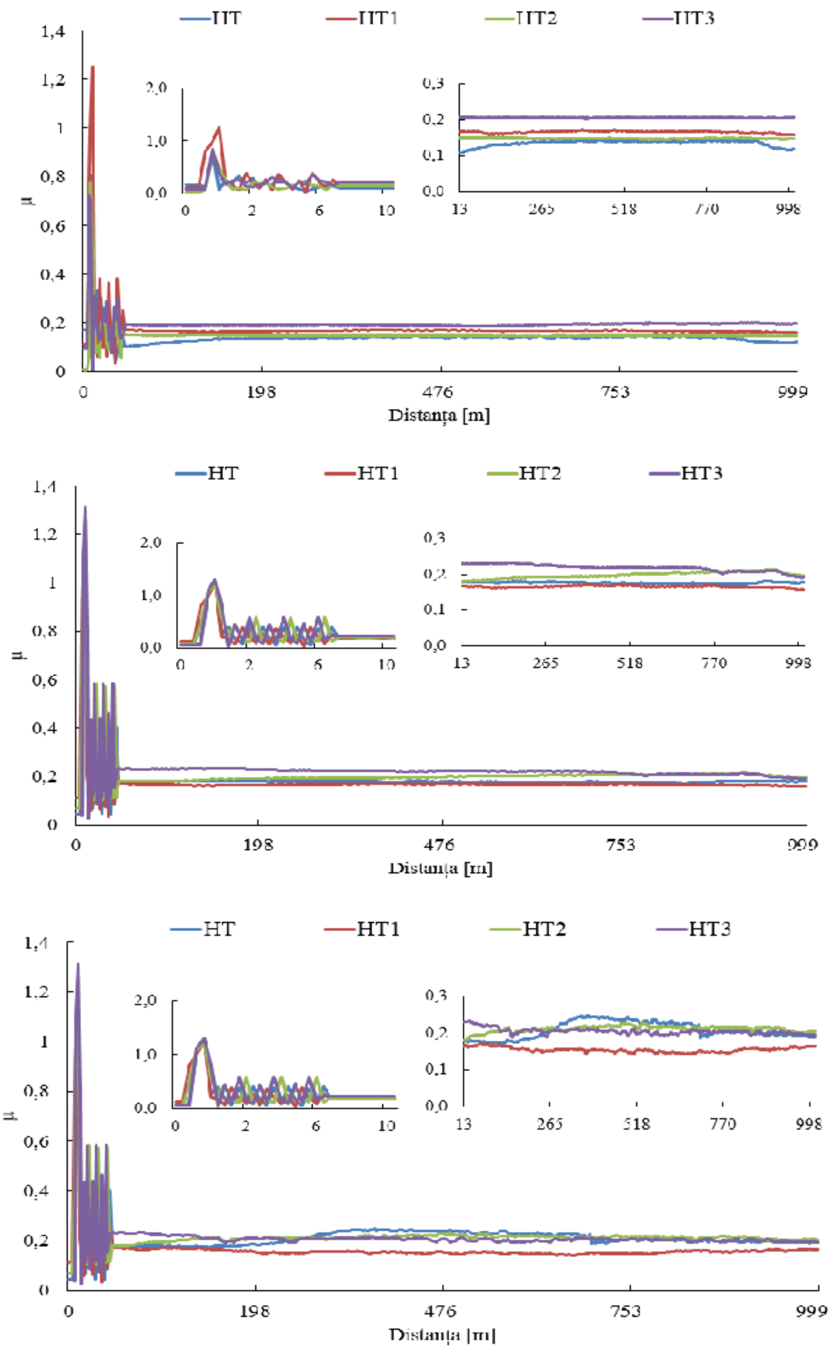


Figure 4.31. Tribological behavior of HT-type materials (above: R1, middle: R2 and down: R3).

It is noted that materials with HT-type epoxy matrix do not observe the increasing evolution behavior typical to the friction coefficient, followed by its stabilization until the test completion.

4.8. Conclusions

After analyzing the results obtained after mechanical testing (compression, bending and tribology) of materials, it is possible to outline the following conclusions:

The compression tests for ferrite-modified composite materials revealed poor mechanical results due to the presence of modifying agent in the polymer volume, which plays the role of tension concentrator.

The amount of modifying agent and its uniform dispersion in the polymer volume lead to an improvement in the mechanical properties of formed materials.

Barium ferrite, used as modifying agent in the case of C1 material confered it low properties on compression in the deforming stage, material cracking occurring very fast, even since the beginning of testing, compared to the other materials, C2 and C3, which showed a behavior better even than that of the unmodified epoxy system.

Irrespective of the nature of the modifying agent used, the dispersion amount and mode in the polymer volume, the composite material formed suffers visible degradations.

Frequently, an improvement in some properties is followed by a decrease in other properties.

The best responses to the three-point bending test were received from the materials with E-type epoxy matrix, then the materials with C-type matrix, followed by the HT-type materials.

Evolution of the friction coefficient for the R1 working conditions is poor for all materials studied regardless the type of epoxy matrix.

There is an increase in the values of the friction coefficient inversely proportional to the value of applied force during the tribological tests.

The wear rate is very low in the case of all materials for the R1, R2 working conditions where the values of working forces were the highest,15 N and 10 N.

CHAPTER 5.

ANALYSIS OF THE THERMAL AND HYDRO-THERMAL PROPERTIES OF NANOFERRITE-MODIFIED COMPOSITE MATERIALS

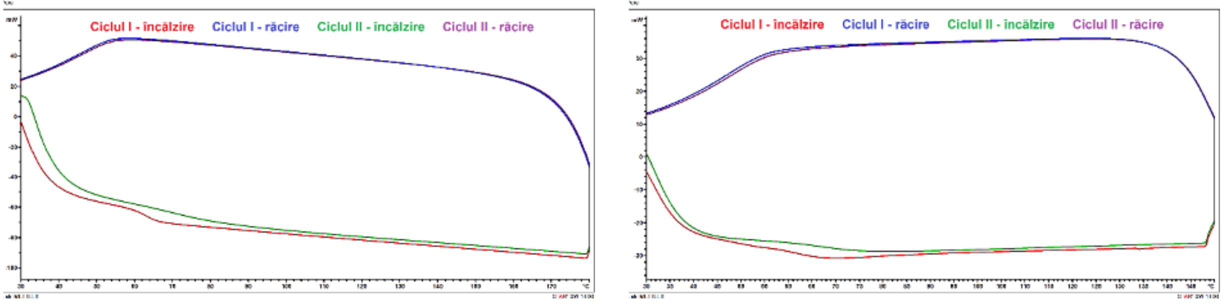
5.1. Overview

5.2. Determination of the Specific Heat

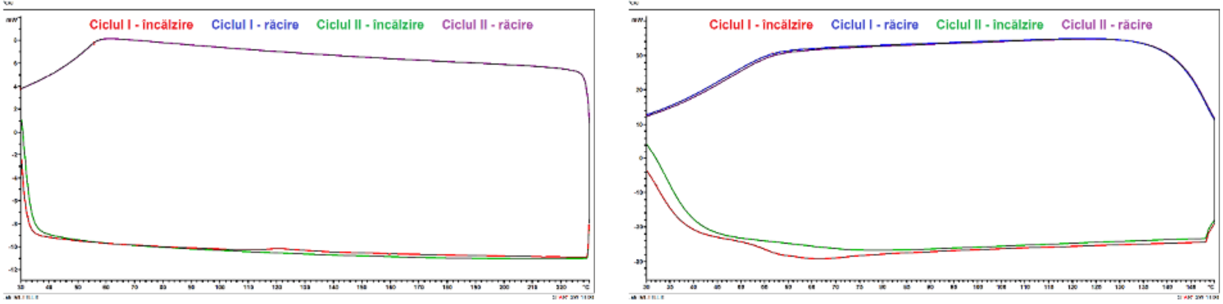
With a view to determining the specific heat was used a Differential Scanning Calorimeter DSC Mettler Toledo. This device is equipped with a sensor for the control of atmospheric conditions within the cell and which ensures the corresponding symmetry between the sample to be analyzed and the reference sample.

5.3. Results and Discussions

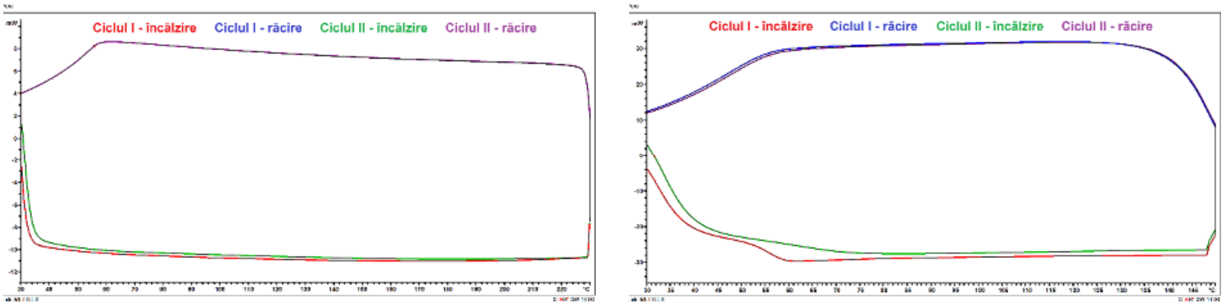
In Figure 5.1. are plotted the energy absorption curves (in the form of heat) for all elements that contributed to making the formed composite material, as follows: base materials or epoxy resin, modifying agent in the form of barium ferrite, respectively strontium ferrite and modified polymeric materials. These curves consist of two cycles of heating and two cycles of cooling the material during a complete temperature cycle ranging between 30 – 150°C.



Epoxy resin C **C1 material**



Barium ferrite **C2 material**



Strontium ferrite **C3 material**

Figure 5.1. The curves of energy absorption (in the form of heat). Base materials (left) and modified polymer materials (right)

The range of interest within this study, for the materials with ferrite-modified epoxy matrix is between 70-120°C. For this range of values have been carried out comparative charts of the homogeneous epoxy system, respectively of the composite materials modified with ferrites containing different epoxy matrix (Figure 5.2.).

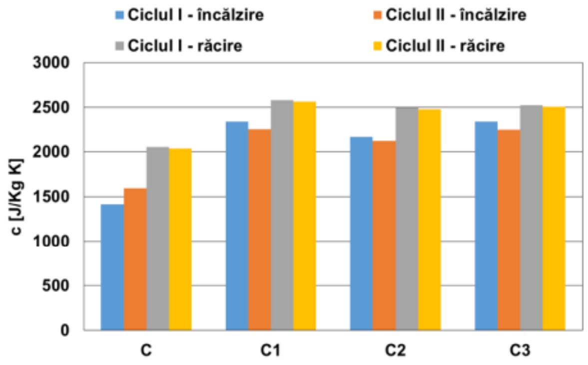
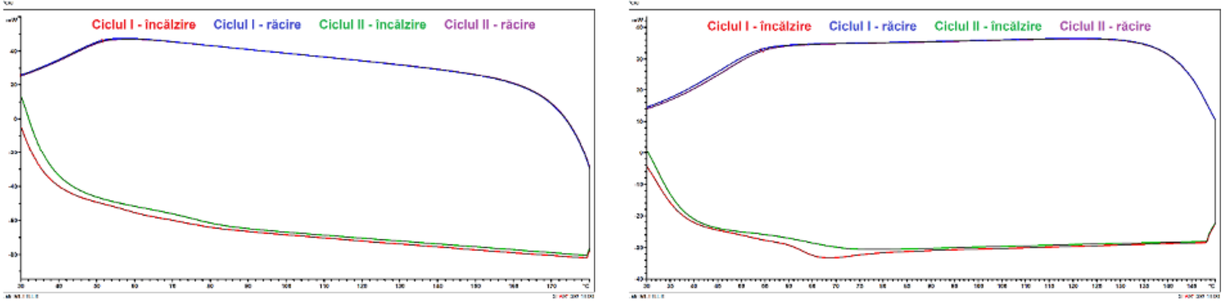
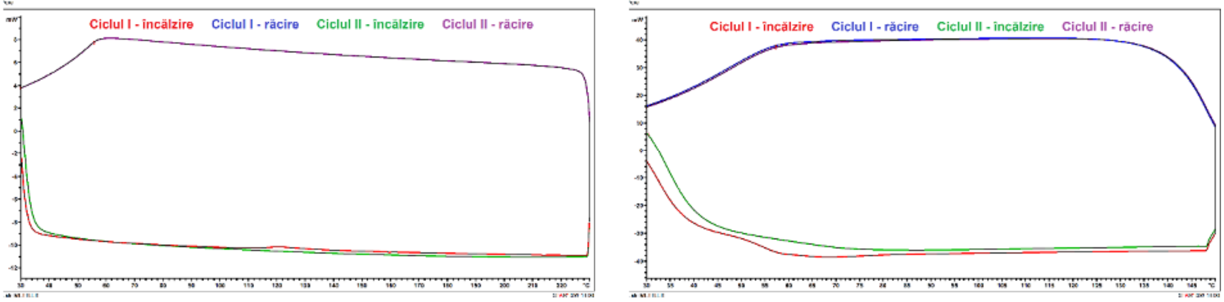


Figure 5.2. The specific heat determined on the range 70-120 ° C for materials with C-type epoxy matrix.

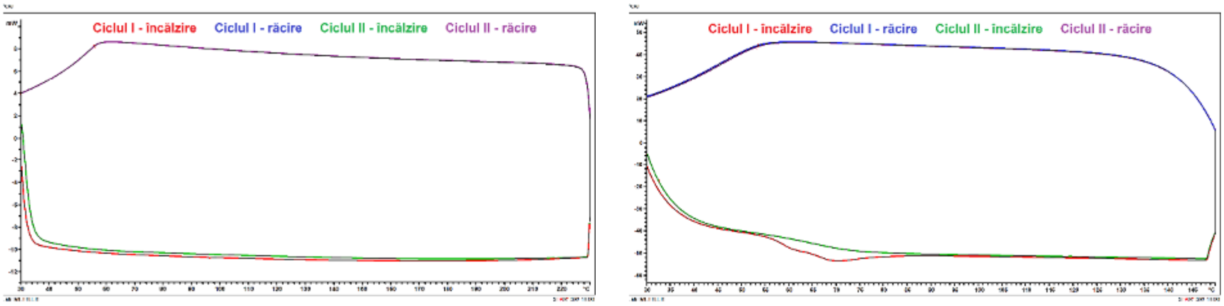
Analyzing the curves shown in Figure 5.3., we can state that the type of modifying agent and its combination is successful, the proof being the absorption curves of energy (in the form of heat), plotted in Figure 5.3.



E Epoxy resin **E1 material**



Barium ferrite **E2 material**



Strontium ferrite **E3 material**

Figure 5.3. The curves of energy absorption (in the form of heat). Base materials (left) and modified polymer materials (right).

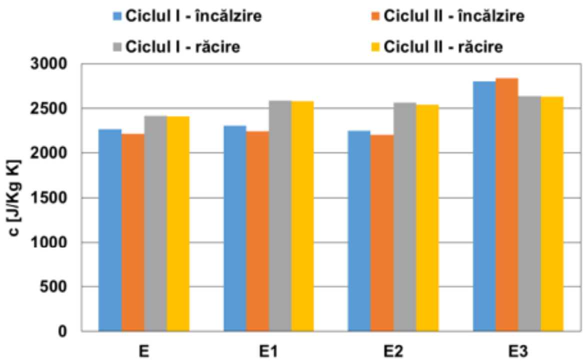
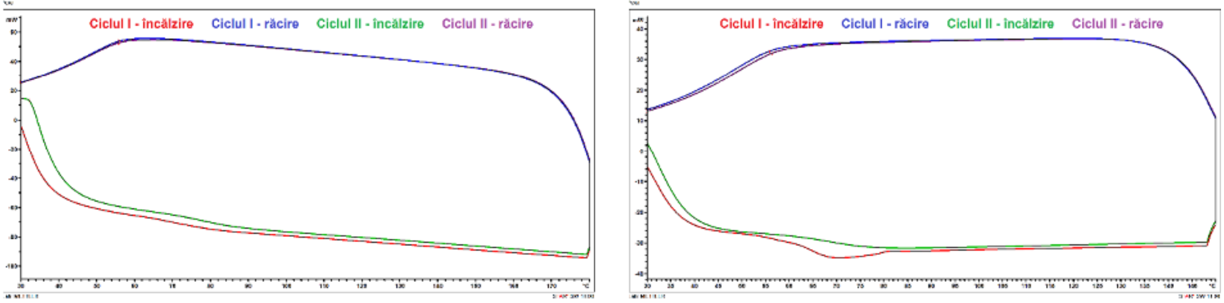


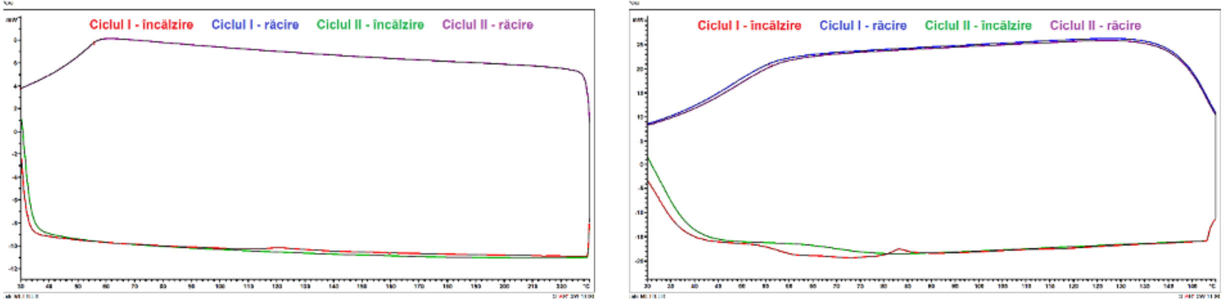
Figure 5.4. The specific heat determined on the range 70-120°C for materials with E-type epoxy matrix.

In the case of materials with E-type epoxy matrix is observed that, when heated, the amount of modifying agent and the combination of modifying agents and matrix is a success. Thus, there can be noticed higher values of the specific heat for E3 material (Figure 5.4.). During cooling have not been observed significant variations in the specific heat values for the materials with E-type epoxy matrix.

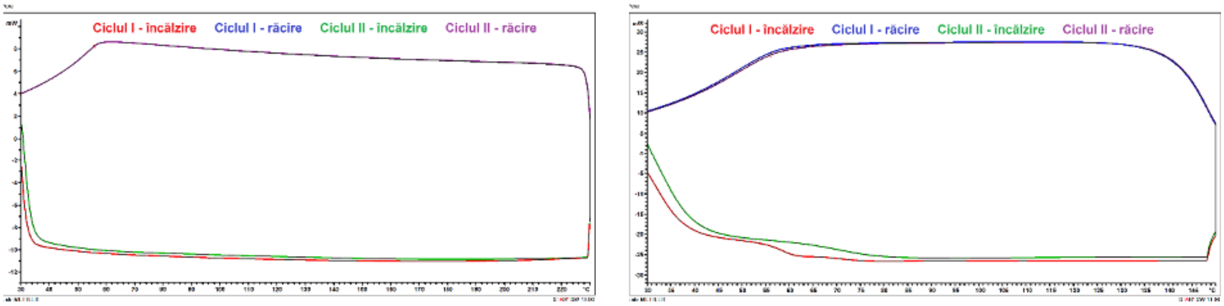
On the same temperature range of 70-120°C of concern in this study there have been made plots in the form of histograms shown in Figure 5.6., where you can observe the behavior of modified materials depending on the modifying agent and the amount used.



HT epoxy resin **HT1 material**



Barium ferrite **HT2 material**



Strontium ferrite **HT3 material**

Figure 5.5. The curves of energy absorption (in the form of heat). Base materials (left) and modified polymer materials (right).

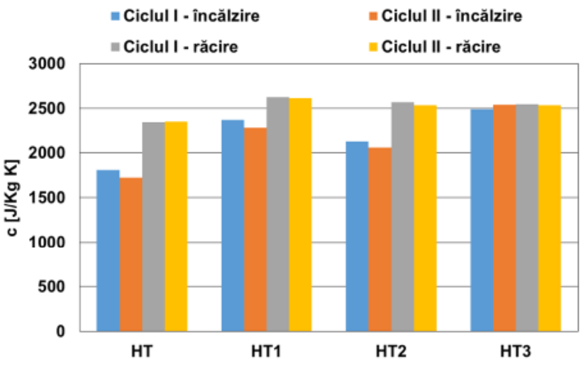


Figure 5.6. Specific heat determined on the range 70-120°C for materials with HT-type epoxy matrix.

The highest values of specific heat during heating were recorded for the materials with HT-type epoxy matrix modified with nanoparticles of barium ferrite (HT1 and HT3 materials) (Figure 5.6.). In the case of HT3 material, the average of specific heat values on the studied interval can be also influenced by the modifying agent amount in the polymer structure. On cooling, there have not been observed significant variations in the specific heat values for the materials with HT-type epoxy matrix, the range of specific heat values for the materials modified being maintained constant.

Before and after determining the amount of specific heat, the samples were weighed in order to be determined the mass loss. This loss is influenced by: the presence of residual water in the polymer and other volatile compounds being in the polymer mass in the form of oxygen and carbon dioxide resulted from the chemical reactions (Figure 5.7.).

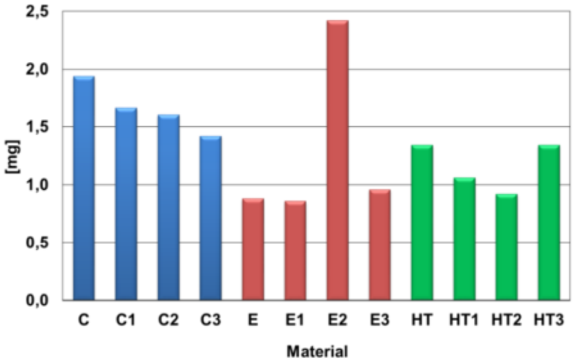


Figure 5.7. Mass loss of epoxy matrix composite materials

Generally the largest values of mass loss were recorded in the case of materials with C-type epoxy matrix, while the smallest were recorded for materials with E-type epoxy matrix.

5.4. Determination of Hydro-Thermal Properties

5.5. Results and Discussions

The calculating formulas for the determination of each parameter in this study were as follows:

– *the amount of water absorbed per cycle* was determined as follows:

$$M_{abs} = \Delta m$$

– *water absorption per surface* was determined as follows:

$$Abs_{surface} = \frac{\Delta m}{A}$$

– *specific absorption* was determined as follows:

$$Abs_{specifică} = \frac{\Delta m}{M_i}$$

In Figure 5.8. it results that the highest degree of water absorption is found in materials with C-type epoxy matrix and the other two materials with E and HT-type epoxy matrix present a lower absorption rate. For the materials with C and HT-type epoxy matrix modified with nanoparticles of barium ferrite, the absorption degree is higher than in the unmodified material (Figure 5.8.).

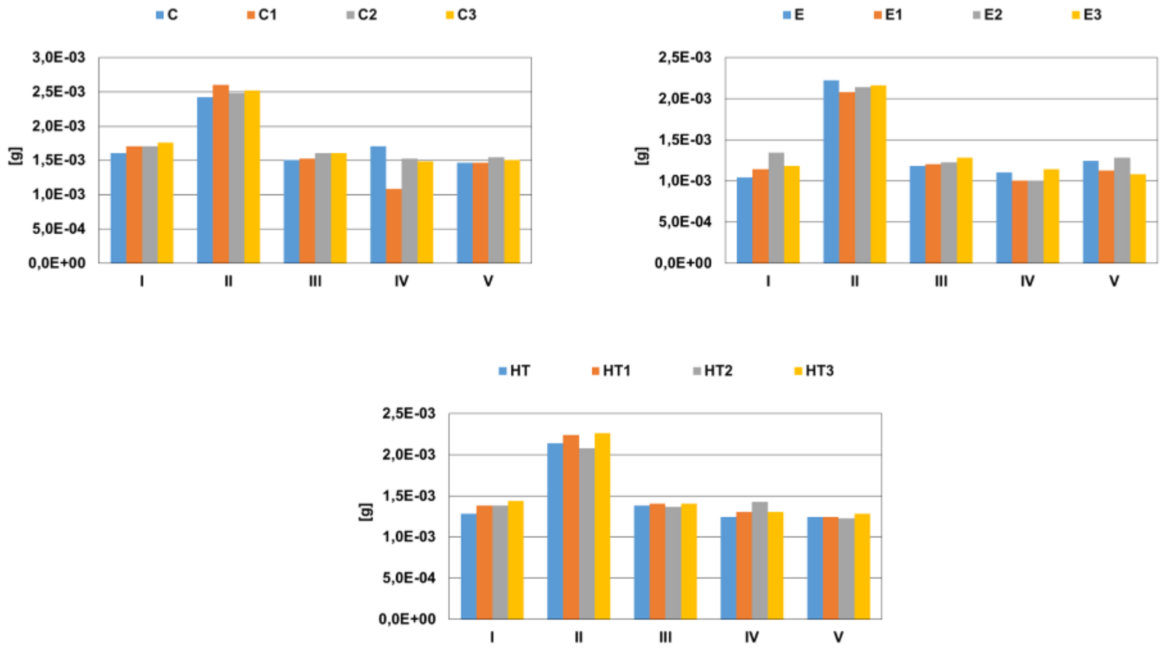


Figure 5.8. Absorption degree for the ferrite-modified epoxy materials.

It can be seen that materials with C-type epoxy matrix modified with strontium ferrite show saturation presents starting from the III rd. cycle, while materials modified with strontium ferrite show super saturation starting with cycle IV (Figure 5.8.).

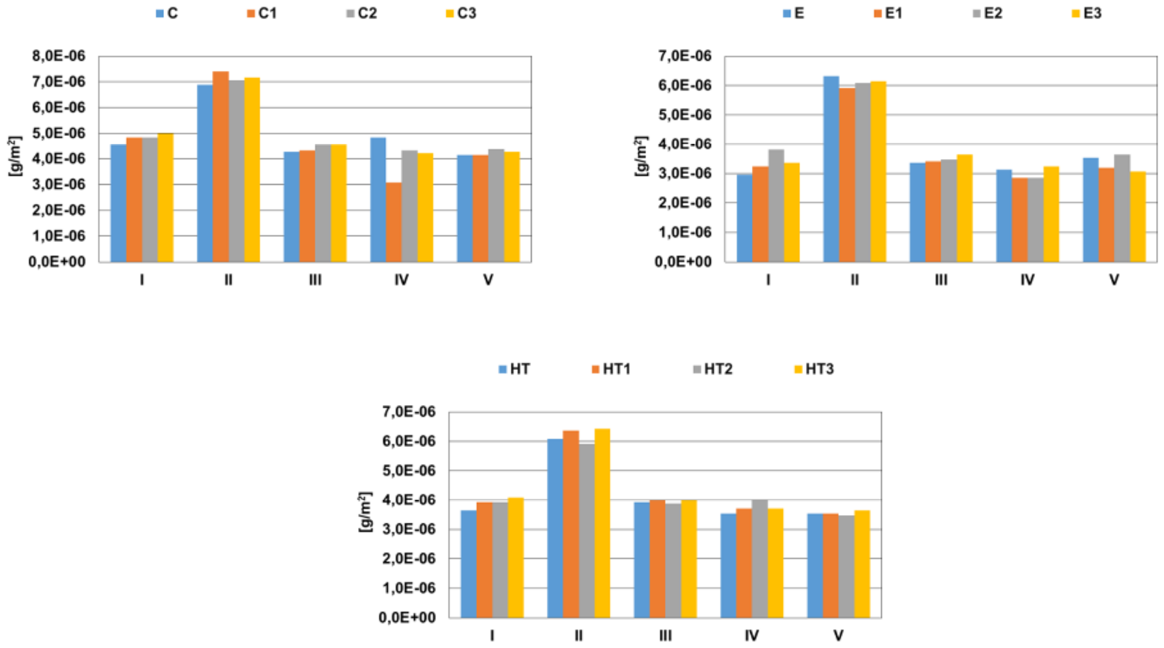


Figure 5.9. Absorption per surface for the ferrite-modified epoxy materials.

Materials with the same type of matrix, but unmodified, show an increase in the absorption degree in cycle IV with values lower than those obtained in the IInd cycle, following which there is a saturation in the last cycle. The absorption degree per surface is very small for all materials studied, regardless of the epoxy system type, modifying agent type or its quantity.

In Figure 5.10. can be seen the hydrothermal fatigue behavior of the materials studied.

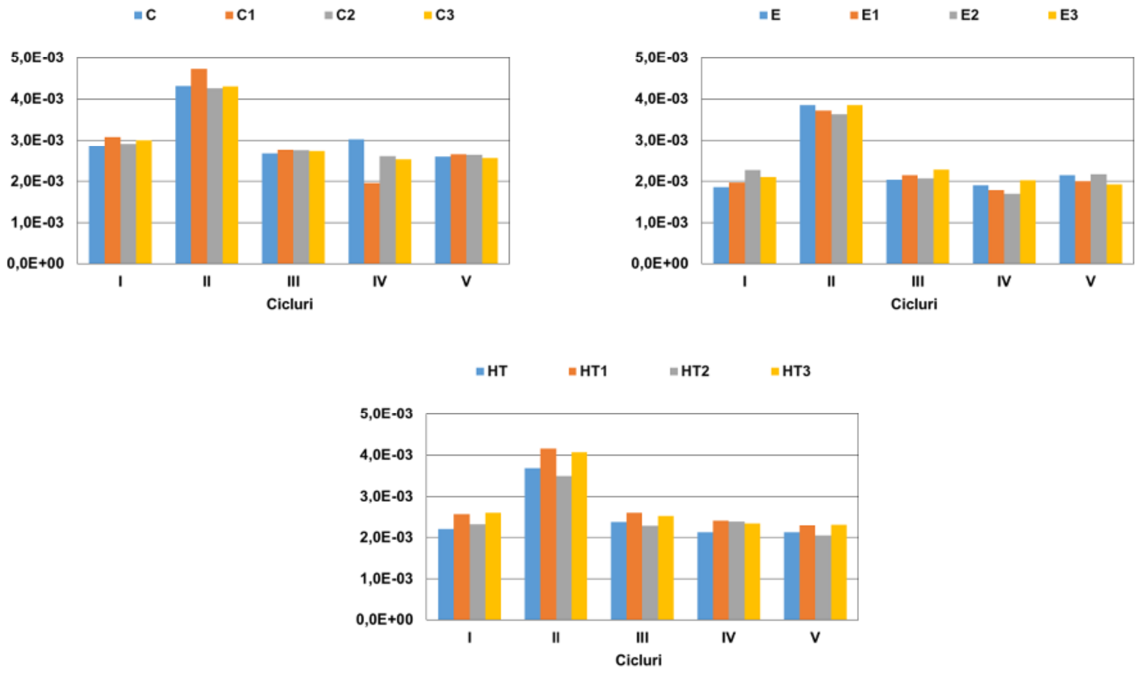


Figure 5.10. Specific absorption for the ferrite-modified epoxy materials

The specific absorption was determined depending on the absorption degree and sample mass following the last heat treatment applied.

5.6. Conclusions

Following the comparative analysis per heating cycles, the different behavior and higher values of the specific heat are due to the chemical interaction of epoxy matrix with the modifying agent. Also the interaction between the two modifying agents has caused an improvement of the thermal properties of materials formed.

The specific heat values obtained for the materials with epoxy matrix modified with nanoparticles of barium and strontium ferrite are generally higher compared to the specific heat values determined in the case of unmodified epoxy systems;

Better thermal properties were seen in materials where both ferrites were used as modifying agent compared to the materials where one type of modifying agent was used.

The loss of mass is visible in every material from, irrespective of the matrix type and amount of modifying agent added to the matrix volume.

From the study of hydro-thermal behavior in the materials analyzed was observed that, after the second cycle, epoxy materials modified with ferrite nanoparticles have reached the saturation level (a phenomenon that prevents the water absorption on the surface of the material).

It was seen that there were no changes in the absorption degree values in epoxy materials with modified with ferrite compared to the absorption values of unmodified epoxy materials.

The absorption degree per surface in materials with epoxy matrix unmodified and ferrite-modified, did not lead to their deterioration.

CHAPTER 6.

ANALYSIS OF ELECTROMAGNETIC PROPERTIES IN COMPOSITE MATERIALS MODIFIED WITH NANOFERRITES

6.1. Overview

6.2. Determination of Electrical Conductivity by the Electro-technical Measurement Method

In the process of determining the electromagnetic properties for composite materials with modified epoxy matrix, it has been used an experimental device, LCR meter type Protek9216A, indicating five fixed frequencies of measuring several pairs of parameters.

6.3. Results and Discussions

The relative variations of material electrical conductivity measured through the electro-technical method are determined in relation to the parameter values corresponding to the homogeneous epoxy systems, grouped by type of epoxy matrix used and plotted according to the operating frequency of the measurement system (Figure 6.1.).

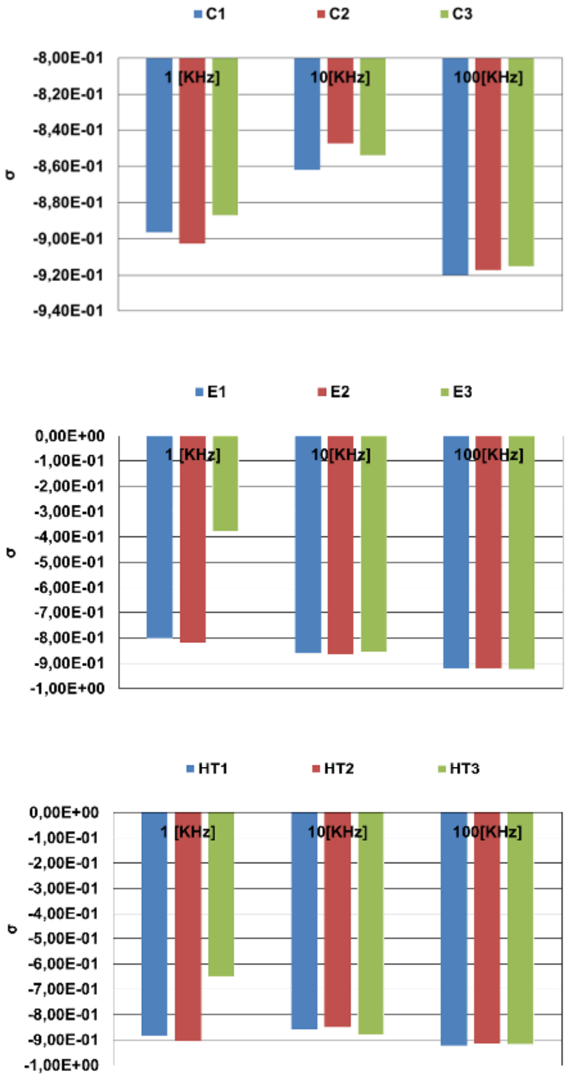


Figure 6.1. Relative electrical conductivity of epoxy composite materials modified with ferrite, measured by the electro-technical method.

6.4. Determining the Dielectric Permittivity by the Electro-technical Measuring Method

6.5. Results and Discussions

The value of dielectric permittivity measured in E-type epoxy systems increases directly proportional to the quantity of the added modifying agent, a fact leading to the idea that the modifying agent confers the material good dielectric properties (Figure 6.2.).

With reference to the value of operating frequency it can be seen that the value of measured dielectric permittivity decreases gradually, regardless of the type or quantity of modifying agent used. In the case of determining the dielectric permittivity in the material, the stability range is between the frequency values of 10-100kHz.

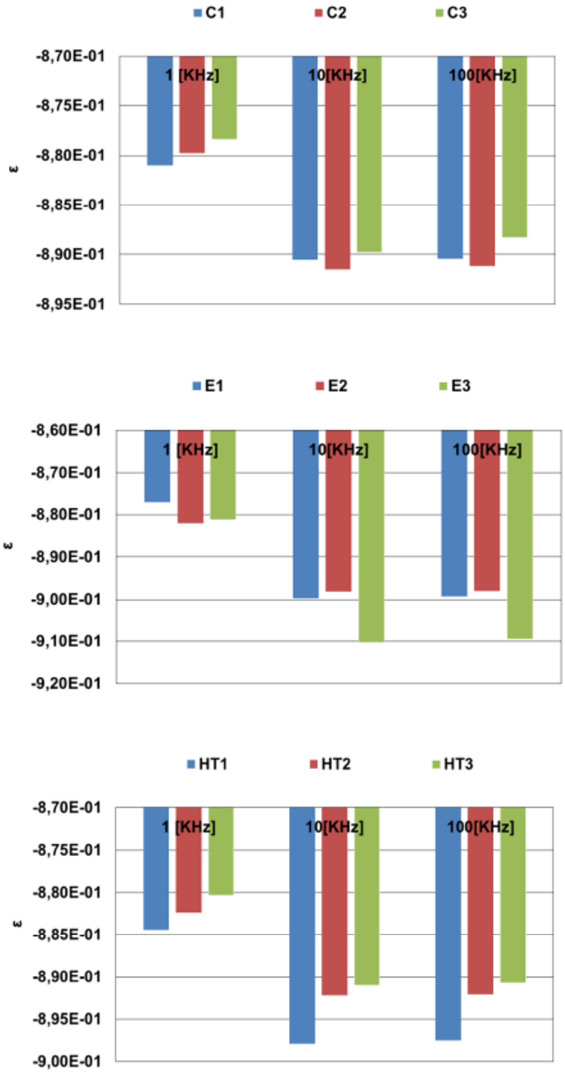


Figure 6.2. Relative dielectric permittivity in epoxy composite materials modified with ferrite, measured by the electro-technical method.

The values of dielectric permittivity measured in the materials volume are almost identical. It is observed that there are no differences that would lead to the conclusion that a material has better dielectric properties than another material in the same category.

The small variations identified may lead to an assumption on the fact that there has been a certain homogeneity of the material, even if on some parts there have been small variations.

6.6. Magnetic Permeability Determination by the Electro-technical Measurement Method

6.7. Results and Discussions

Variation in the relative magnetic permeability for composite materials with ferrite-modified epoxy matrix is shown in Figure 6.3.

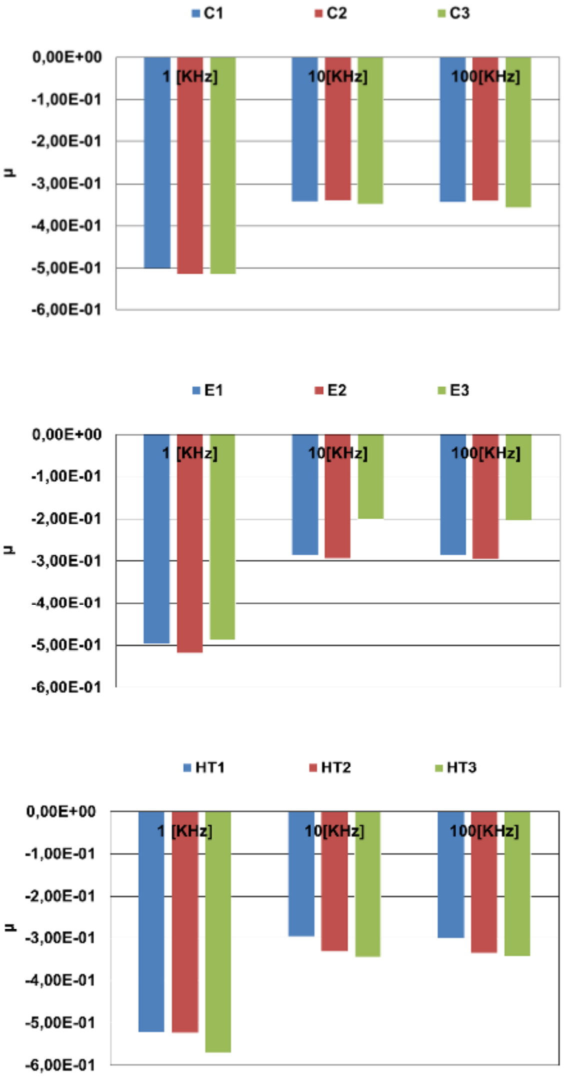


Figure 6.3. Relative magnetic permeability in epoxy composite materials modified with ferrite, measured by the electro-technical method.

In Figure 6.3. there can be observed large variations in the magnetic permeability values for materials with modified epoxy resin, measured at a frequency of 1 kHz, while in the case of other modified epoxy resins, the magnetic permeability is equal.

6.8. Determination of Electrical Conductivity through the Method of Measuring the Insulation Resistance

6.9. Results and Discussions

The results of measurements on the areas of concern are shown graphically, where the following notations are used:

M (sample) – average of the measurements in the plate area where no magnetic field was applied,

P (parallel to the applied magnetic field) – average of the measurements in the area where was applied magnetic field during forming, (measurements performed parallel to the applied field),

A (antiparallel to the applied magnetic field) – average of the measurements in the area where was applied magnetic field during forming, (measurements performed antiparallel to the applied field).

If we refer to the electrical conductivity values measured by the same method for the materials formed in magnetic field, we can say that there are some differences, which can be considered the effects of the presence of modifying agent, particularly to the antiparallel measurement in relation to the magnetic field direction (Figure 6.4.)

As a consequence, the value of electrical conductivity measured outside the magnetic field is higher, reason for which we can say that these materials have good electrical properties of the magnetic field area.

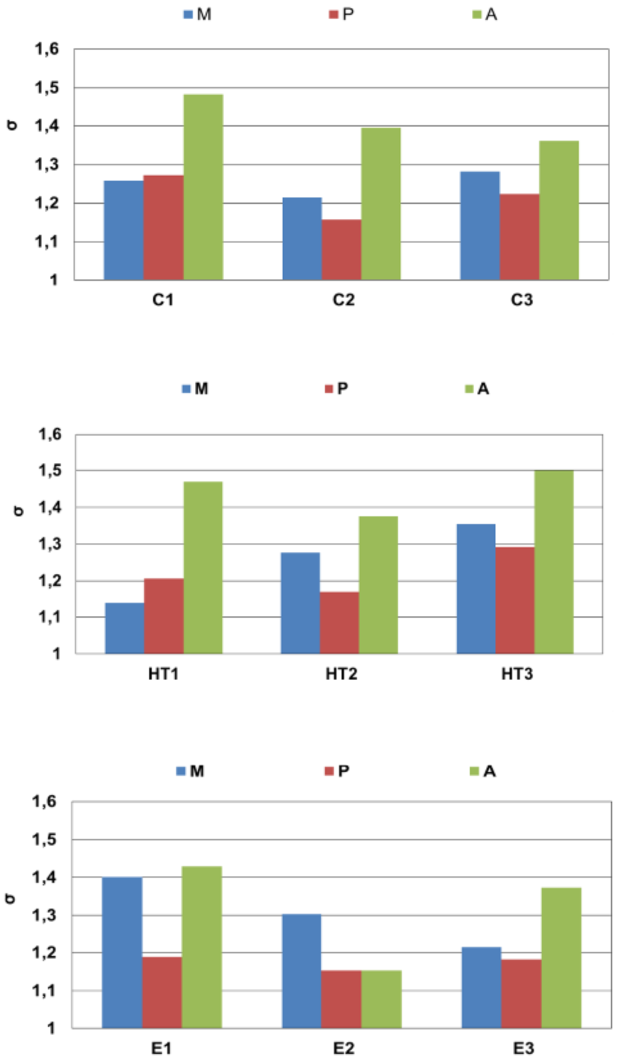


Figure 6.4. Relative electrical conductivity of epoxy composite materials modified with ferrite through the method of measuring the insulation resistance.

In the case of materials with HT-type epoxy matrix modified with ferrites, the electric conductivity values measured by the A method, on the application area of the magnetic field are better. This can be seen particularly in the case of materials where the amount of modifying agent used is higher. In areas where no magnetic field was applied, electrical parameters determined by the two points measuring method presents low values.

Following the measurements carried out on composite materials with epoxy matrix of C, E, HT types, modified with ferrites, it is noted that the electrical conductivity values determined by the method A are higher than the electric conductivity value as measured by other methods. We can say that the application of magnetic field during material forming did not influenced significantly electrical conductivity values measured by the P and M methods of measuring.

6.10. Conclusions

The introduction of ferrite nanoparticles in the polymer structure leads to an improvement in the electromagnetic properties of the materials.

In the case of determining electric parameters using the LCR meter, it has been found that materials modified with barium an strontium ferrites had values of the electrical conductivity increasing in direct proportion to the measuring frequency.

Concerning the dielectric permittivity measured on the composite materials modified with barium ferrite, it has recorded variations depending on the modifying agent and frequency of measuring.

Measurements carried out by the two-point method, using the Terra Ohm Meter, showed higher values of electrical conductivity, determined by indirect A polarization for composite materials with C and HT-type epoxy matrix.

The application of magnetic field during the formation of formed materials influenced differently the electrical conductivity values, depending on the type of epoxy matrix, using the two-point measuring method.

CHAPTER 7.

GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND PERSPECTIVES OF CONTINUING THE RESEARCH

This paper started from the need to study the behavior of new classes of composite materials modified with ferrites.

In the paper it was intended to deepen some aspects concerning the influence of additive and additive concentration on the mechanical and tribological behavior of these materials. Also, the doctoral dissertation has also performed a study of the electromagnetic, thermal and hydro-thermal properties.

Thus, the research conducted has outlined the following general conclusions:

- The complex program of research applied allowed the characterization of the mechanical, tribological, electromagnetic, thermal and hydro-thermal behavior of composite materials modified with ferrites;
- Through the Raman, SEM, SEM-EDAX analyzes, it was possible to identify additives of barium and strontium ferrite in the structure of polymeric materials formed,
- Based on mechanical tests (on compression and bending) was possible to determine the influence of the type of additive material, and of concentrations of additive material on tensile strength, elasticity modulus and tear deformation. The mechanical tests have shown a good repeatability of the results obtained for all types of nanoparticles used;
- For each working condition (R1 – testing speed of 0.66 [m/s], 15N force, distance of 1000 m; R2 - testing speed 1 [m/s], the force of 10N, 1000 m distance; R3 - speed of testing 2 [m/s], 5N force, distance of 1000 m) there have been identified the wear mechanisms that are typical for each type of additive material used,
- The effects of additivation are significant as concerns the thermal properties of materials with epoxy matrix analyzed, compared with the electromagnetic properties where the effects of the additive / additives used do not have a particular significance,
- Combination of the two additives, barium ferrite and strontium ferrite has led to the significant improvement of thermal parameters values compared to using these additives separately within the same epoxy matrix,
- Adding additives in epoxy matrix did not influences the absorption degree of water on the surface of formed materials;
- The effects of modifying agent are very important concering the thermal properties of materials formed and analyzed, while in case of electromagnetic properties, the modifying agent effects have no significance.

ORIGINAL CONTRIBUTIONS OF THE THESIS

1. Elaboration of polymeric composite materials with epoxy matrix through additivation with ferrite nanoparticles (of barium and /or strontium) used in different concentrations.
2. Designing and carrying out a complex program of research concerning the mechanical, tribological, electromagnetic, thermal and hydro-thermal behavior of composite materials modified with ferrites.
3. Association of mechanical studies (tests of compression, bending and tribological) with metallurgical studies (micrographic structure analysis and use of SEM and EDAX microscopy, Raman spectroscopy) enabled to highlight and evaluate the tear surface obtained from mechanical tests as well as the mechanisms of destruction through wear.
4. Emphasizing the favorable effect of ferrite nanoparticles on the thermal properties of composite materials formed.
5. Own method of evaluating the hydro-thermal parameters of composite material modified with ferrites.
6. Complementing new experimental data of mechanical, tribological, electromagnetic,

thermal and hydro-thermal studies regarding the influence of ferrites used as an additive in forming composite materials with epoxy matrix.

PROSPECTS TO CONTINUE THE RESEARCH

- Determining the influence of the magnetic field applied to composite materials during polymerization on the tensile mechanical properties.
- Study of the influence of other systems for testing on the tribological behavior of composite materials modified with ferrites.
- Determination of the degree of thermal expansion of the composite materials with epoxy matrix modified with barium and strontium ferrites, using the TMA analysis (Thermomechanical analysis).
- Development of other recipes of composite materials with a different type of epoxy matrix (L-type) based on ferrites (different concentrations, particle sizes, different types of ferrites, etc.).

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