PhD THESIS

ABSTRACT

STUDY REGARDING THE PROPERTIES OF ORGANIC SOLVENTS MODIFIED EPOXY SYSTEMS

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Galaţi

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„DUNĂREA DE JOS" UNIVERSITY OF GALATI

Doctoral School of Mechanical Engineering

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Conform modificărilor aduse Codului studiilor universitare de doctorat prin Hotărârea Guvernului României nr. 134/2016 și de Regulamentul de organizare și funcționare al CNATDCU aprobat prin Ordinul Ministrului Educației Naționale și Cercetării Științifice nr. 3482/24.03.2016;

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Prof. dr. ing. Iulian Gabriel BÎRSAN

RECTOR

CONTENT

1. Introduction

The purpose of this study is the creation of new composites modified with organic solvents endowed with multifunctional properties. Thus, we wish to create composites with enhanced electric properties, without affecting their mechanical characteristics.

The continuous development of new materials with enhanced properties in order to be used on a large scale requires that the current development stage of humanity be characterised, as compared to previous stages and taking into account the contribution brought and demanded by composites, as the age of composites. Unlike traditional materials, composites are thus created so that they adapt, through their properties, to the requirements of use. As their design is based on the characteristics of the components, according to the desired field of use, composites must possess certain properties.

The initial idea of the study was to create groups of polymeric composites which, together with an electrolyte, would allow the storage of the energy of the electric field for its subsequent use. Such a system is called structural battery in literature and it represents a challenge in the current scientific research not only for physicists and chemists, but also for the manufacturers or designers of composites. Such materials could be used for the creation of reinforced composite structures and thus it would be possible to obtain composite structures with a double purpose at least: protection (through mechanical properties) and storage of energy.

The inorganic agents for the three epoxide systems were chosen with a view to obtain composite materials which, eventually, would allow the storage of the energy of the electric field along the simple principle of chemical cells with iron and nickel (known mainly for their durability). For this, a mixture of nickel, nickel oxide, nickel azotate, zinc and lithium hydroxide was used for one type of material and a mixture of iron dust and iron oxide for the other material (the two types of materials being the electrodes of the cell). Unfortunately, the alteration of the three epoxide systems with inorganic agents proved to be a failure (from the perspective of using them for the intended purpose), the tests carried out to prove the hypothesis failing mainly due to the fact that the created materials had no pores and, therefore, did not allow the penetration of the electrolyte. Consequently, the study was directed towards analysing the possibilities of obtaining porous epoxide materials. In this stage, we analysed the possibility of using polysulfone (polymer which forms porous structures) mixed with the epoxy resins. The tests performed for the dispersion of polysulfone in the three types of epoxy resins also had poor results, therefore, based on the experience of some of the colleagues from the Research-Development Centre for Composites with Thermosetting Matrices, the study continued with the analysis of the dispersion of polysulfone solutions in epoxy resins.

Literature recommends three highly efficient organic solvents for polymers. All these solvents were used for modifying the properties of the three analysed epoxy systems in order to outline the effect of their presence within the volume of the polymer upon the properties of the created materials. Moreover, using these solvents, it is possible to include other organic agents in the volume of the polymer which, given the proper treatment (heating, irradiation), are decomposed (chemically) and lead to the appearance of nanometric structures.

2. Composite materials. Current trends

2.1. Classification of composite materials

Composite materials are made of different types of materials. They offer a unique combination of mechanical and physical properties which cannot be encountered in one material only. They have low density, resistance to high temperatures, as well as a good response to impact which recommend their use [1], [2] in the most common or uncommon applications.

Composite materials are defined as systems of solid, deformable bodies, obtained through macroscopic combinations of several materials with different properties.

Concomitantly with the evolution of research in the field of composite materials, they were defined in various ways. If four decades ago a composite material was defined as the mixture of at least two materials of different kinds in order to obtain a third one with different properties, a composite material is currently defined as a material formed of at least two phases which do not interact chemically and induce to the created material superior properties through interphases.

2.2. Epoxy resins

Epoxy resins are thermosetting materials used widely due to their special mechanical and thermic characteristics. Epoxy resins are of high interest as they pertain to the category of practical materials, for instance, they may be used as structural adhesives, covering agents or polymer matrices [3].

An important factor in the design of composite materials is the amount of fibres of the reinforcing agent as it influences the mechanical and thermo-mechanical properties of the resulting material. In order to obtain a material with properties useful for a certain application it is important to know the way in which the performance modifications of composite materials depend on the amount of the reinforcement fibres. Three decades ago, one of the concerns in the field of composite materials was the influence of the amount of reinforcement fibres on the properties of the created material [4,5,6,7,8], thus, it was noticed that the inclusion of fragile fibres in the thermosetting and thermoplastic matrices leads to composite materials with a low resistance to erosion.

2.3. Polymers – composite materials

The polymer, as its name suggests, is a substance formed of poly (several) and mers (or monomers), where the monomer is the basic or structural unit of the polymer. These basic units are connected through covalent (most of the times) chemical bonds which form a chain. The polymerisation degree of a polymer is equal with the number of repeating basic units or the ratio between the mass of polymer chain, M and the mass of the basic unit, m. If the polymerisation degree is low, containing several basic units, the substance will be called oligomer and makes the connection between common substances and polymers.

Therefore, composites whose polymerisation degree equals 50 are called oligomers and composites with a higher polymerisation degree are polymers.

Epoxy resins are widely applied due to their remarkable performances [9] and have made the object of a myriad of patents and technical publications [10].

Recent advances in the field of intrinsically conductive polymers (ICPS), as well as in the field of conductive polymer composites (CPC) filled with natural fibres are being systematically reviewed. The possibilities of using natural fibres as fillers for ICPS and CPC in order to obtain conductive fibres with unique characteristics, such as electrical conductivity, mechanical strength, which made it possible to use them in new and interesting applications, including,

aerials, chemical sensors, tissue engineering, neural probes, biosensors, bio-servomotors, fuel cells etc. [11].

Soft magnetic composites (SMC) are remarkable as magnetic materials made of small isolated ferromagnetic particles. They possess certain excellent mechanical and electromagnetic properties, for instance, extremely low losses and relatively low losses of energy at medium and high frequencies (due to an insulating layer between the iron powder particles, eddy currents are minimised). The manufacturing process manages to ensure cheap mass production and, consequently, it can compete with traditionally used materials, such as FeSi steels or magnetic ferrites at a similar or even lower production cost [12], [13], [10], [14], [15].

In lithium-ion battery systems, the separator plays a key role in terms of performance, thus polymer composites and polymer mixtures have been frequently used as battery separators due to their specific properties.

A battery separator can be obtained in two stages, namely, first of all, the salts are dissolved in a solvent and subsequently added to a host polymer in order to ensure proper mechanical stability.

With the inclusion of ferroelectric materials in the polymer matrix it is to be expected that the transport number of lithium increases and, consequently, ionic conductivity too, due to the polarisation of the fillers.

Most polymer matrices display a fairly low dielectric constant, having a limitation of the dissociation of electrolyte salts, thus, by adding ferroelectric ceramics, with a high dielectric constant, the polarity of the composite increases and may also improve the lithium / electrolyte interface.

2.4. Modifiers

In order to obtain optimal performances of the composite material and, implicitly, with minimum costs, a variety of additives or modifiers are used [16].

Thus, the introduction of certain additives in the polymer composites leads to the improvement of dimensional stability, increase of the elastic modulus, decrease of the heat expansion coefficient, increase of the resistance to abrasion [17], [18], therefore, all composite materials contain an additive, with different concentrations, in order to obtain the desired properties.

Compared to fibres, particles are more easily obtained and embedded in the matrix material, thus, powders can be classified as follows:
- according to origin - organic and inorganic;
- according to size - nano, micro, macro;

According to the studies [19, 20, 21, 22] on the environmental impact of polymer wastes, there is an increasing interest in creating new classes of biodegradable polymers. As a consequence, the creation of a new class of composites which meets all the necessary characteristics requires high costs. The optimisation of the production costs of biodegradable composites imposes the use of some cheap additives, components.

In order to increase the degree of biodegradability of composites, α-D-glucose is added to the polymers, according to the studies [23], [24], [25], [26], [27], [28]. Alpha-D-glucose is a ring biological monosaccharide with terminal hydroxyl groups which can be used to a selective transformation of the resin [29], [30]. As glucose is one of the nutritive substances of metabolism in the body, it has good biological compatibility for the use of composite materials modified with glucose in the medical field [28].

D-glucose derivatives may also be used as additives for epoxy resins, according to the studies [31, 32, 33] as they are compatible and allow polymerisation.

By adding glucose to polymers, the obtained composite is a shape-memory material which has the ability to return to its original shape in ratio of 70% [34,35].

2.5. Solvents used for diluting resins, dissolving additives

The solvent is more efficient at dissolving a material if it possesses functional groups, therefore, it is preferable that the material is of the same nature as the solvent (organic nature).

In order to avoid unwanted reactions between the material and the solvent, it is necessary to know the chemical reactivity of the solvent.

For instance, dimethyl formamide, methyl cellosolve, 1-metoxi-2-propanol, N-methyl-2-pyrrolidinone (NMP) increase the chemical stability of the epoxy matrix, reducing the neutralisation capacity of the composite material [36].

Solvents are currently widely used for the production of asymmetrical polysulfone membranes, the separation performance of the membrane depending very much on the polarity of the used solvent, so that, the most used solvent is N-methyl-2-pyrrolidinone (NMP). This solvent was added due to its characteristics of non-polar solvent which improved the flawless formation of polysulfone membranes. Therefore, the properties of the solvent may impose new, improved characteristics of the final material, here, the most important characteristic of the solvent, N-methyl-2-pyrrolidinone (NMP) being its polarity [37, 38, 39].

The main criteria for a successful mixture are:
- mixing at constant speed;
- mixing in one direction only;
- avoid oscillatory movements so as to prevent air bubbles from getting into the resin which would cause damages to the finite material.

3. Goals of the research

Based on the analysed bibliographical resources concerning the formation, characterisation and testing of composite materials obtained with epoxy resins, the importance of the additives, solvents used in the formation of materials in terms of the role they have in the modification of the properties of epoxy resins, an analysis of the composite materials with modified epoxy matrix could be done. Following such analyses, it was found that the tests with polysulfone dissolved directly into the components of the epoxy systems proved to be inefficient [40] and, consequently, solvents must be used. On the other hand, the use of certain solvents produces, through the presence of the solvent molecules in the volume of the polymer, changes to its properties.

Initially, the study was designed to investigate the possibility of obtaining structural batteries by using cheap materials which were meant to improve certain properties or, through the simple presence of certain pulverous materials in the volume of the polymer, would allow the use of the obtained polymer composite as electrode of a battery. At this stage, the goals were the following:

- bibliographic analysis of the types of existing batteries;
- determining the batteries most susceptible of being reinterpreted in terms of composites;
- analysis of the availability of materials;
- execution of the composite materials modified with powders
    • selection of polymers;
    • determination of powders (if needed, their production);
    • establishing the strategies for powder dispersion;
    • establishing the mass fractions of powders;
- analysis of the properties of the formed materials;
- structural analysis of the formed materials;
- analysis of the energy storage capacity.

All of these goals have been reached in the initial stage of the study. Unfortunately, the last goal, although attained, led to the conclusion that the obtained materials cannot be used as electrodes for the creation of a structural battery, first of all because the obtained materials allowed no contact between the electrolyte and the active components of the electrodes (inorganic powders) because the latter were covered by an insulating polymer layer. A solution in this respect could be the increase of the polymer porosity without essentially modifying its mechanical properties (thus excluding the production of epoxy foam).

Based on the other bibliographical analyses, we chose the solution of the polymer mixture between epoxy resin and polysulfone. Polysulfone is a polymer used for obtaining the membranes for waste water treatment and, therefore, it makes it possible to obtain porous structures. In this second stage, the following goals were set:

- analysing the solubility of polysulfone in the components of the three used epoxy resins;
- finding optimal solutions for the dispersion of polysulfone in the volume of the epoxy resin;
- analysing the behaviour of mixtures during polymerisation;
- analysing the properties of the obtained materials.

From these goals, only the first was reached and most unfavourably as to the initially declared goal, that is, irrespective of the types of the used external physical agents – mechanical, thermic, undulatory, electromagnetic – none of the six chemical substances (two for each epoxy system, the resin and the reinforcement) proved to be polysulfone solvents and did not allow its dispersion in the volume of the respective substance.

Therefore, in a third stage of the study, it was suggested to use a solvent for the solvation of polysulfone and to introduce this solution in the pre-polymer mixture of each epoxy system. Unfortunately, the use of this method presupposes, first of all, to know the way in which the use

of the solvent modifies the properties of the epoxy systems to be able to understand subsequently which the effect of the polysulfone solution is.

Due to these reasons, we chose three solvents in which we know that polysulfone is soluble [128] and thus use solutions to modify the three epoxy systems. Concomitantly with the use of the solvent we had the idea of using it for placing in the volume of the epoxy resins organic substances which, through decomposition, would lead to the creation of either porous or nanostructured materials. Finally, the goals of the study are:

- bibliographic study concerning the organic solvents;
- determination of the organic solvents to be used;
- identification of the organic materials which, through thermic decomposition, could lead to the nanostructuration of a polymer;
- study of the solubility of these organic substances in the solvents of polysulfone;
- creation of modified epoxy materials through the addition of solvents;
- creation of composite materials with epoxy matrices modified with starch and glucose solutions;
- analysis of the mechanical properties of solvent-modified materials;
- analysis of the mechanical properties of starch and glucose-modified materials;
- analysis of the electromagnetic properties of modified epoxy systems;
- analysis of the thermal properties of the obtained materials..

4. The forming of composite materials and the extraction of test pieces

For obtaining composite materials we used as modifiers inorganic compounds (iron oxide and iron powders, nickel powders, nickel nitrate, zinc nitrate and lithium hydroxide), solvents (DMF, NMP and 1.4 D) and organic compounds (starch and glucose).

Some agents have agglomeration tendencies and, in order to avoid this problem, dispersants are introduced in the pre-polymer mixture, which can be either liquid or powders. The agglomeration of particles in matrices leads to the weakening of the mechanical properties, all such agglomerations being considered flows in the polymer network and acting – in the case of mechanical tests – as effort concentrators. Physically, the presence of agglomerations leads to the creation of materials which cannot be considered isotropic media and, therefore, require laborious analyses for the determination of the characteristic parameters. From the category of pulverous dispersion agents, we know: starch, clay and talc.

The homogenisation of the mixtures made between a component of the epoxy system (resin or hardener) or of the pre-polymer mixture (resin-hardener mixture in state of gel) and the agent used for modifying some of the polymer properties represents also a challenge and can be done differently for liquid solutions which can be homogenised through mechanical mixing and, respectively, powders – especially micro or nanometric, cases in which mechanical mixing may be accompanied by mixture ultrasounding and temperature control so as to ensure the viscosity conditions of the mixture [41].

For the achievement of the desired composite materials, we used three types of epoxy resin, Epiphen RE4020/DE4020 (manufacturer: Bostik), Epoxy resin HT 2 (manufacturer: R&G), and Epoxy resin C (manufacturer: R&G).

4.1. Used materials

The materials used for forming composites with modified polymer matrix, according to previous studies, have been selected to be compatible and the interphases between them to allow the achievement of enhanced properties as compared to epoxy resins, therefore, we will present below the characteristics of the used resins, of the modifiers, additives, as well as of the solvents used for the forming of these new composite materials.

The forming of a polymer composite material with better properties than the used epoxy resins presupposes covering several stages:

- establishing the polymer matrix, according to density in polymerised state, the polymerisation time and the ambient temperature, the temperature reached during polymerisation, the manoeuvrability presupposed by the gel time, toxicity;

- establishing the type of additive and its nature: the size of particles, the behaviour upon dispersion in the pre-polymer and the capacity to dissolve in solvents.

4.1.1. Epoxy resins

For obtaining the proposed composite materials, we used the three above-mentioned epoxy resins, noted in this paper E, H and C. We selected these three resins as they are the most used due to their qualities, very good resistance to moisture and to ultraviolet radiations, excellent adhesiveness and, after complete polymerisation, good resistance to heat, transparency and, last but not least, polymerisation is achieved at ambient temperature in maximum 24 hours.

All three epoxy systems ensure a long enough gel time so that the homogenisation of additives is done completely, that is, for casting in the previously established matrices. The chosen matrices were 14x14 cm plates, used for the electromagnetic characterisation, followed

by the extraction of test pieces with the water jet cutter, used in traction, as well as cylinders for the test pieces used in tribological characterisation, compression and bending mechanical tests.

4.1.2. Additives and property modifiers

Based on the bibliographic studies concerning batteries, in line with the goal to obtain cheap composite materials, we chose to use iron and nickel for the electrodes of the active element (accumulator). Ni-Fe batteries proved to be the most efficient (although their large mass makes them rather difficult to use), practically presenting an infinite number of recharging cycles. This is why we tested the hypothesis of obtaining composites (with epoxy matrix) loaded with iron and, respectively, nickel, which could be used as electrodes and which would (subsequently) allow the formation of reinforced composites, thus obtaining structural batteries. Loading consisted in loading the epoxy resins with iron and iron oxide powders and, respectively, nickel and nickel oxide. In the design stage, analysing the real possibilities of obtaining the desired materials, we decided to use zinc powder as well, next to the nickel powder, as well as sodium hydroxide in order to intensify the electropositive character. Obviously, metallic powders do not interact with the epoxy matrix when it is polymerised, but, as subsequently proven, are affected during their dispersion in the components of the epoxy system, especially due to the presence of hydroxyl groups in the molecules of Bisphenol A.

The used organic modifiers were also chosen due to the fact that they are found in most 'green' plants, therefore, given to their origin, we may say they are renewable materials. Thus, we aimed at creating biodegradable composite materials and purchase costs for the modifiers are low. Based on these considerations, we used as modifiers starch brought from a supermarket in Galați and 99.5% purity glucose from Sigma Aldrich.

4.1.3. Solvents

After choosing the organic modifiers, we made solubility tests in three organic solvents and noticed that starch dissolves in each solvent, with no other special intervention or thermal condition, through stirring only. Concerning solubility tests for glucose, it took 15 minutes of stirring at a constant temperature of 50°C to dissolve in N,N-dimethyl formamide (DMF) and 30 minutes in 1-metil-2-pyrrolidinone (NMP).

N,N-dimethyl formamide is an organic solvent, commonly abbreviated as DMF, it belongs to the class of dipolar aprotic solvents, has the appearance of a colourless liquid, mixable with water and with all the organic liquids.

1-metil-2-pyrrolidinone, abbreviated as NMP, is used in industry as paint additive for covering surfaces or as solvent for cleaning, degreasing and dilution. 1-metil-2-pyrrolidinone (NMP) is an organic compound, colourless liquid, mixable with water and with most of the common organic solvents.

1,4-Dioxane, often simply called Dioxane, because the other isomers, respectively 1,2 and 1,3 are rare. 1,4-Dioxane is a heterocyclic organic compound and it will be hereinafter referred to as 1,4-D.

4.2. The forming of composite materials

For the formation of materials, several stages were covered:
- determining the method of dispersion of inorganic powders and organic modifiers;
- establishing the type of matrix;
- obtaining the dispersions of inorganic powders in the volume of epoxy systems;
- obtaining 50% concentration solutions with solvents and organic modifiers.

According to the desired part, achieved in keeping with the properties to be determined and taking into account the possibility of extracting the test pieces required for the tests, according to the standards imposed by the equipment and devices used in determining the properties, the composite materials were formed by moulding for obtaining plates and, respectively, cylinders.

Two plates (in glass matrices) and six cylinders (in low-density polypropylene matrices) were formed for all the designed materials.

4.2.1. The forming of composite with inorganic modifiers, Nickel and Iron

In order to reach the first two goals, we made two types of materials in which most of the used inorganic modifiers were Fe and Ni, with all the three available epoxy systems. Given that, at present, the most efficient batteries are Ni-Fe batteries, the study focused on their use as modifiers of the polymer properties with the purpose of identifying the possibility to use the formed composites as elements of structural batteries.

Tabel 1 Names of materials formed with inorganic modifiers.

Pos.	RESIN	EPIPHEN Reference	HT2 Reference	C Reference
1	Nickel	EN	HN	CN
2	Iron	EF	HF	CF

4.2.2. The forming of composite with organic modifiers

For comparing future results we first formed materials with the three unmodified epoxy resins, then with epoxy resins modified with 10% solvent of the amount of used epoxy resin. The amount of resin was established after calculating the volume necessary for casting two plates and six tubes, also taking into consideration a 10% addition for losses.

Consequently, after making the solubility tests of the two additives in the chosen solvents, we made 50% solutions which we used as modifiers for the three epoxy resins and, implicitly, obtained new composite materials.

According to the above method and the exposed conditions, we obtained 18 composite materials, modified with a 50% solution, 9% mass ratio, 9 composite materials modified with a 10% solvent and 3 reference materials. In the table below, you will find the names of the obtained materials, 30 materials in all, out of which 27 are modified composite materials.

Tabel 2. Names of materials formed with organic modifiers.

Pos.	RESION SOLUTION	EPIPHEN E0	HT2 H0	C C0
1	DMF	E1	H1	C1
2	DMF Starch	E2	H2	C2
3	DMF Glucose	E3	H3	C3
4	1,4 - D	E4	H4	C4
5	1,4 - D Starch	E5	H5	C5
6	1,4 - D Glucose	E6	H6	C6
7	NMP	E7	H7	C7
8	NMP Starch	E8	H8	C8
9	NMP Glucose	E9	H9	C9

4.3. Extraction of test pieces

The extraction of composite materials from the cylindrical matrices was made by destroying the cylindrical tube through mechanical methods. For each set of parameters of the composite material to be characterised, we prepared test pieces of the sizes required by the standards of the used equipment and devices.

After the extraction of test pieces from the cylindrical matrices, the first operation was to remove one centimetre from each end of the tube (one had plastilin impurities, the other because of the convex shape of the formed material, due to the contraction). For this operation, as well as for the extraction of test pieces with the sizes required by the standards of the equipment to be used for the mechanical (bending, compression) and thermal characterisation of composite materials, we used the lathe – Micomat 10.

For the extraction of test pieces required for traction tests, we used the water jet cutter – IWM CTA1313U.

5. Equipment used for analysing the properties of the materials formed with inorganic and organic modifiers

For determining the properties of the new composite materials formed with inorganic and organic modifiers, we used the equipment below:
- TMA/SDTA 840 – for determining the heat expansion coefficient;
- DSC – for determining specific heat;
- Tribometer – TRM 1000 – for the tribological characterisation of the formed composite materials;
- Mechanical testing machine - INSTRON 8802 – used for compression, bending and tension tests;
- RLC-meter - Protek 9216A – for the analysis of electric conductivity.

5.1. TMA/SDTA 840

For determining the heat expansion coefficient of the materials modified with inorganic agents, both the shape and the sizes of the test piece were dictated by the characteristics of the device, a thermomechanical analyser (TMA). The required test pieces were extracted from the composite material cast in the shape of cylinders in disks with thicknesses between 0.4 and 1.4 mm. According to the method, the specimen was subject to heating, with a heat rate of 10°C/min, and to a force of 0.02N, specific to this type of measurements.

5.2. DSC

For determining the specific heat of the materials modified with inorganic agents, we used a differential scanning calorimeter (DSC). For the characterisation of the obtained composite materials, we extracted 5 test pieces of each material, measuring 6 mm in diameter and 5 mm high. The method of determining specific heat using the DSC is a technique in which the temperature difference between the test piece and a reference material is measured as temperature function. The test piece and the reference material are subject to a controlled heating-cooling programme [42], [43], [44]. The heating effect which appears in the case of a phase transition or physical-chemical process is recorded as heat flux difference, translated in electronic signal, amplified and then processed by the software of the DSC [45], [46].

5.3. Tribometer – TRM 1000

The tribometer is used for examining and stimulating the friction and abrasion processes under sliding load.

Tribometer TRM 1000 is manufactured by Wasau, and according to the manufacturer's description, during the standard testing procedure, a standing specimen (PIN or ball) is pressed onto the frontal surface of a rotating disk placed above, with a defined normal force.

Tribological tests are meant to determine the friction coefficient on sliding and the afferent wear. These tests are necessary for understanding the tribological properties of the composite materials and the areas in which they will be used.

5.4. Mechanical testing machine - INSTRON 8802

Measurements performed with this equipment had the purpose of determining the mechanical properties of the materials subject to compression, bending and tension tests.

According to the data provided by the manufacturer, this mechanical testing machine, when combined with the Bluehill software and the adequate accessories, is ideal for performing a wide range of static tests, such as tension, compression, bending, shearing, displacement and friction tests.

The bending, compression and tension tests made were performed at ambient temperature and the tested specimens were extracted using the above-mentioned devices, according to the standard afferent to each testing method.

5.5. RLC-meter - Protek 9216A

For the electromagnetic characterisation of composite materials we applied the method described in [47] using the same experimental device. The electromagnetic tests of the materials are performed according to a sinusoidal regime, therefore, for determining these properties the used RLC-meter was Protek 9216A which has five fixed measuring frequencies, with digital display which allows the simultaneous recording of the pairs of parameters:
- R – Q (electric resistance – quality factor);
- R – Q (inductance – quality factor);
- C – D (electric capacity – dielectric loss);
- C – R (electric capacity – electric resistance).

We use plate-type specimens, cleaned with ethylic alcohol prior to testing in order to prevent any measurement errors.

6. Results and discussions

6.1. The thermal properties of composite materials modified with inorganic agents

Specimens were taken from the formed composite materials according to the standard imposed by the equipment used for analysing the thermal properties. Thus, for TMA and DSC the following testing method was established, having two heating – cooling cycles, every 10 degrees Celsius, up to a maximum temperature of 180 degrees and a minimum temperature of 30 degrees, which was also the starting temperature for the experiment:

- At 30 degrees Celsius – isothermal for 2 minutes;
- Increase of temperature with 10 degrees per minute up to 180 degrees Celsius;
- At 180 degrees Celsius – isothermal for 2 minutes;
- Decrease of temperature from 180 degrees to 30 degrees;
- Isothermal for 2 minutes at 30 degrees;
- Increase of temperature with 10 degrees per minute up to 180 degrees Celsius;
- At 180 degrees Celsius – isothermal for 2 minutes;
- Decrease of temperature from 180 degrees to 30 degrees;
- Isothermal for 2 minutes at 30 degrees.

6.1.1. Heat expansion coefficient

Generally, for polymers, the expansion coefficient is approximately ten times higher than for metals which, in their turn, have an expansion coefficient higher than ceramic materials.

We present below, in figures 1 – 9, the representatives curves for each tested material, given by the equipment used for determining the heat expansion coefficient.
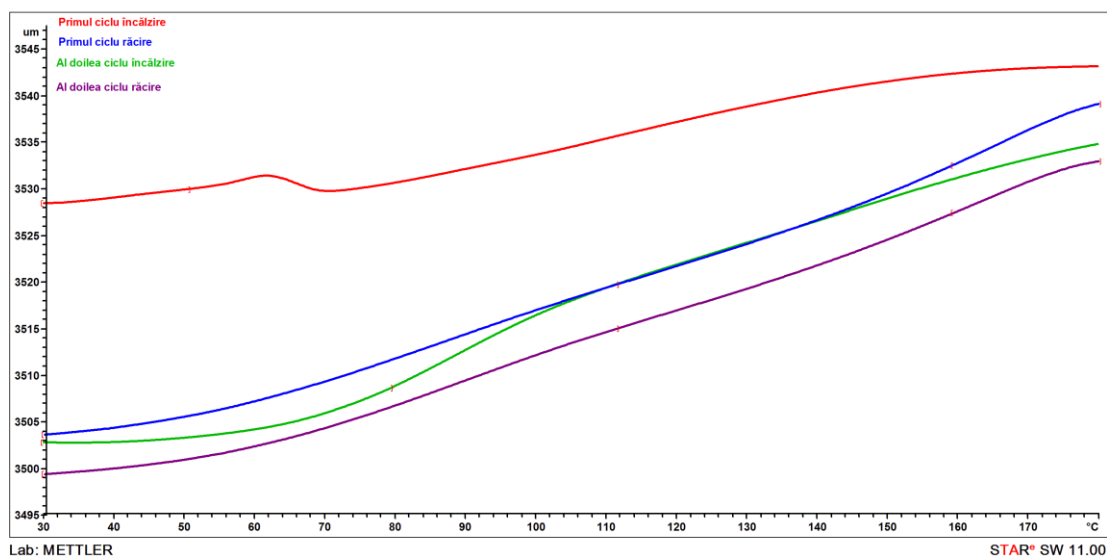
Figura 1. Variation of material C0 thickness according to temperature.
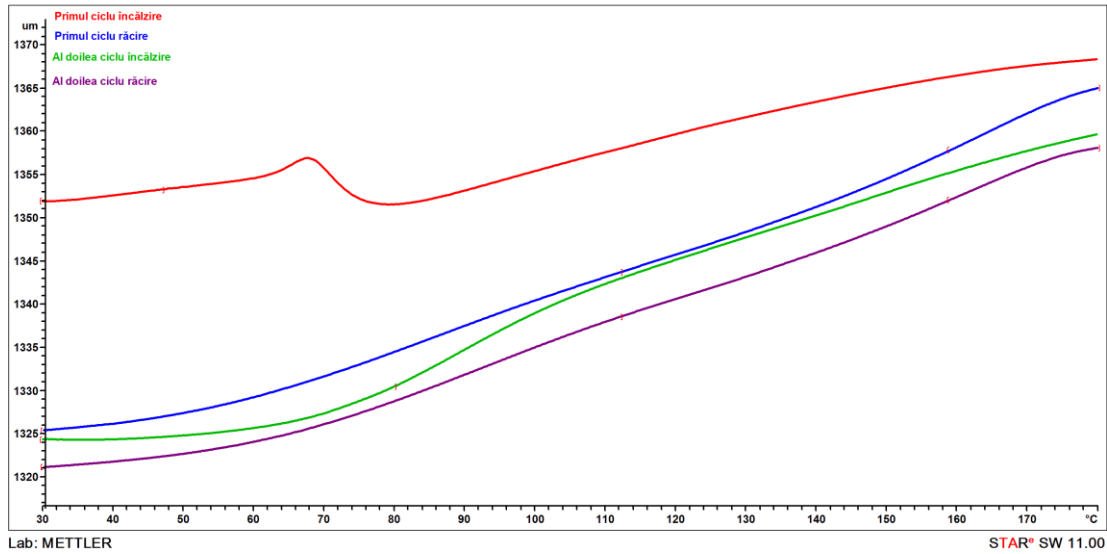
Figura 2. Variation of material CN thickness according to temperature.
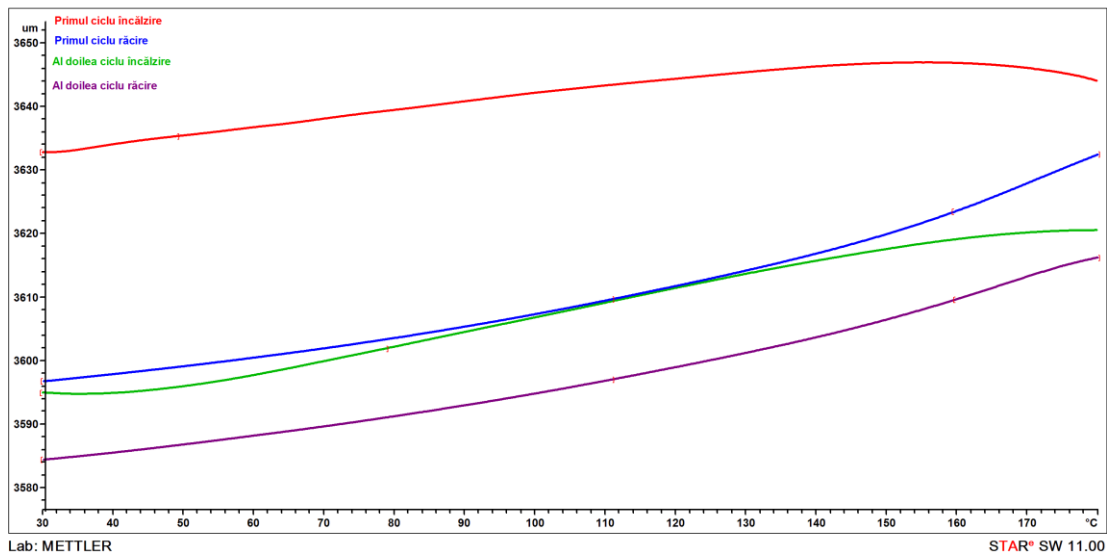
Figure 3. Variation of material CF thickness according to temperature.
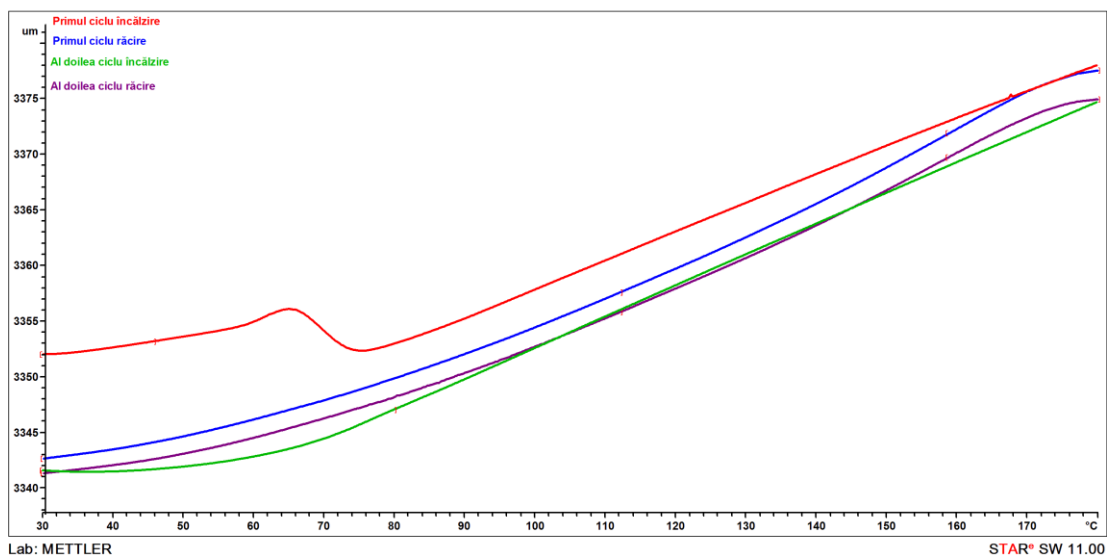
Figure 4. Variation of material E0 thickness according to temperature.
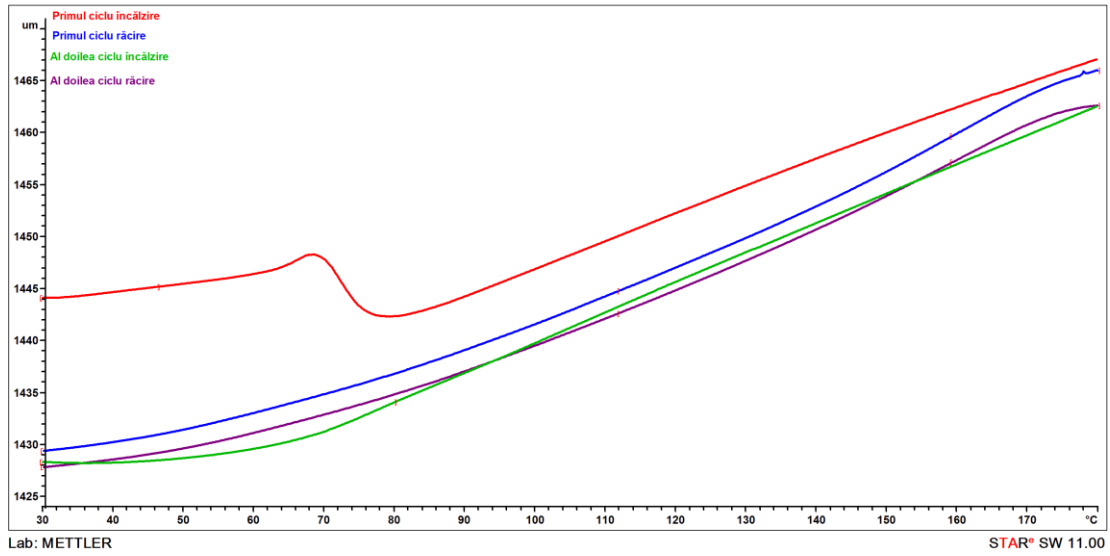
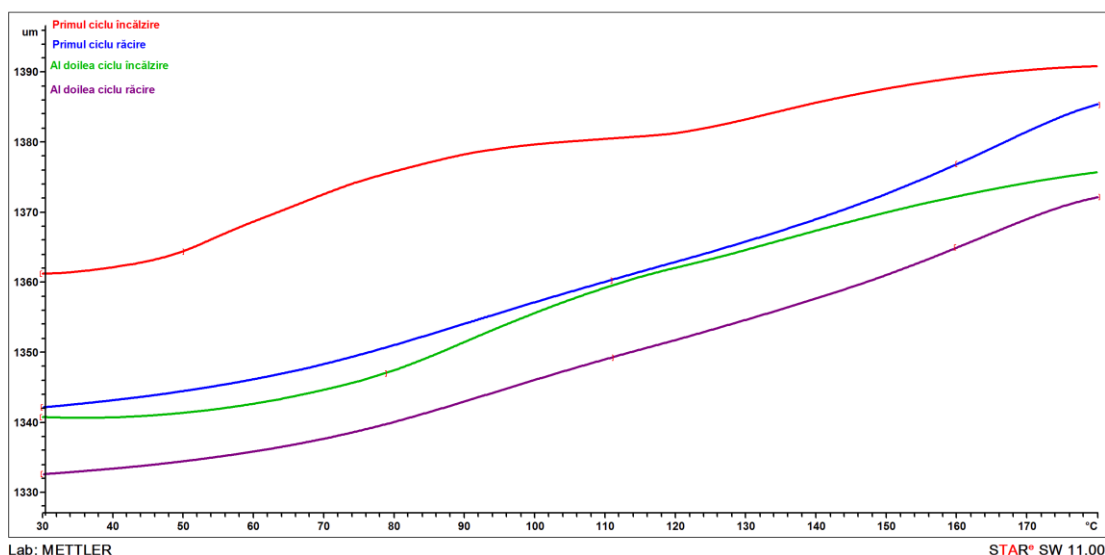*Figure 5. Variation of material EN thickness according to temperature.*
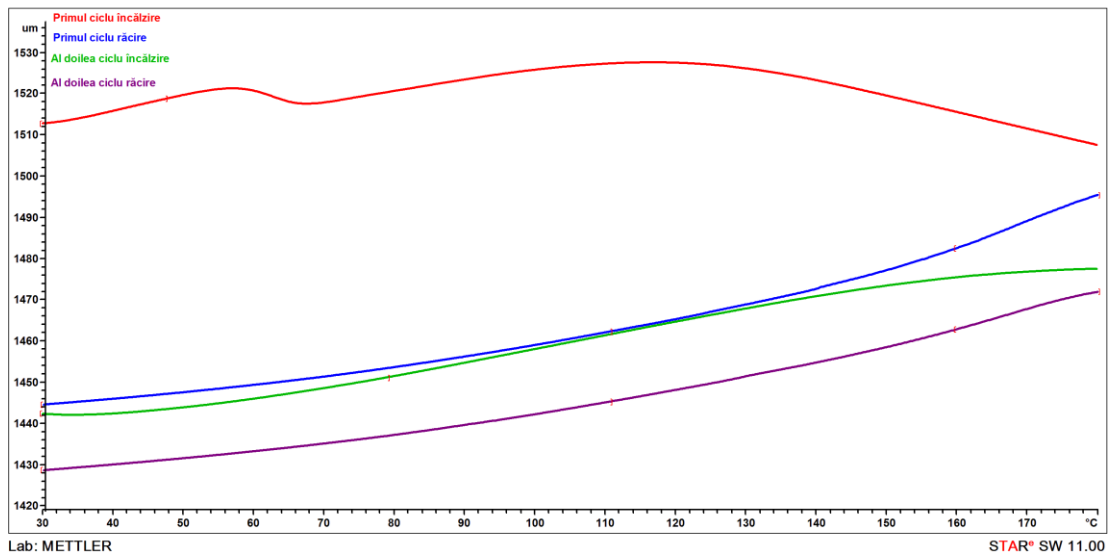
Figure 6. Variation of material EF thickness according to temperature.
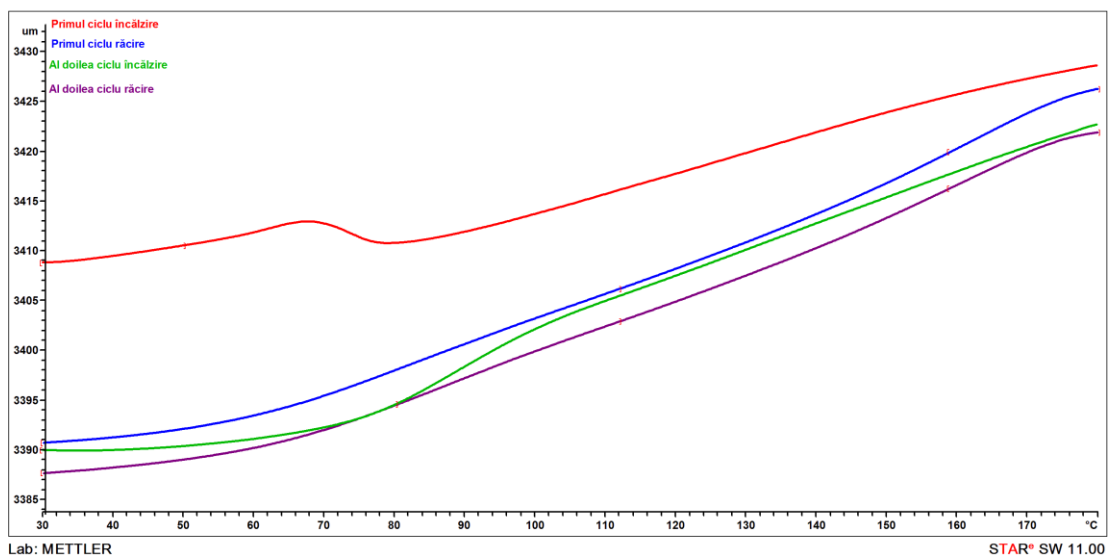
Figure 7. Variation of material H0 thickness according to temperature.
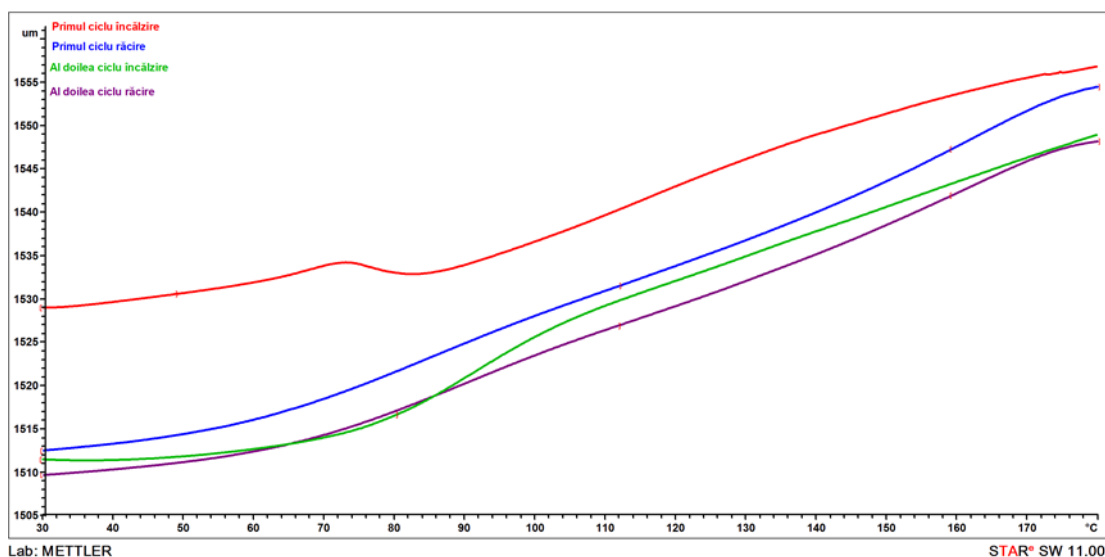
Figure 8. Variation of material HN thickness according to temperature.

Figure 9. Variation of material HF thickness according to temperature.

In heat tests, standard recommendations are to make determinations for two heating-cooling cycles, the sought results being measured on the last cooling of the procedure. Given that the specimens analysed in this study are made of polymer materials or modified polymer materials, we must take into consideration the behaviour of polymers upon heating (and cooling, for special technical possibilities), beyond the limits recommended by the de polymer manufacturer.

The thermomechanical analysis performed with the purpose of determining the linear expansion coefficient of the composite materials obtained through the modification of the three epoxy resins with iron and iron oxide and, respectively, nickel, nickel oxide, nickel nitrate, zinc and lithium hydroxide revealed the following:

- generally, the expansion coefficient of the polymer used as matrix has lower values than the expansion coefficient of modified materials;

- the first thermal cycle of the method used for determining the expansion coefficient may be interpreted as a material reinforcement treatment;

- polymers display, on the first heating segment, at 60-70°C, critical points which disappear after heating at 180°C;

- the critical points appear on the first heating segment for the nickel-modified materials as well but they are shifted to the right (towards the 70-80°C temperature range);

- iron and iron oxide modified polymer matrices manifest – on the first heating segments – different behaviour as compared to the polymer matrices and the nickel-modified materials which may lead to the conclusion that chemical interactions occur between the components of the epoxy systems (most probable Bishpenol A) and dispersed powders;

- the values of the expansion coefficients (final determinations – the last cooling segment) do not follow any rule given that in the case of resins C and E the highest expansion coefficient is presented by the nickel-modified materials and, in the case of resin HT, the iron-modified materials;

- subsequent analyses are required for the identification of the chemical reactions which occur between the epoxy resins and the mixture of iron and iron oxide.

6.1.2. Specific heat

In the case of polymers, the analysis of this parameter is even more important if we take into consideration that all polymers present phase transitions (undetectable at macroscopic level), such as the glass transition. Concerning composite materials, the mixture rule allows the evaluation of this parameter provided that the proportions of the components in the final material and the values of the specific heats are known. There are not, however, when applying the mixture rule, restrictions or corrections concerning the sizes or shapes of the phases dispersed in the matrix so that the value of the specific heat of a polymer in which an iron nail was placed shall be, by applying the pattern, the same with that of the same amount of polymer in which a mass of iron filings was dispersed equal with the mass of the nail. Previous studies carried out by the Polymer Composite Laboratory (and presented in the doctoral theses of our colleagues) outlined the fact that the mixture law does not lead to acceptable results in the case of powders dispersed in polymer matrices, especially in the case in which the volume fractions of dispersed phases are small.

The higher the specific heat of a part is, the higher may be its dimensional stability. From this perspective, the results obtained through the DSC (differential scanning calorimetry) technique are analysed on the same temperature ranges as the thermomechanical analysis: 60 - 70°C, 80 - 100°C and 110 - 140° and, as in the case of the thermomechanical analysis, the study concerning both heating and cooling. The specimen heating programme is the same as the one used in the TMA analysis.

In figures 10-18 we can see the most representative heat fluxes through specimens on two heating segments and two cooling segments.
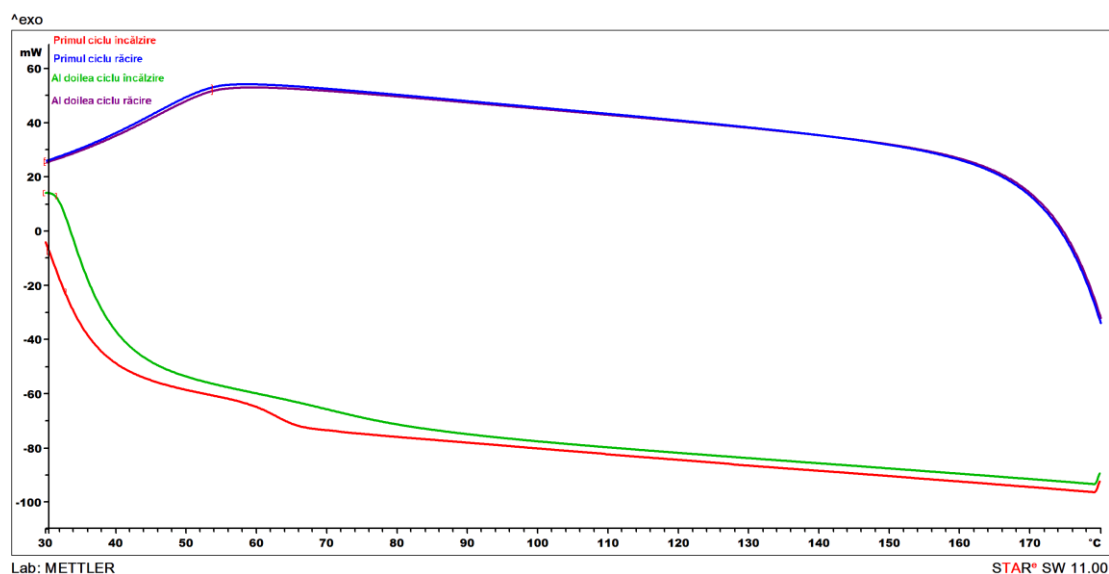

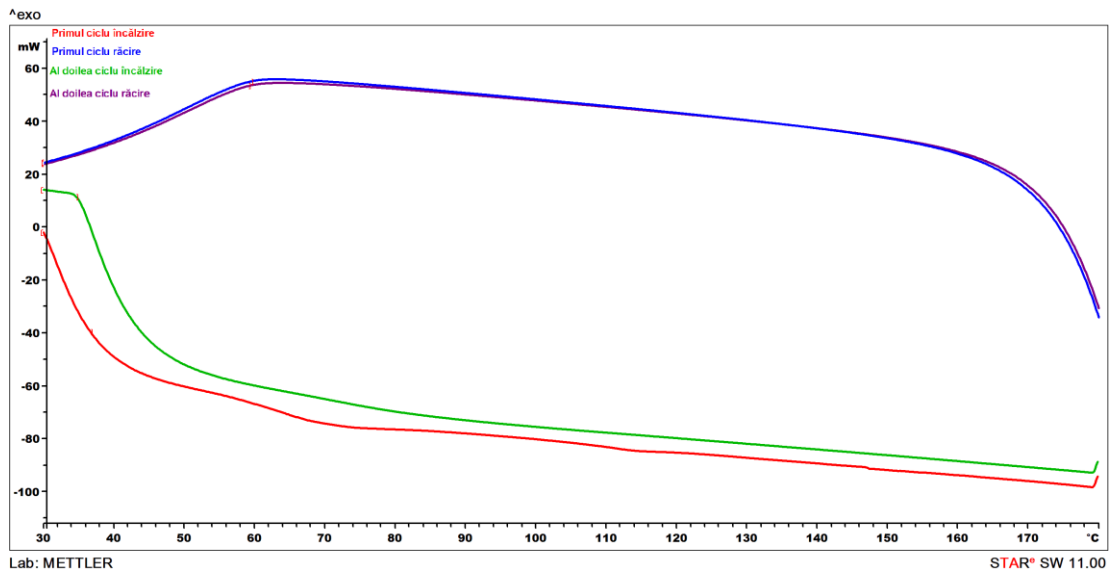*Figure 10. Energy absorption of material C0 according to temperature.*

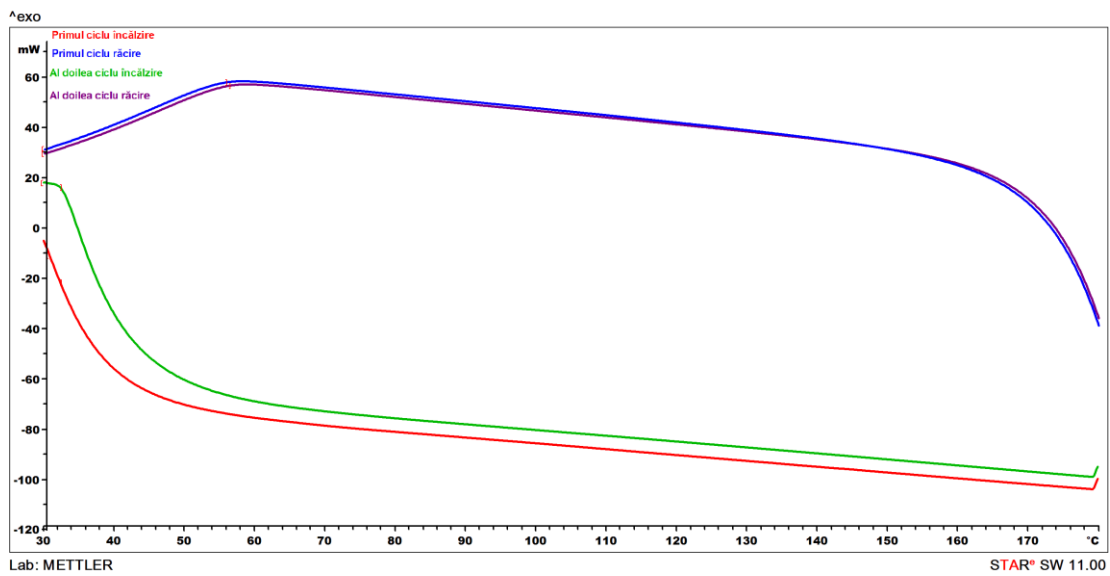*Figure 11. Energy absorption of material CN according to temperature..*

Figure 12. Energy absorption of material CF according to temperature..
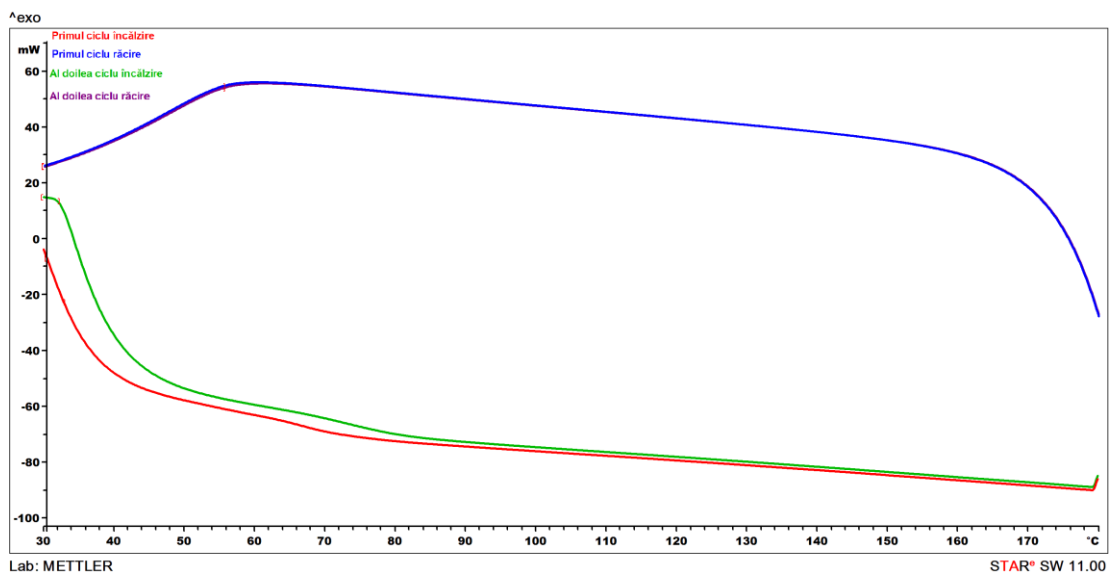

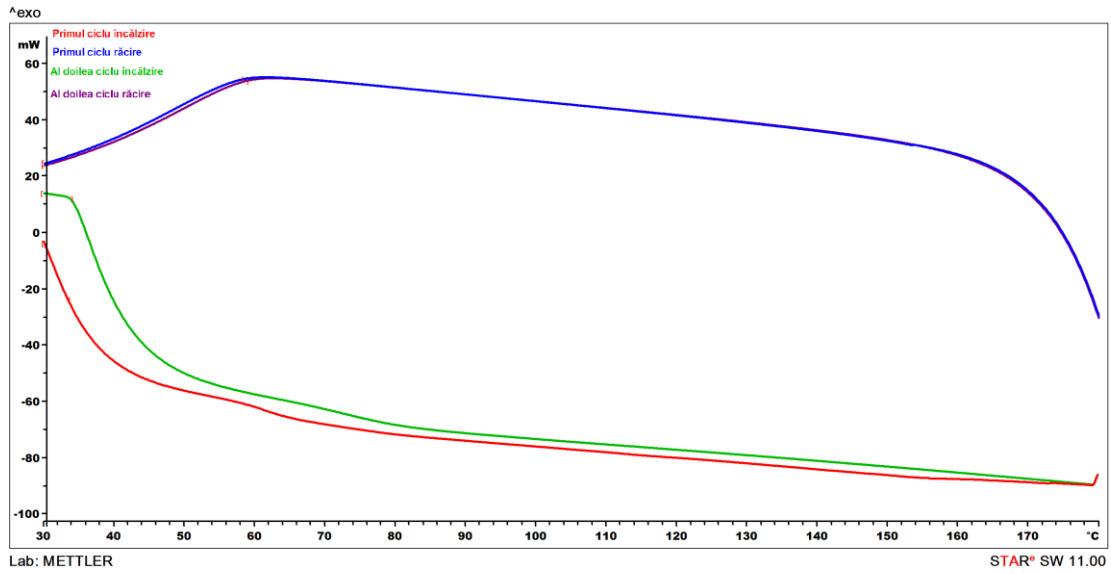*Figure 13. Energy absorption of material E0 according to temperature.*

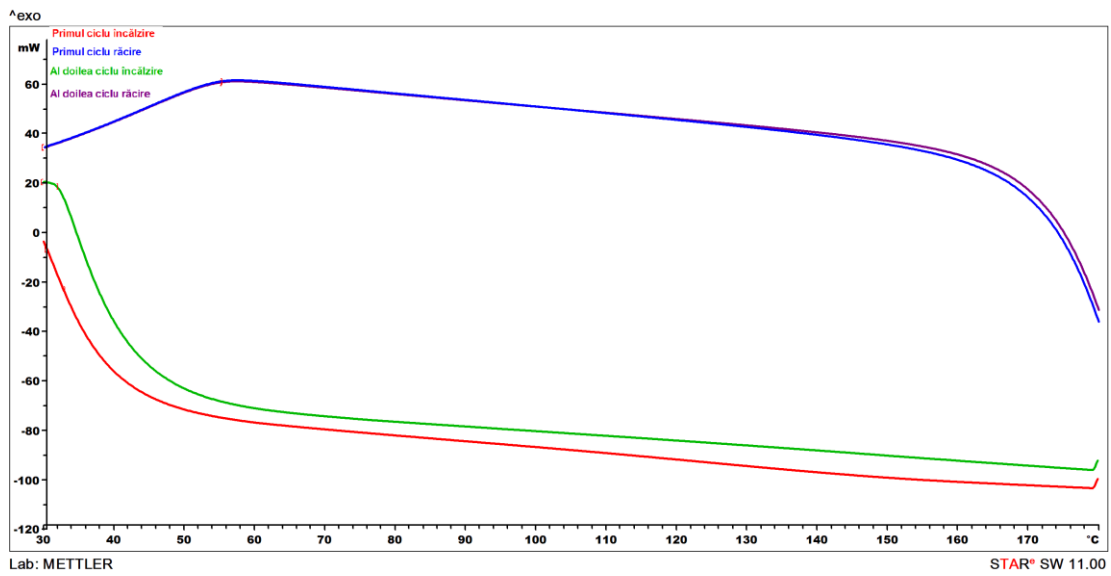Figure 14. Energy absorption of material EN according to temperature..

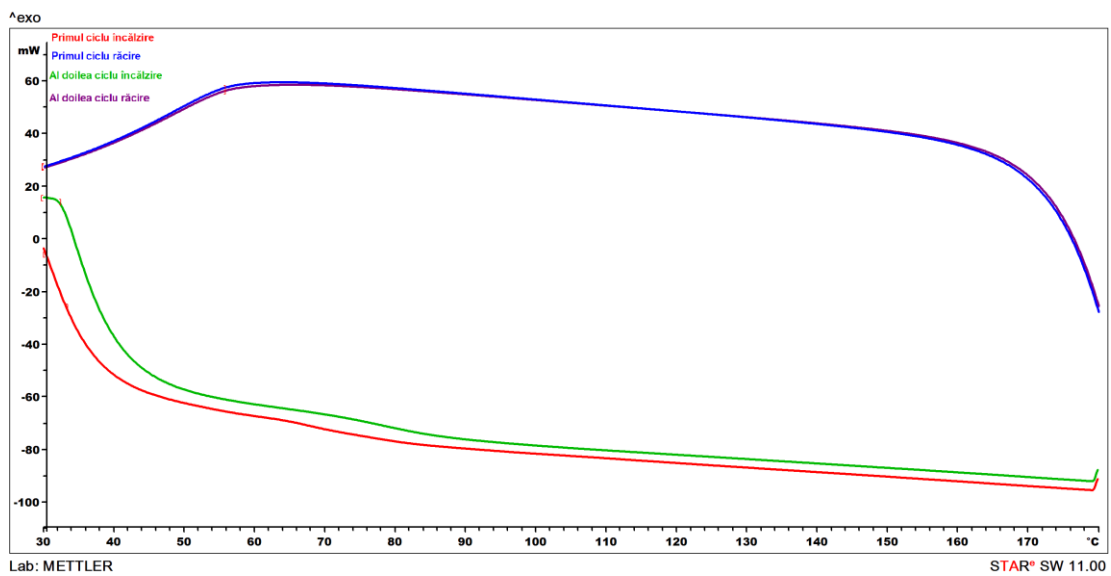Figure 15. Energy absorption of material EF according to temperature.

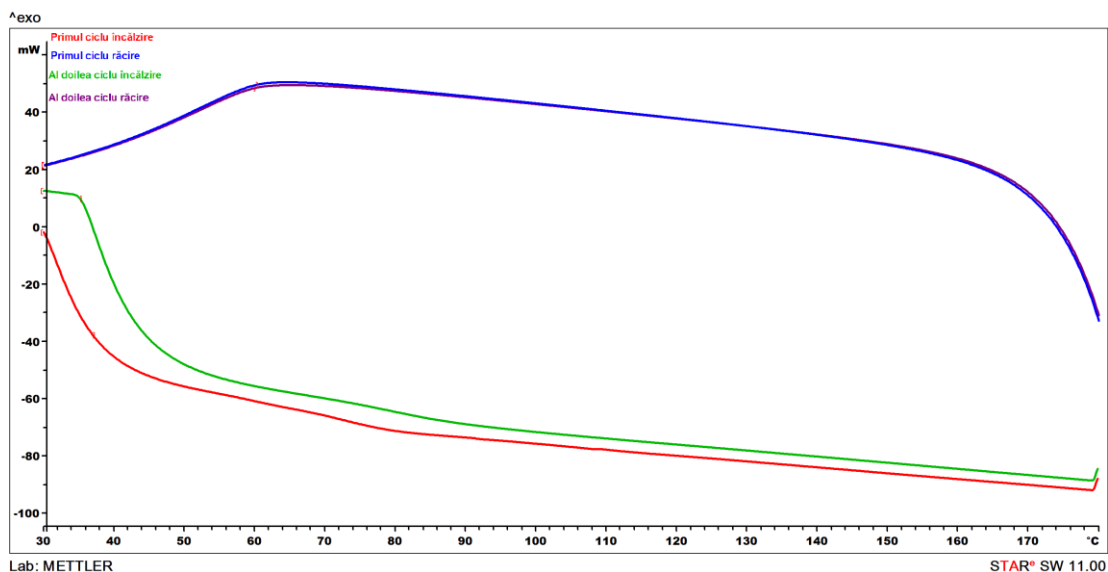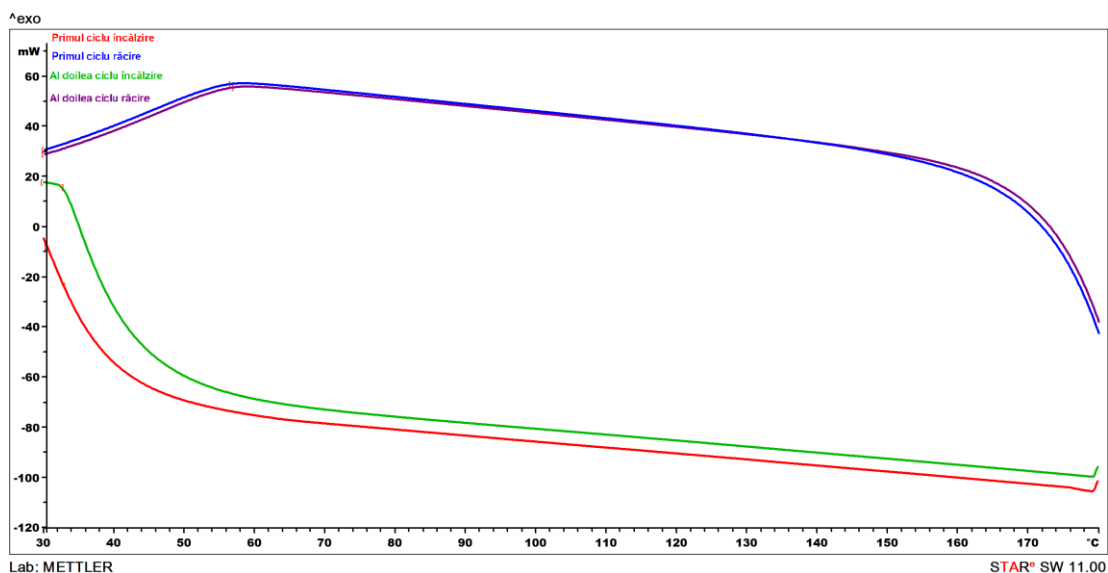Figure 16. Energy absorption of material H0 according to temperature.

Figure 17. Energy absorption of material HN according to temperature.

Figure 18. Energy absorption of material HF according to temperature.

The first remark concerning the above graphic representations is that, like in the case of thermal analysis, there are phase transitions in the 60-70°C temperature range. These are visible both in the case of the three analysed polymers (C0, E0 și H0) and in the case of nickel, nickel oxide, nickel nitrate, zinc and lithium hydroxide modified polymers. As with thermal analysis, we can see that these critical points are shifted to the right in the case of modified polymers, as compared to polymers themselves. Additionally, we notice that in the case of iron and iron oxide modified materials, these critical points do not appear on the heating curves (the same as in the case of thermomechanical analysis), which confirms the hypothesis of the existence of some chemical reactions which alter the structure of the polymer.

The DSC analysis of the materials proposed to be used as electrodes of the structural batteries, compared with the polymers used as matrix revealed the following aspects:

- the values of the specific heat parameter are higher on the first cycle of the test than on the second cycle, for each polymer;

- generally, polymers, present a slow linear dependency of the specific heat on the value of the temperature at which it is determined;

- iron and iron oxide modified materials have lower values of the specific heat than those of the basic polymer which, on the one hand, may be explained based on the existence of certain

chemical reactions between the agents used for the modification of properties and polymers in the dispersion phase of these agents and, on the other hand, confirm the fact that in this case the mixture rule cannot be applied;

- nickel, nickel oxide, zinc and lithium hydroxide modified materials have the highest values of the specific heat;

- we should perform detailed chemical analyses to be able to identify the chemical reactions which take place at the dispersion of iron and iron oxide in the pre-polymer mixture of epoxy systems.

6.1.3. SEM structural analyses of the materials modified with inorganic agents

In the current context of the scientific and technological development of composite materials, the morphological and structural characterisation at a nano and even atomic scale through the various modes of operation of an electronic microscope represents an important method of study. For the microscopic analyses of the materials modified with iron, iron oxide, respectively, nickel, nickel oxide, nickel nitrate, zinc and lithium hydroxide, the specimens were torn and the fractured surface was analysed.

The purpose of the modification of the three polymers with metallic agents was to use them, eventually, as electrodes for structural batteries. The electric testing failed. The lack of pores large enough to allow the access of the electrolyte to the active elements (metallic powders). The structural analysis reveals the fact that these elements are, in fact, covered in the polymer (insulating) so that the liquid agent (electrolyte) could not reach them anyhow. In order to use such a material as electrode, its metallic particles should be left exposed.

From the perspective of the subsequent execution of structural batteries (from other starting positions), these materials should not present special mechanical properties as, in the structure of the material, they shall be protected by other polymer layers or reinforced polymer layers.

The purpose of the SEM analyses in the case of epoxy composite materials modified with inorganic agents was to obtain information concerning the presence of the modifier in the volume of the material, as well as its dispersion degree. The performed analyses started from 1000x, 5000x 10 000x and, in the end, 50000x.

In the case of materials which contain iron powder and iron oxide, there isn't a good connection between the epoxy matrix and the modifier, noticing powder agglomerations, which may affect the tribological properties and may influence electrical properties. The distribution differences of the modifier in the matrix can also be seen in the thermal behaviour of the composite materials.

6.2. The tribological properties of the composite materials modified with organic agents

The tribological properties of the modified composite materials are influences by the effect of temperature, the speed of surfaces which come into contact and the pressing force.

According to the different studies, it results that friction takes place due to the molecular – mechanical interactions of the bodies which come into contact [48], [49].

The tribological tests for the composite materials were performed in three different regimes of load and sliding speed, on a distance of 1000m.

The three regimes were noted R1, R2, and R3, characterised by the force-velocity pair (F, v) as follows: R1 - (5N, 2m/s); R2 - (10N, 1 m/s); R3 - (15N, 0,66m/s). The friction coefficient and the wear rate of the materials were studied at ambient temperature. Three tests were made on each material, in the three previously established regimes, and the results are the average values for each material.

Figures 19, 20, 21 depict the evolutions of the friction coefficient for composite materials formed with epoxy resin C in the three testing regimes. For all the materials and for all the three testing regimes, we notice a transition regime on the first three-four sliding meter, after which friction become stabilised. For the basic polymer (in this case epoxy resin C), we see that, practically, the value of the friction coefficient does not change during testing for regimes R1 and R2 while for regime R3 we notice a sudden drop of the parameter value, followed by a slow decrease. Among these materials, C1 has the closest behaviour to the basic resin (resin diluted with N,N dimethyl formamide), the other materials presenting a growing evolution of the friction

coefficient upon sliding, according to the sliding distance. This evolution, corroborated with the remark that the values of the friction coefficient during sliding are higher for any other material apart from C0 (basic resin) may be accounted for by the fact that the addition of solvents causes the softening of the material, on the one hand and, on the other hand, the local increase of temperature amplifies this effect.
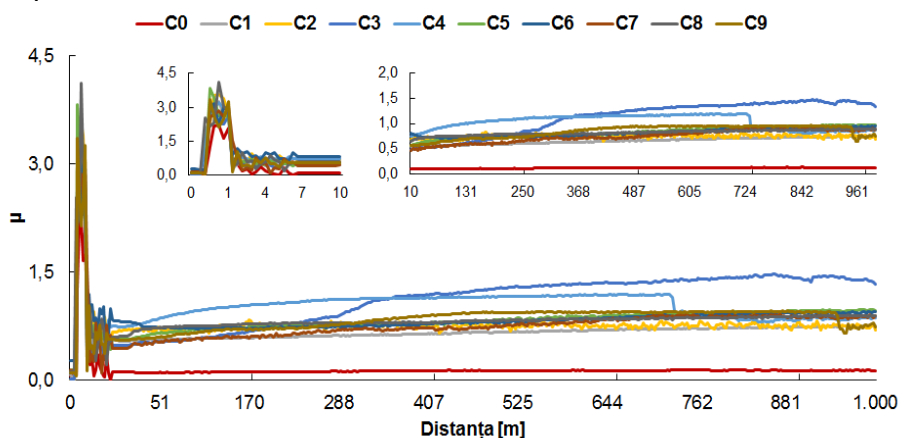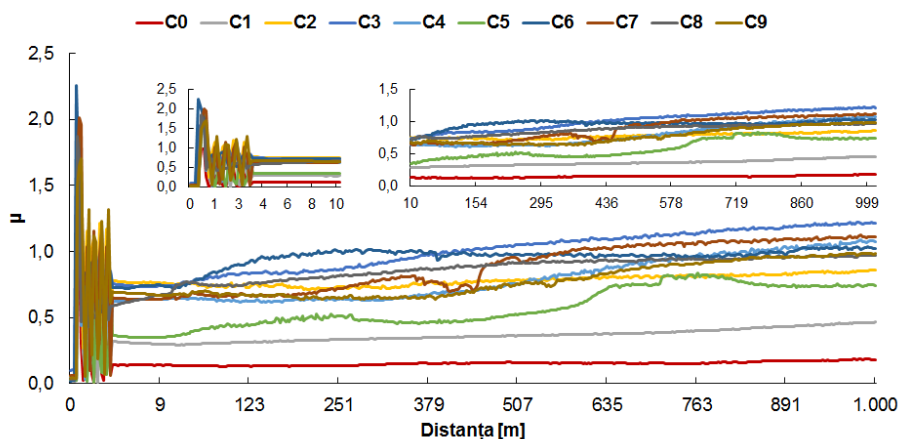
Figure 19. The evolution of the friction coefficient on group C (R1).

Figure 20. The evolution of the friction coefficient on group C (R2).
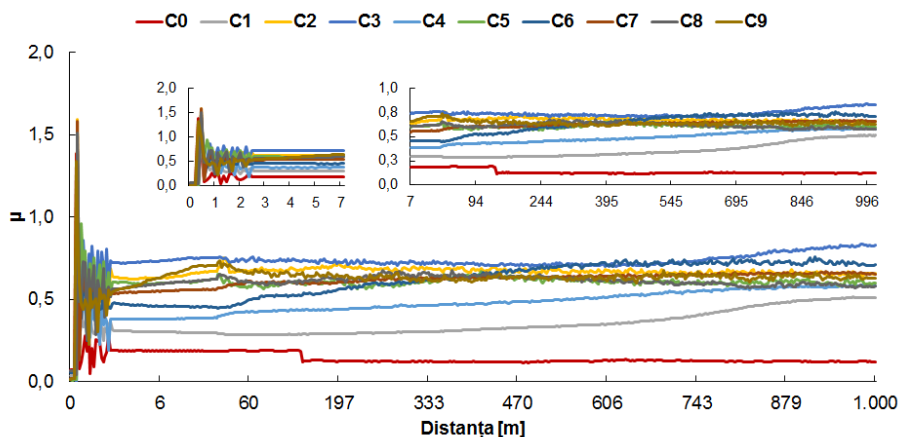
Figure 21 The evolution of the friction coefficient on group C (R3).

- for all the materials, C1, C2, C3, we notice the increase of friction coefficients during the test, as well as the fact that material C1 behaves almost the same as C0 (reference material);

- all the materials, C4, C5, C6, have an increased value of the friction coefficient (in relation to C0), but, after the transition stage of the sliding, the values remain constant, without a great influence of the glucose or starch present in the polymer;

- in materials C7, C8, C9, we notice a continual increase of the friction coefficient during the sliding, the best behaviour being that of material C7.
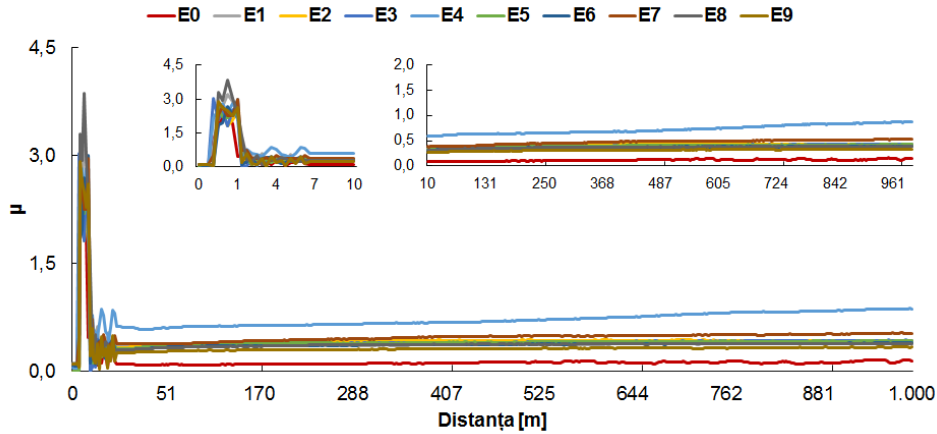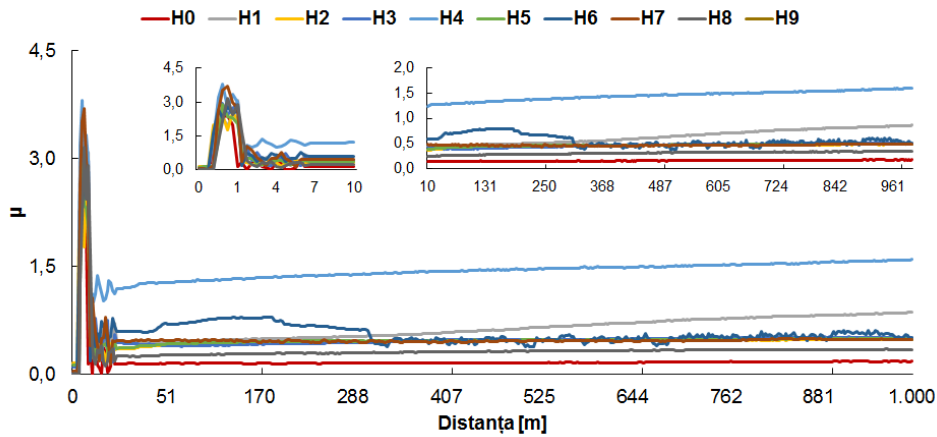

Figure 22. The evolution of the friction coefficient for type E materials (R1).
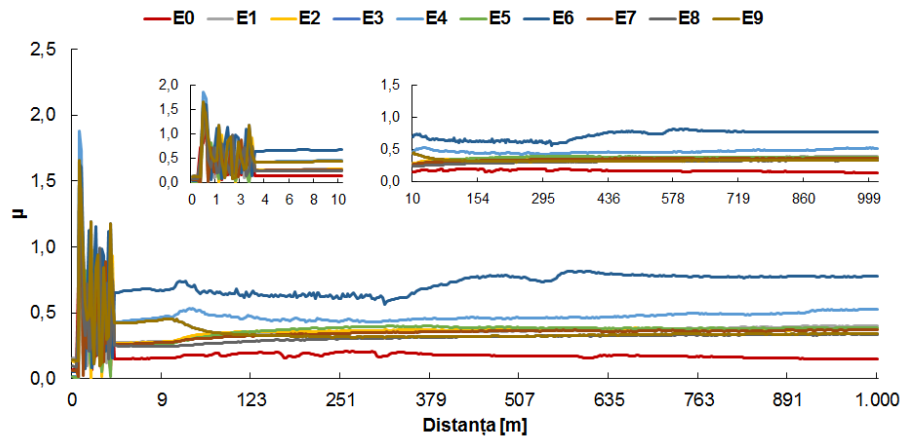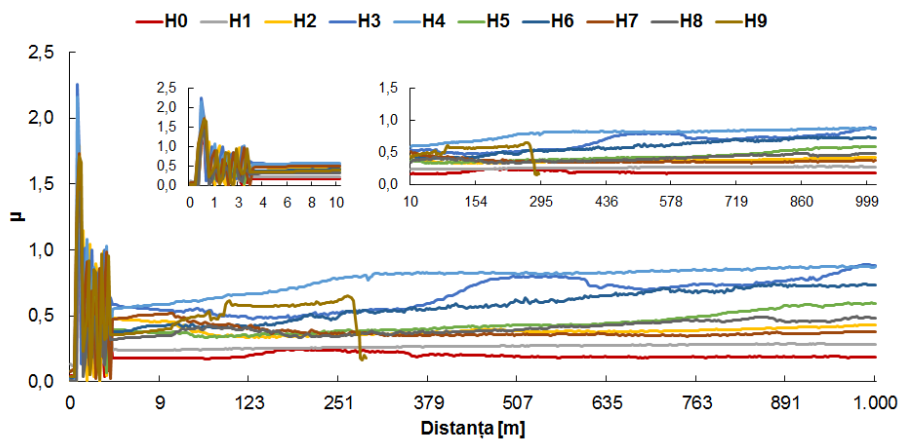

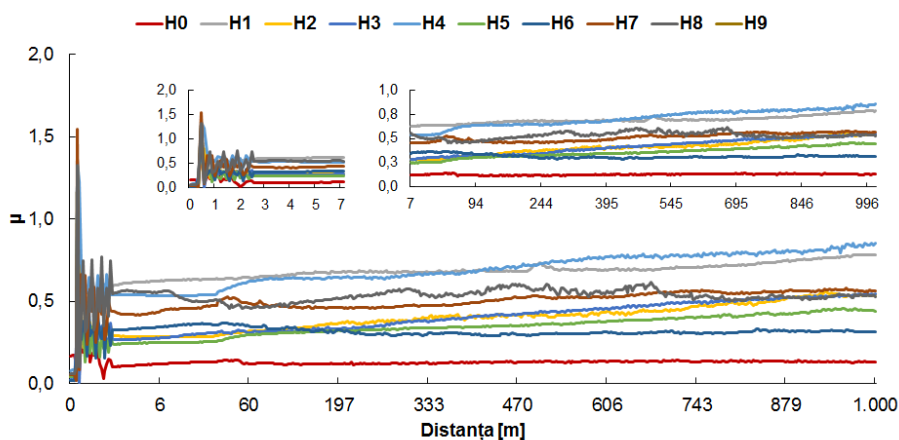*Figure 23. The evolution of the friction coefficient for type E materials (R2).*
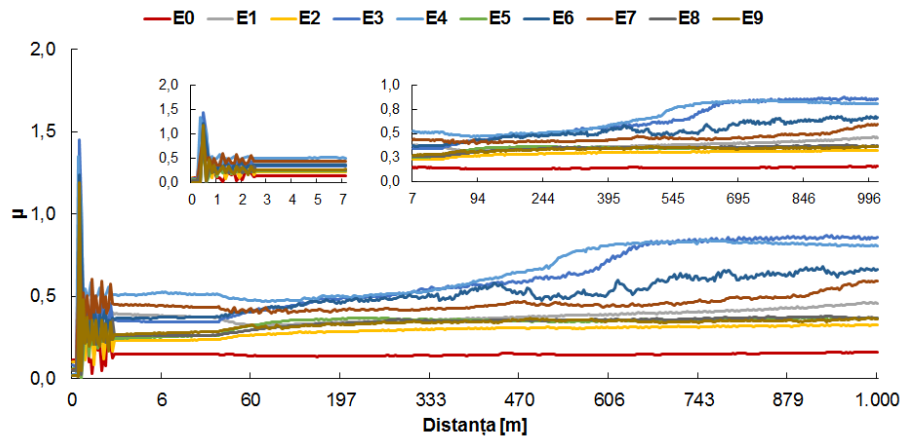
Figure 24. The evolution of the friction coefficient for type E materials (R3).

From figures 22, 23, 24 we can see that, in the case of materials formed with type E epoxy resin, there are random evolutions of the friction coefficient in the final stages of the test. Compared to the previously presented materials, however, the evolutions of the friction

coefficients are more grouped, except for the materials in which 1-4 Dioxane was introduced . Materials E have almost the same friction behaviour irrespective of the type of the type of the resin modifier, which denotes that epoxy resin E is the least affected (from a tribological perspective) by the presence of the modifier in the three used epoxy resins. In regime R1, all the materials obtained based on Epiphen RE4020-DE4020 epoxy resin have the most grouped behaviour, without any variations of the studied parameter.

Figure 25. The evolution of the friction coefficient for type H materials (R1).

Figure 26 The evolution of the friction coefficient for type H materials (R2).

Figure 27 The evolution of the friction coefficient for type H materials (R3).

Concerning the composite materials formed with type H epoxy matrix, the situation is rather different as some of the tests failed. As we can see in figures 25, 26 and 27, for some of the

composite materials, it was impossible to obtain an evolution curve of the friction coefficient. Thus, all the solvents used as additives for H epoxy resins decreased its basic properties and the value of the friction coefficient increased. HT epoxy resin (as we will see in the mechanical tests) is the hardest of the studied epoxy resins and its modification with organic solvents significantly changes the tribological behaviour of materials.

The specific wear rates for all the tested materials are presented in tables 3, 4 and 5 for each group of composite materials.

Table 3. Wear rate for type C materials.

Materials	Wear rate [g/Nm]		
	R1	R2	R3
C0	1.00E-07	3.70E-07	1.05E-06
C1	0.00E+00	4.00E-08	0.00E+00
C2	2.40E-07	3.10E-07	2.07E-07
C3	0.00E+00	4.00E-08	3.60E-07
C4	1.40E-07	1.10E-07	9.33E-08
C5	0.00E+00	2.00E-07	1.73E-07
C6	1.40E-07	2.30E-07	2.93E-07
C7	1.80E-07	1.40E-07	1.33E-07
C8	0.00E+00	1.40E-07	2.07E-07
C9	6.00E-08	1.20E-07	1.93E-07

Table 4. Wear rate for type E materials.

Materials	Wear rate [g/Nm]		
	R1	R2	R3
E0	0.00E+00	0.00E+00	0.00E+00
E1	0.00E+00	0.00E+00	0.00E+00
E2	8.00E-08	3.00E-08	0.00E+00
E3	0.00E+00	3.00E-08	2.67E-08
E4	0.00E+00	0.00E+00	0.00E+00
E5	0.00E+00	0.00E+00	0.00E+00
E6	0.00E+00	0.00E+00	0.00E+00
E7	0.00E+00	0.00E+00	2.67E-08
E8	0.00E+00	0.00E+00	0.00E+00
E9	0.00E+00	1.00E-08	3.33E-08

Table 5. Wear rate for type H materials.

Materials	Wear rate [g/Nm]		
	R1	R2	R3
H0	2.00E-08	0.00E+00	0.00E+00
H1	0.00E+00	0.00E+00	0.00E+00
H2	0.00E+00	2.00E-08	1.33E-08
H3	0.00E+00	6.00E-08	1.33E-08
H4	0.00E+00	0.00E+00	1.33E-08
H5	0.00E+00	0.00E+00	0.00E+00
H6	6.00E-08	4.30E-07	0.00E+00
H7	0.00E+00	1.00E-08	0.00E+00
H8	0.00E+00	1.00E-08	0.00E+00
H9	1.00E-07	1.00E-08	6.67E-09

Analysing the data presented in the tables above, we can see that the highest wear rate corresponds to material C0 (C epoxy resin) tested in R3 (the highest value of the loading force and, respectively, the lowest value of the sliding speed). For many of the tested materials, the friction wear rate could not be evaluated due to the absence of material losses. In this respect,

Epiphen RE4020-DE4020 epoxy resin seems the least affected by the introduction of the organic solution or starch or glucose solutions in the matrix, followed by HT epoxy resin and, in the end, C epoxy resin.

The tribological analysis carried on the three epoxy resins modified with solvents and, respectively, starch and glucose solutions, revealed the following:

- the transitional regime takes place (for each tested material and for each regime) over the first four meters of sliding, at most;
- the values of the friction coefficient upon sliding among the pins made by the unmodified epoxy resins on the steel disk are practically constant for each type of polymer and for each regime of the tribological regime;
- adding the solvents or the starch or glucose solutions in the three solvents in the polymer matrices leads to the softening of the matrices with effects on the evolution of the friction coefficients between the tested material and steel;
- for the materials made based on E epoxy resin (Epiphen RE4020-DE4020), the profiles of the evolutions of the friction coefficients are almost identical and are more grouped for regime R1 than in the case of the two other resins;
- for all the tested materials, it is found that in the regimes with a high loading force and low sliding speed, there are great dispersions of the friction coefficient values;
- in the case of C epoxy resins, N,N dimethyl formamide modifies the least the tribological behaviour of materials;
- 1-4 Dioxane produces the greatest changes to the tribological behaviour of Epiphen RE4020-DE4020 epoxy resin, as in the case of HT epoxy resin;
- the lowest friction wear rates are noticeable in the case of materials based on E resin, followed by those on H resin and, at last, the materials based on C resin.

6.3. The mechanical properties of the composite materials modified with organic agents

For testing and determining the mechanical properties of the composite materials, we used INSTRON 8802 mechanical testing machine, described under point 5.4. Five specimens were used for each of the tested materials, the tests performed with this equipment focusing on the mechanical properties of the materials subject to bending, compression and tension.

6.3.1. Mechanical properties on compression

The compression testing standard for plastic materials ASTM D695 – 15 imposed the parameters as well as the size of the specimens. Thus, the specimens were cylinders, extracted with the Micomat 10 lathe, having a diameter of 8 mm and a height of 160 mm.

Figures 28, 29, 30 present the curves of the compression tests for composite materials obtained with C, E and H epoxy matrix for noticing their behaviour compared to the reference material.
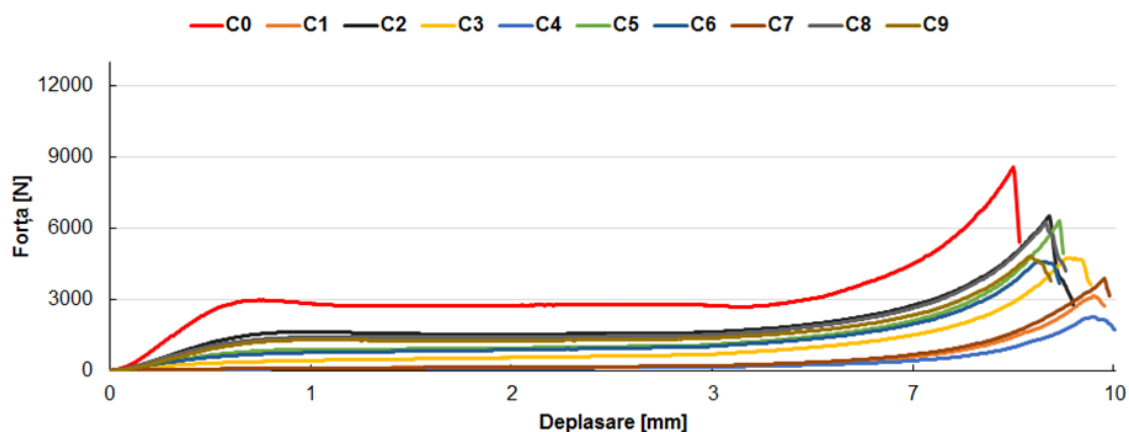

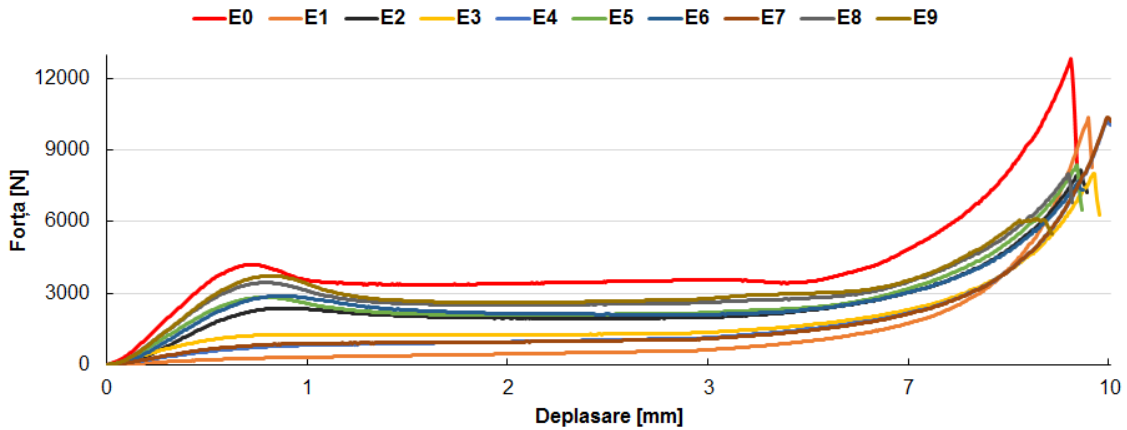*Figure 28. Compression test curves for type C materials.*

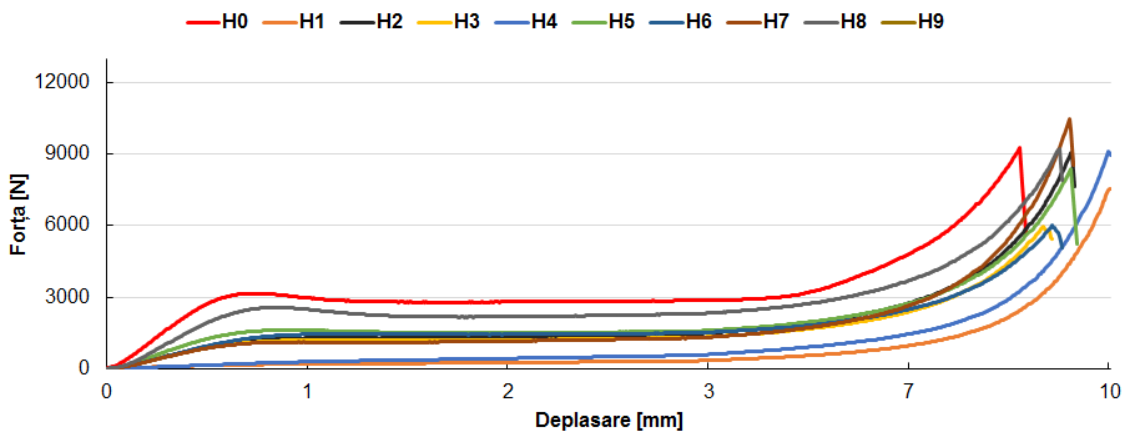*Figure 29. Compression test curves for type E materials.*

Figure 30. Compression test curves for type H materials.

The curves above present a typical behaviour of the thermosetting polymers upon compression, with an elasticity area (deformations under 1 mm), followed by a compaction area in which, practically, loading does not suffer any changes, but specimen cracks occur and, in the end, the breakage of the material, the final peak on the load curves representing the area in which the material can no longer be fractured. The testing programme requires to establish a movement speed of the upper pan, accompanied by the continual measurement of the load force.
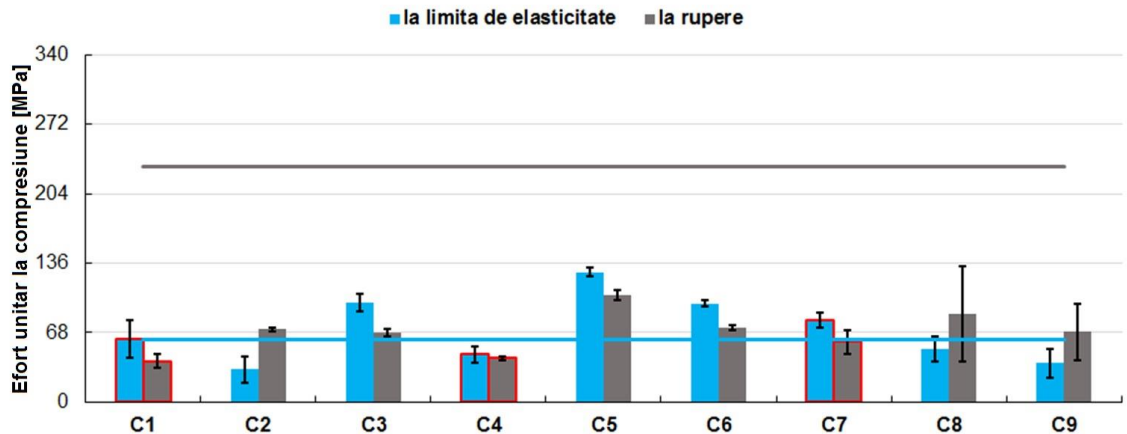
Figure 31. Unit stress of type C materials upon compression.
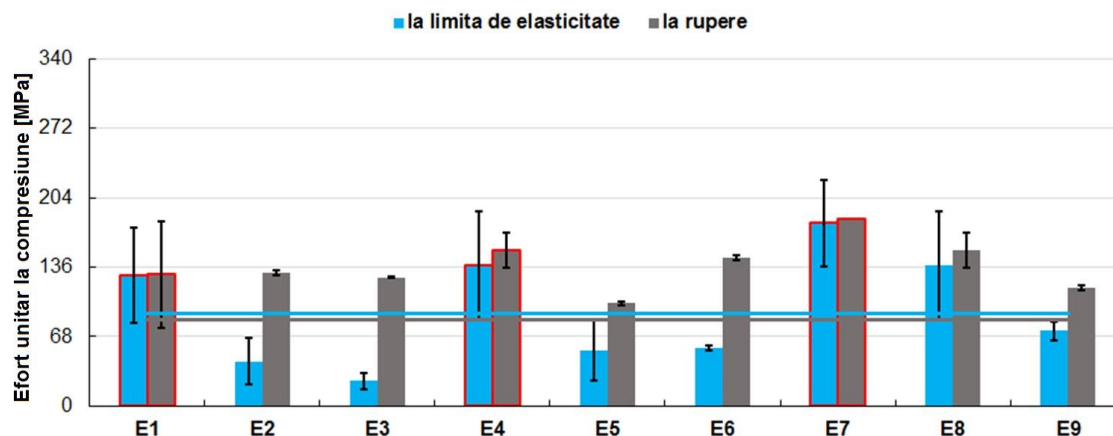
Figure 32. Unit stress of type E materials upon compression.
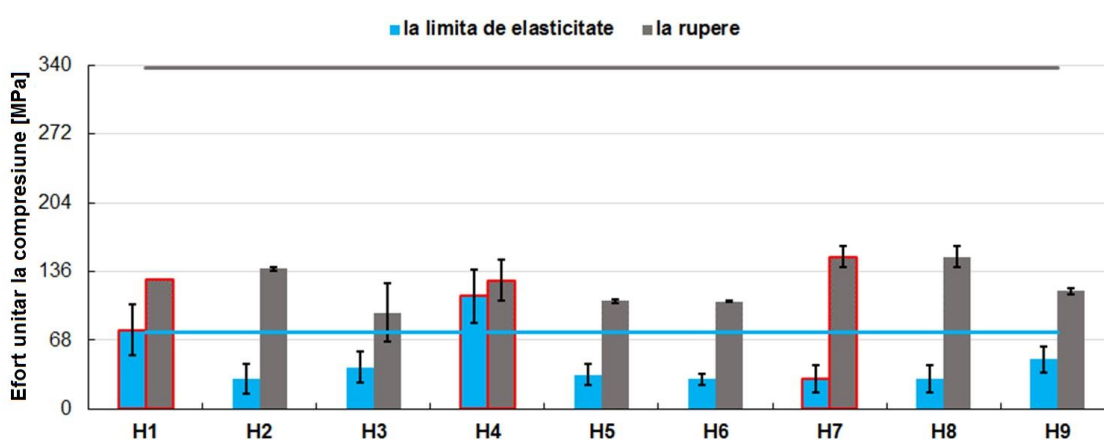
Figure 33. Unit stress of type H materials upon compression.

According to figures 31, 32, 33 which contain the experimental data (averaged on three specimens) concerning unit stress on compression, we may infer the following:

- significant changes of the unit stress value at the elastic limit for Epiphen RE4020 – DE4020 epoxy resin diluted with any of the three used solvents (the value corresponding to the unmodified resin in represented by the lighter solid line);

- for C epoxy resin, the only higher value of the unit stress at the elastic limit is represented by the polymer diluted with 1 methyl – 2 pyrrolidone, while the presence of N, N dimethyl formamide does not seem to change the value of the parameter;

- for HT epoxy resin, a slight growth is given by dilution with 1-4 Dioxane, while, as in the case of C epoxy resin, N, N dimethyl formamide does not modify, practically, the value of the parameter;

- for most of the studied materials, the value of the stress unit at the elastic limit for the materials modified with starch and, respectively, glucose solutions, are smaller than the parameter value corresponding to the modified epoxy resin (the only exceptions being material E8 modified with starch solution in 1 methyl – 2 pyrrolidone and materials C5 and C6 modified with starch, respectively, glucose solutions in 1-4 Dioxane), indicating a loss of elasticity of these materials;

- for materials C5 and C6 it is interesting that the presence of organic agents, starch and glucose, corrects the effects of the solvent presence (1-4 Dioxane);

- with respect to the stress unit on breakage, we may easily notice that the values of this parameter for all the modified materials are inferior, respectively, to the value of the unmodified resin (the darker lines in the representations above).

According to figure 34 afferent to materials C5, C8, E4, E7, H2, H7, we notice their ability to regain their original shape.
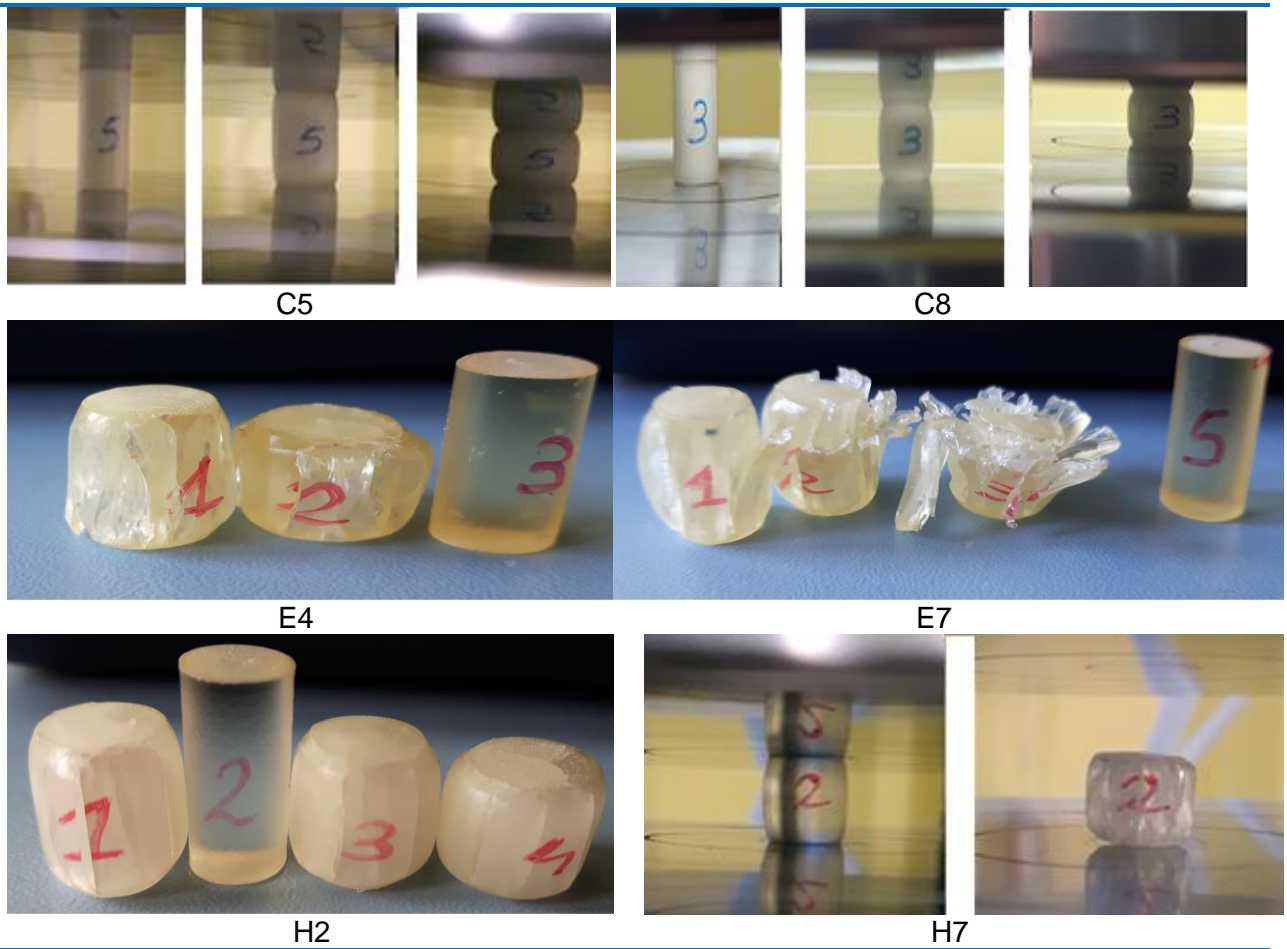
Figure 34. The behaviour of materials on compression.

You will find below the charts for the compression deformation at the elastic limit and brakage of materials modified with organic agents.
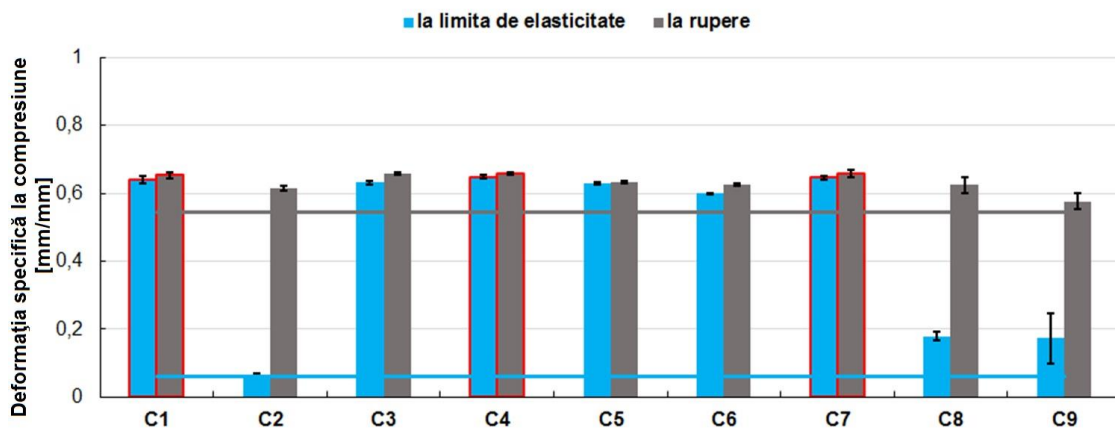

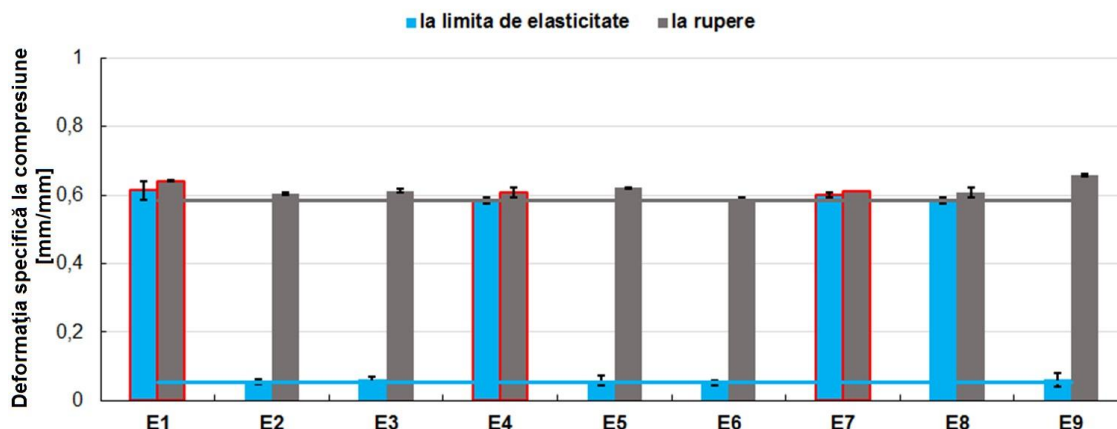*Figure 35 Compression deformation of type C materials.*
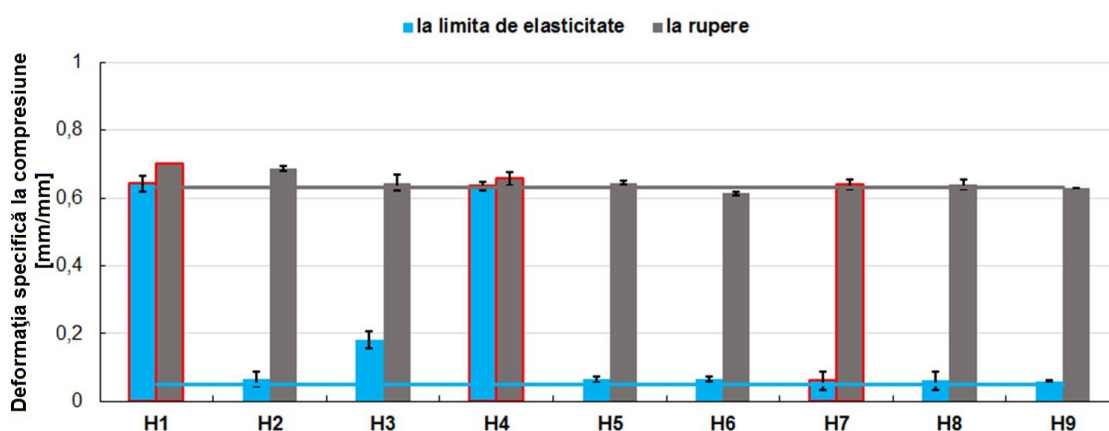
Figure 36. Compression deformation of type E materials.

Figure 37. Compression deformation of type H materials.

According to figures 35, 36 and 37 afferent to the compression deformation of materials, we notice that compression deformation at the elasticity limit increased as compared to the reference material in the case of materials C1, C3, C4, C5, C6, C7, E1, E4, E7, E8, H1, H4. In other words, the dilution of the epoxy matrices with the solvents used in this study raises the deformability level of the basic materials (which are brittle) although this does not mean that the respective materials are not plastically deformed, that is, the complete destruction of the material (through compression) appears later (after a greater deformation) of the specimen. The only exception to this behaviour is HT epoxy resin diluted with 1 methyl – 2 pyrrolidone.

Below, in figure 38, we can see the ability to regain their original shape (of course, with visible effects as to the cracks) of materials E1, E7 and H1 subject to the compression test. In material H1 the tendency is much more obvious than in material E1 (both being polymers diluted with N,N dimethyl formamide) while in material E7 (diluted with NMP) there is a tendency of the splinters not yet detached to return to their initial positions. The study did not include analyses of the factors which affect the recovery speed.
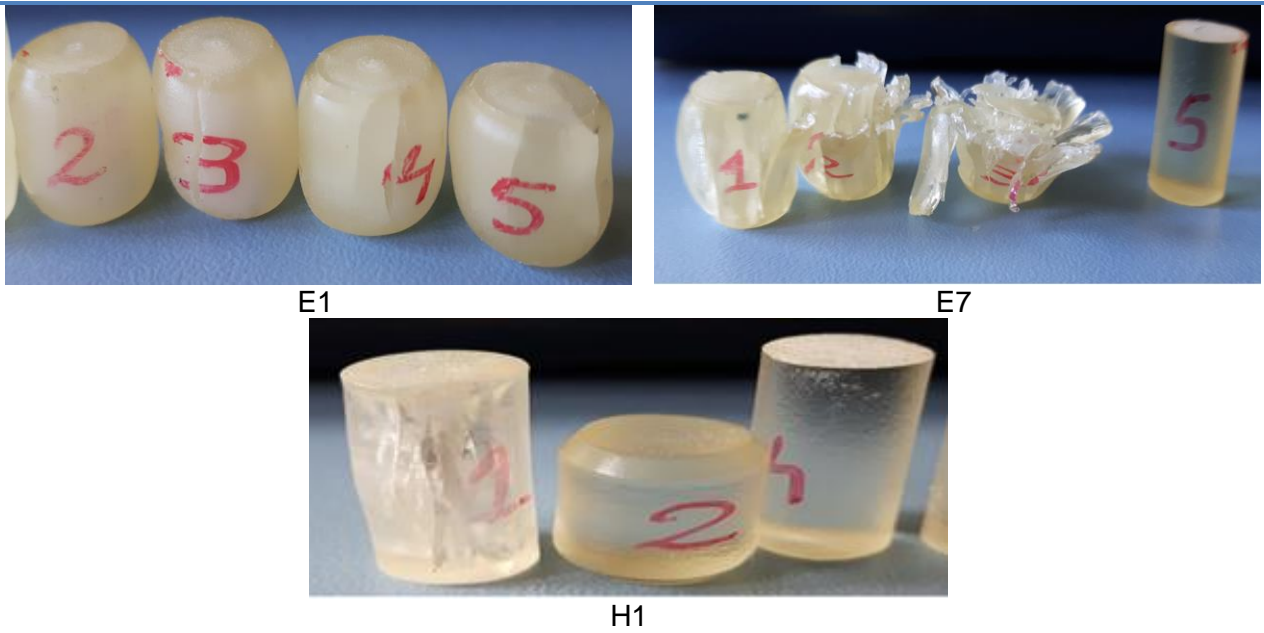
E1

E7

H1

Figure 38. Image of the materials which regain their original shape.

In the following charts (figures 39, 40, 41) we present the values of the compressive modulus of elasticity of the materials belonging to the three classes and we can immediately see that all the modified materials present low values of this parameter as compared to the basic resin.
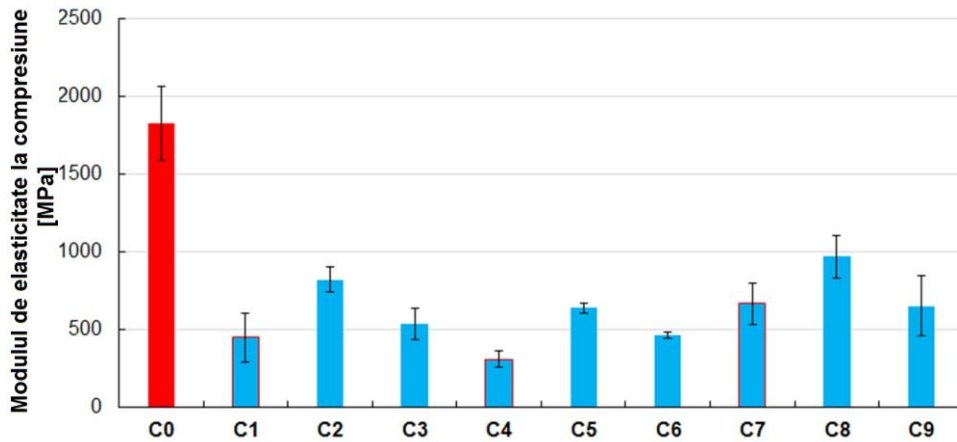

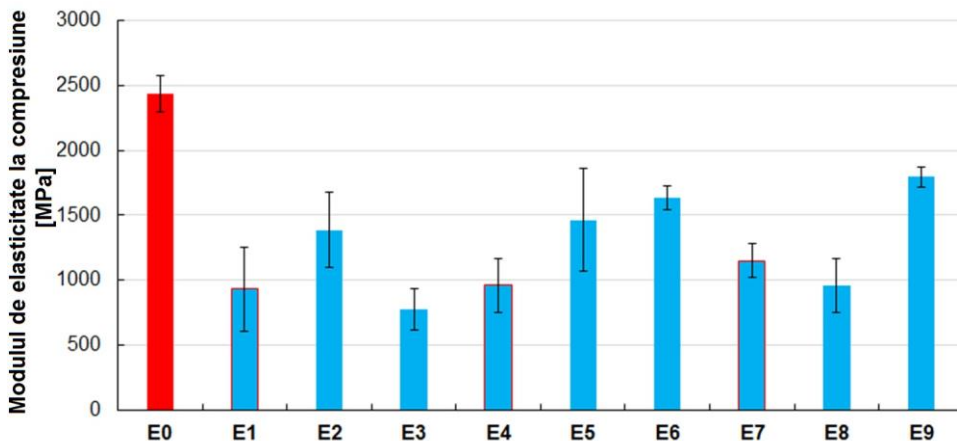*Figure 39 Compressive modulus of elasticity for type C materials.*

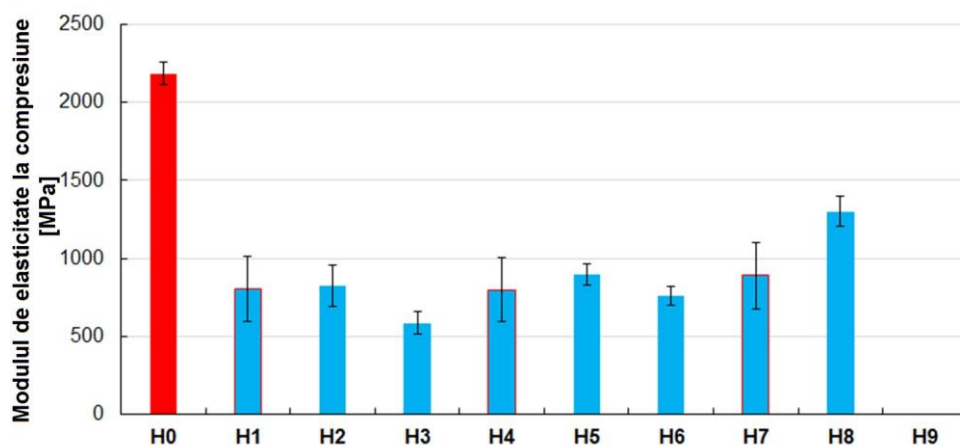*Figure 40. Compressive modulus of elasticity for type E materials.*

Figure 41 Compressive modulus of elasticity for type H materials.

The results of the compression test can be summarised as follows:

- the elastic moduli on compression of the modified polymer materials have lower values as compared to the basic polymers and the highest values correspond to Epiphen RE4020 - DE4020 epoxy resin;

- the unit stresses at the elastic limit of the diluted materials are higher than those of the basic resin for E resin, but for C and H resins they have the same value for the materials diluted with N,N dimethyl formamide, for these two resins, the only diluted systems with higher values of the parameter being H4 (diluted with 1-4 Dioxane) and C7 (diluted with 1 methyl – 2 pyrrolidone);

- for some of the tested materials we noticed the tendency to return to their original shape (even if the specimens are cracked and, in some cases, cracks extend up to the edge of the specimen);

- the dilution of polymers or their modification with starch and glucose solution increases the deformability level;

- the compressive modulus of elasticity has low values for the modified materials as compared to the elastic modulus on compression of the basic polymer and the highest values correspond to Epiphen RE4020 – DE4020 epoxy resin.

6.3.2. Mechanical properties in the three point bend test

The three point bend test of composite materials was carried out according to standard BS EN ISO 178:2003, specific to tests for plastic materials. The tested specimens were cylinders, having a diameter of 8 mm and a total length of 110 mm, and the distance between the supporting pins was of 64 mm.

For each formed material, we tested five specimens – figures 42, 43, 44 below illustrate the curves obtained following the bend tests for the materials formed with C, E and H epoxy resins for noticing their behaviour as compared to the reference material. We see (figure 42) that in the case of materials formed on C epoxy resin, all the bend fracture moduli of plastic materials are detectable. Thus, material C2 breaks along the linear area, materials C8 and C9 break immediately after passing in the flowing area, material C0 breaks after a length flow, material C1 does not break. For E and H resins, fractures (if any) occur after flows (maybe with the exception of material E8) and, in the case of these resins, there are more materials which do not break upon bending.
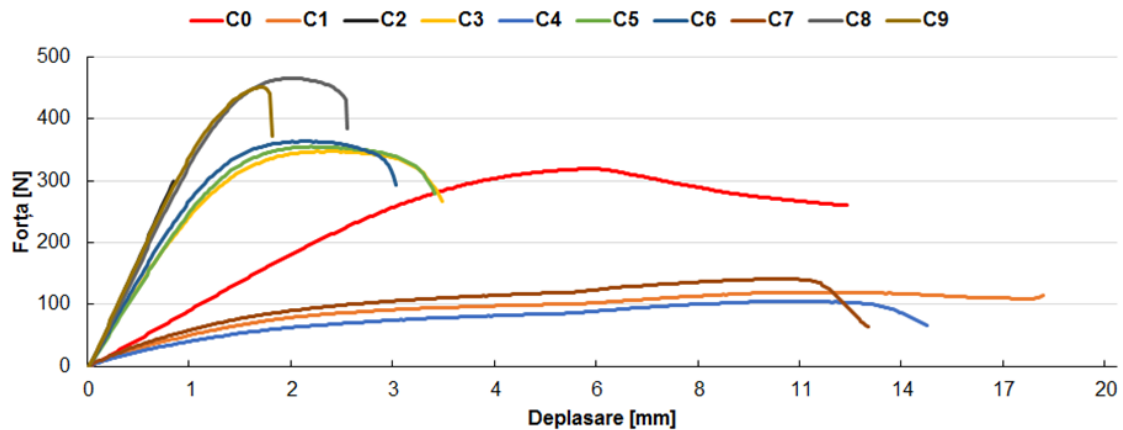
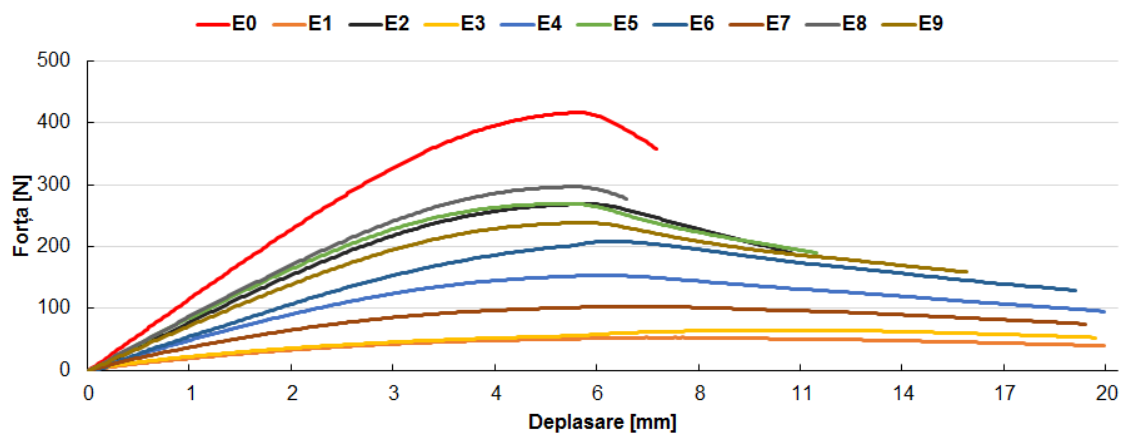*Figure 42. Bend test curves for type C materials.*

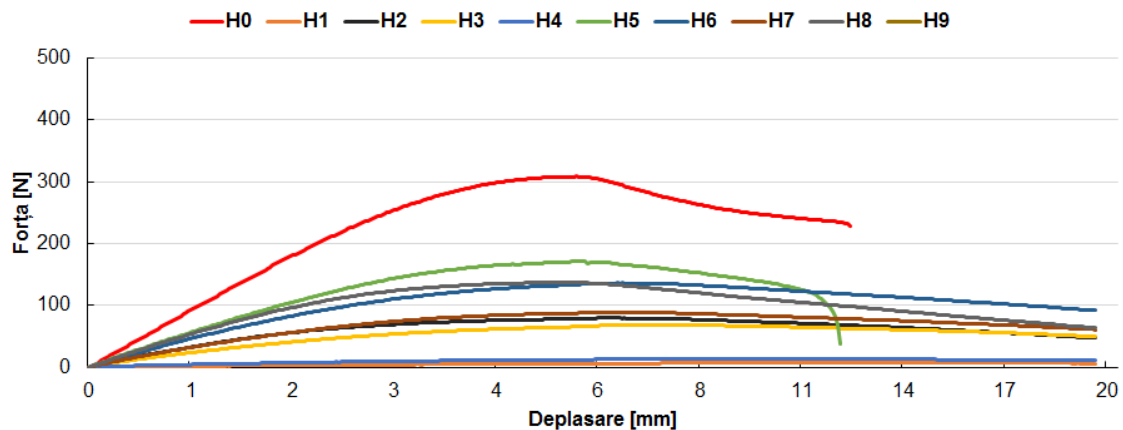*Figure 43. Bend test curves for type E materials.*

Figure 44. Bend test curves for type H materials.

As we will see henceforward, in fact, there are no material flows (specific to plastic materials), the resulting deformations being, sometimes, elastic (meaning that the materials regain their initial shape and size), as in the case of compression tests (again, we did not analyse the factors which determine the recovery speed).

In the charts below we can see the values of the unit stress on bending at the elastic limit and maximum load (given that not all the materials broke through bending and that some of the tested specimens got out of the props during the test).

For materials based on C epoxy resins, all the materials modified with starch or glucose solutions have higher values of the unit stress on bending as compared to the diluted materials (for the same solvent).
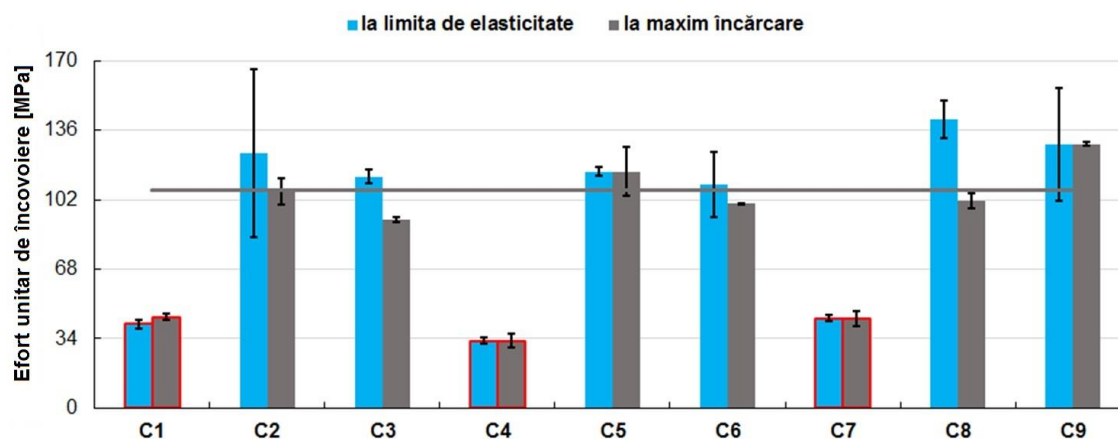
■ la limita de elasticitate   ■ la maxim încărcare

Figure 45. Bend unit stress for type C materials.

■ la limita de elasticitate   ■ la maxim încărcare
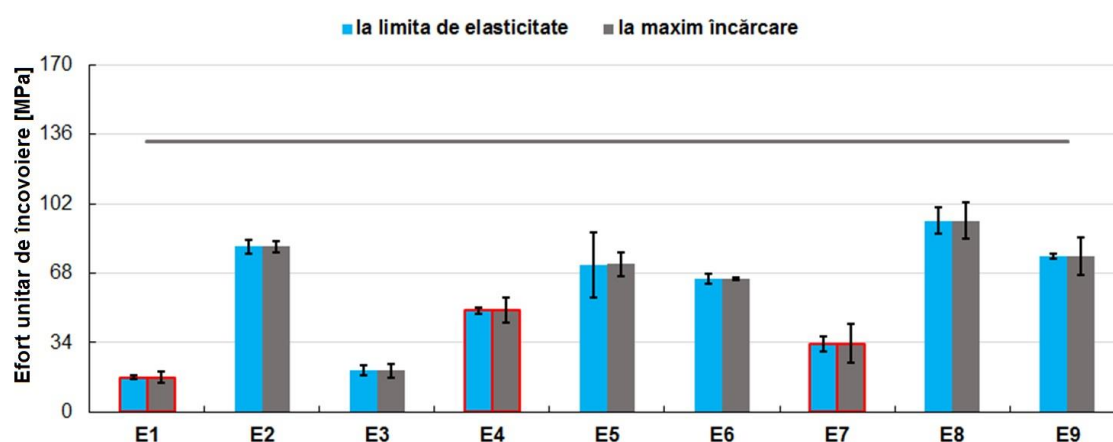
Figure 46. Bend unit stress for type E materials.

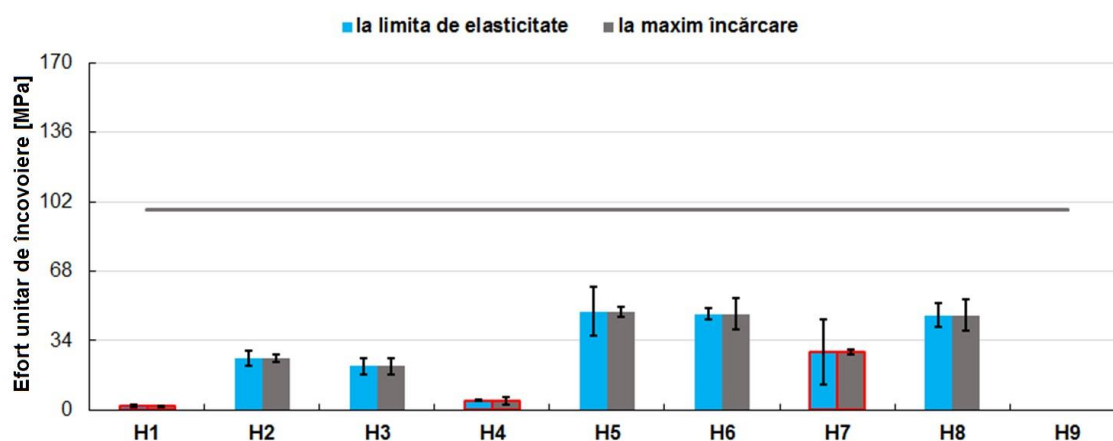■ la limita de elasticitate   ■ la maxim încărcare

Figure 47. Bend unit stress for type H materials.

All the materials of type C (figure 45) modified with solutions of the organic agents have values of the bending unit stress at maximum load comparable with the value of the same parameter for the unmodified epoxy resin. For E resin (figure 46), the values of this parameter (for materials modified with solutions) are situated somewhere half of the value of the unit stress at maximum load of the polymer while for H resin (figure 47), the values are neatly inferior to the value corresponding to the stress unit at maximum load for the polymer. In the case of the same polymer, H, we can see that no determinations could be made for material H9 (the material is too soft), the situation being similar for HT epoxy resin diluted with the first two solvents, N,N dimethyl formamide and, respectively, 1-4 Dioxane. For such a material, it is very interesting to analyse the way in which it achieves an interphase with other reinforcing elements (fibres or

fibre cloth) because, placed inside a layered material, it could contribute to the resistance to shock.

Figures 48, 49, 50 contain the data obtained for the specific bend deformation of the analysed materials – at elastic limit and maximum load. Compared to the value of the specific deformation at maximum load of the polymer, all the diluted polymers record higher values of the parameter – almost double for C epoxy resin (irrespective of the solvent type), slightly increased for Epiphen RE4020 - DE4020 epoxy resin and, in the case of HT epoxy resin, things are slightly different, each solvent producing different effects (but with higher values of the specific deformation as compared to the value of the bending specific deformation at maximum load of the polymer).
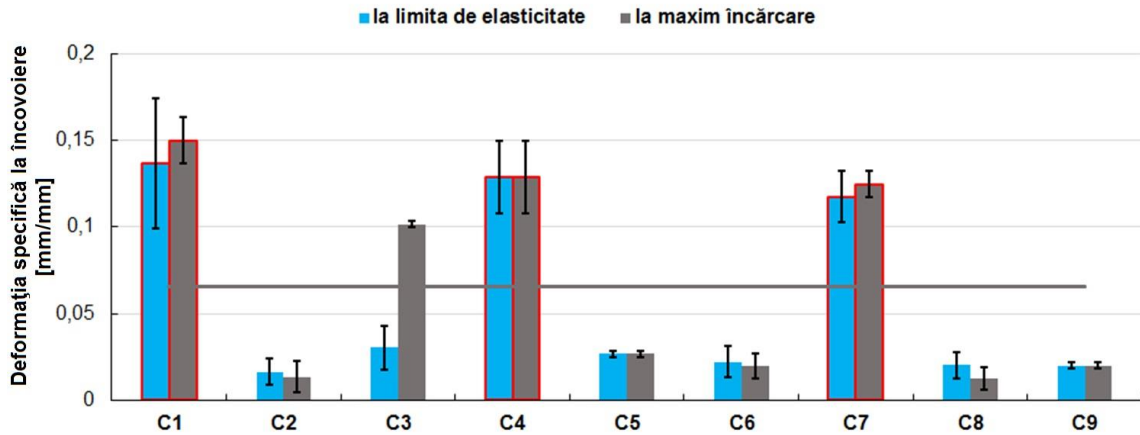

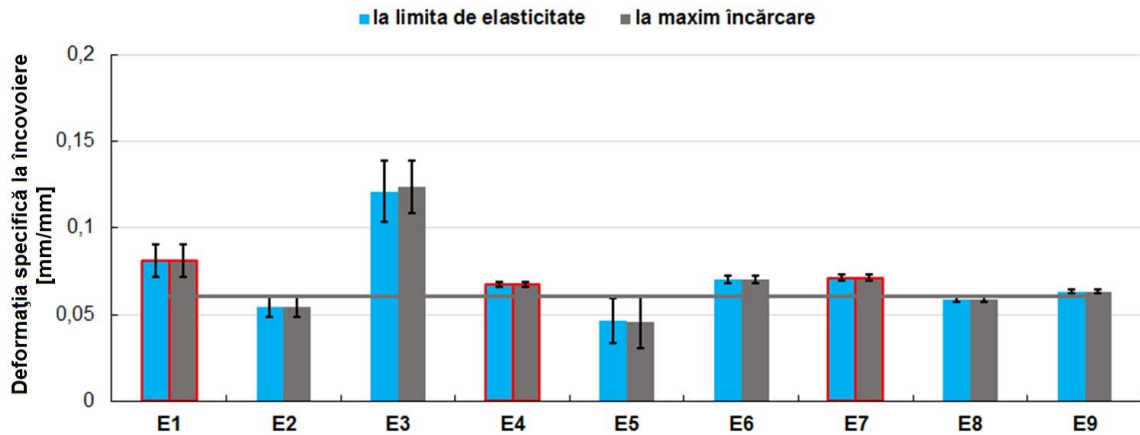*Figure 48. Bend specific deformation for type C materials.*

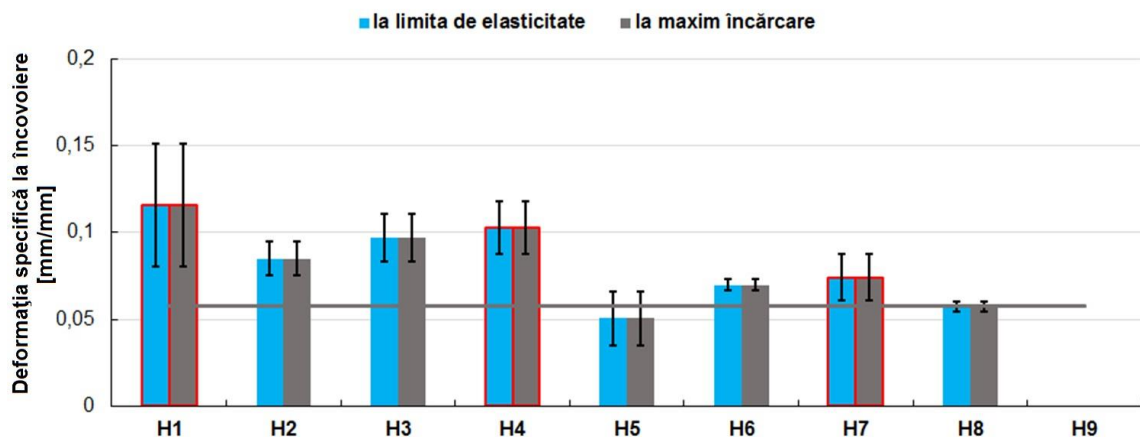*Figure 49. Bend specific deformation for type E materials.*

Figure 50. Bend specific deformation for type H materials.

According to figures 48, 49, 50 , we can say that bend specific deformation at the elastic limit corresponds to the maximum load value for all the tested materials. From these tests, we can see the materials which regain their initial shape, from the great shift as compared to the reference material. Therefore, we may conclude that the selection of the modifiers, DMF, 1,4-D and NMP led to the forming of shape-memory materials.

Regarding the bend elastic modulus (figures 51, 52, 53) we may see that, for C epoxy resin, the materials modified with starch or glucose solution have higher values of the parameter than those of the resin or diluted resin (3-4 times higher).
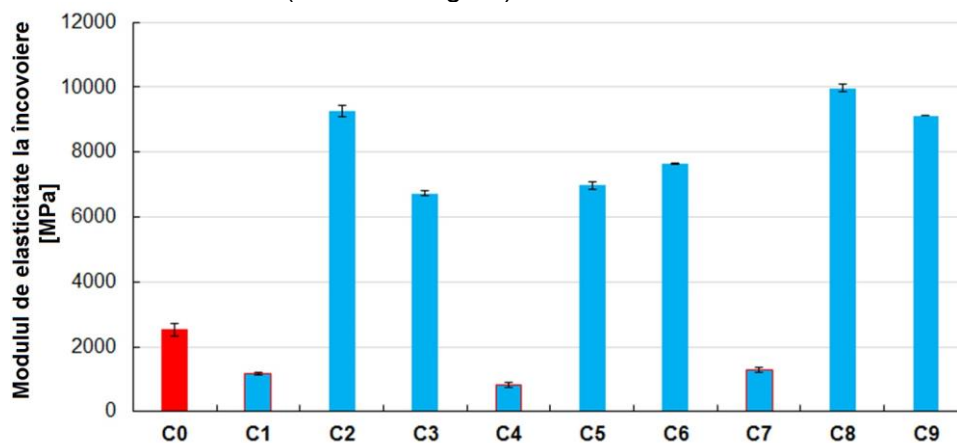
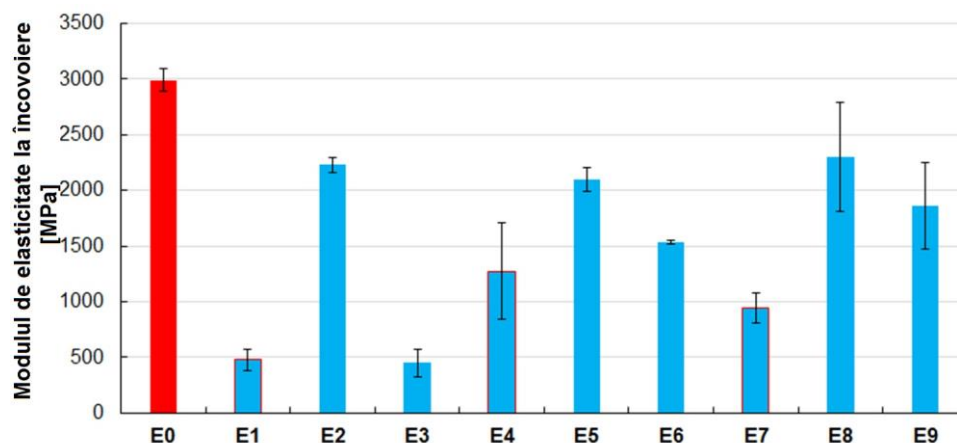*Figure 51. Bending modulus of elasticity for type C materials.*

Figure 52. Bending modulus of elasticity for type E materials.
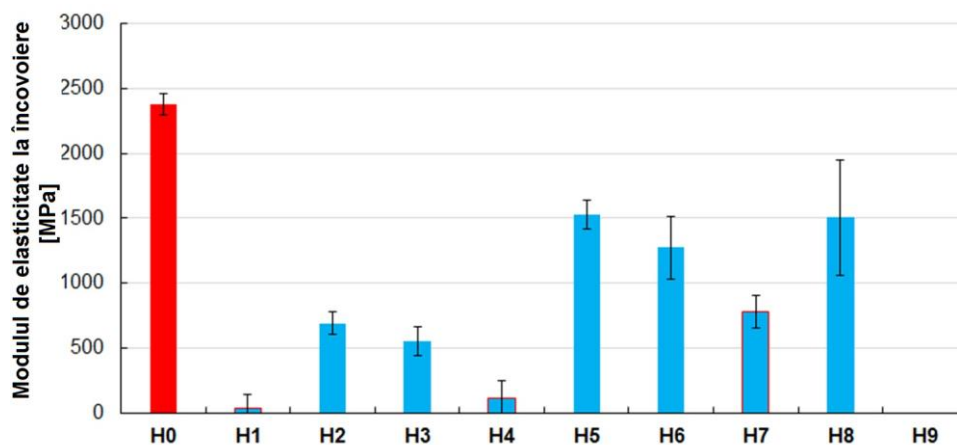
Figure 53. Bending modulus of elasticity for type H materials.

In figures 51, 52, 53 we can see that for C materials modified with solvents, C1, C4, C7 (DMF, 1,4-D, NMP) the values of the elastic modulus are much lower than of the reference material, which we see from the movement value, while the materials which were added solutions C2, C3, C5, C6, C8, C9 have higher values. Therefore, for material C, the content of additives in the solution (starch, glucose) significantly increased the elastic modules as compared to the reference material.

Three point bend tests revealed the following:

- polymer dilution leads, without exception, to the drastic reduction of the compressive modulus of elasticity;

- for C epoxy resin, the materials formed by modifying the basic solution with starch or glucose solution determine a three to five times increase of the bending modulus of elasticity as compared to the value of the parameter recorded for the unmodified polymer;

- for the other two polymers, dilution leads to the reduction of the bending modulus of elasticity as well, but the use of starch or glucose solutions do not cause the effects which appear in the case of C epoxy resin;

- in terms of the three point bend test, C resin is more vulnerable to 1-4 Dioxane (the most drastic reduction of the elastic modulus), while the other two resins are more vulnerable to N,N dimethyl formamide;

- as in the case of compression, material H9 is too soft to be tested in the experimental conditions set for the analyses;

- as the materials present a load characteristic on bending which has a maximum point which coincides with the elastic limit, the values of the unit stress and, respectively, of the polymer specific deformations have equal values for each polymer (whether it is measurement at the elastic limit or maximum load), so that in the representations of those parameters for the modified materials, there is only one line which corresponds to the parameter for the polymer;

- as with compression (but this time there are no cracks of the specimens), there are materials which regain their initial shape after a certain period of time (the factors which influence recovery speed have not been analysed).

6.3.3. Mechanical properties on tension

All the tests were performed by setting a certain movement speed of the upper blade of the testing machine (the same as for the compression and bend tests). In figures 54, 55, 56 we can see the load-deformation curves for the materials undergoing the tension tests and we notice different behaviours of the materials, some break in the elasticity area (fragile materials H0), other break immediately after the elasticity area, other have a flowing behaviour (with fracture in the end, unlike bend tests).

The variety of the profiles of the load curves on tension is an expressive enough indicator for the amplitude of the changes brought about by solvents or by the starch or glucose solutions in these solvents used as modifiers for the polymer properties.
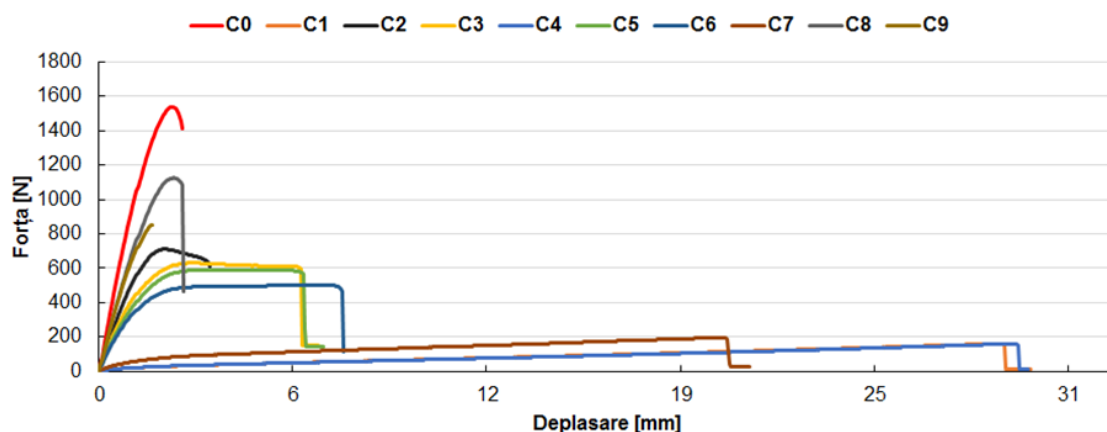

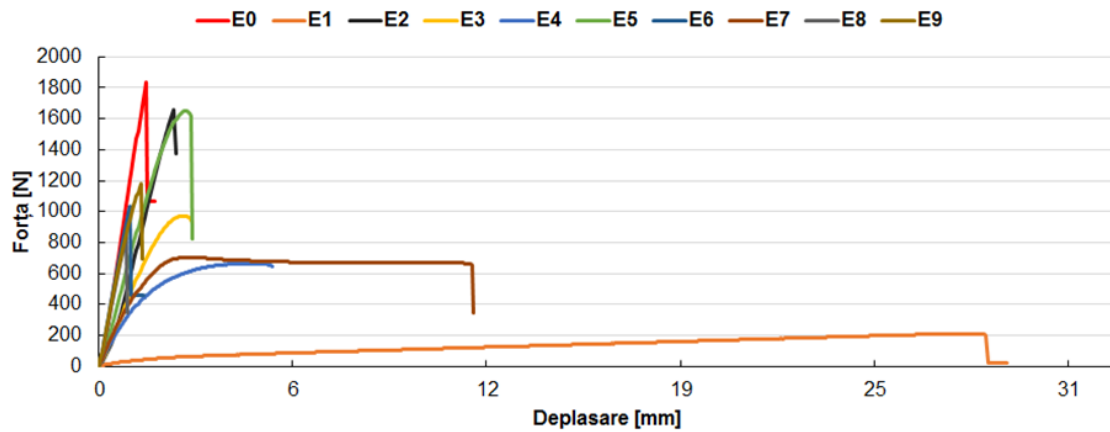*Figure 54. The curves of tensile tests for type C materials.*

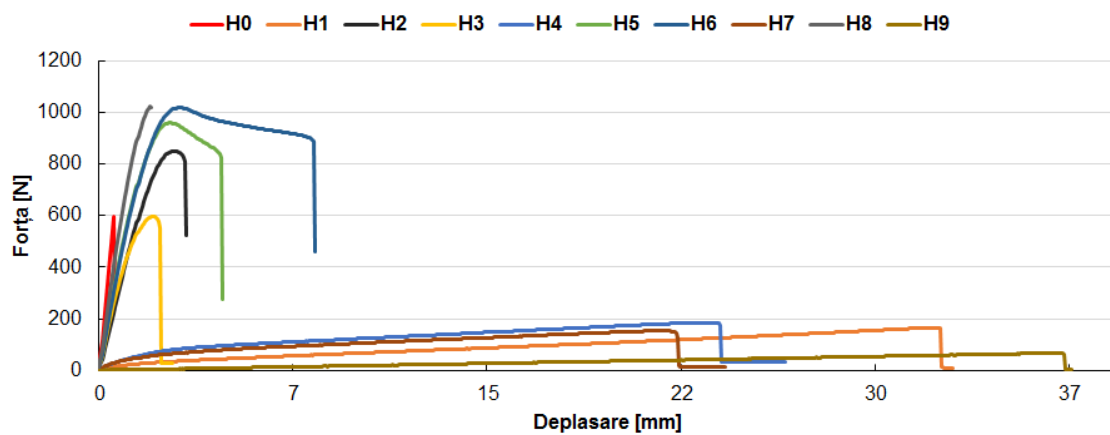*Figure 55. The curves of tensile tests for type E materials.*

Figure 56. The curves of tensile tests for type H materials.

Four specimens were tested for each formed material, the above results being the curves obtained after averaging the individual results. The averages, along with the statistical analysis of the obtained data are performed directly by the software application which controls the testing machine.

As it was to be expected, soft materials record high values of the specific deformation under tension, as we can see in the data from figures 57, 58 and 59. C epoxy resin fails within this category of materials, diluted with any of three solvents and, similarly, HT epoxy resin.
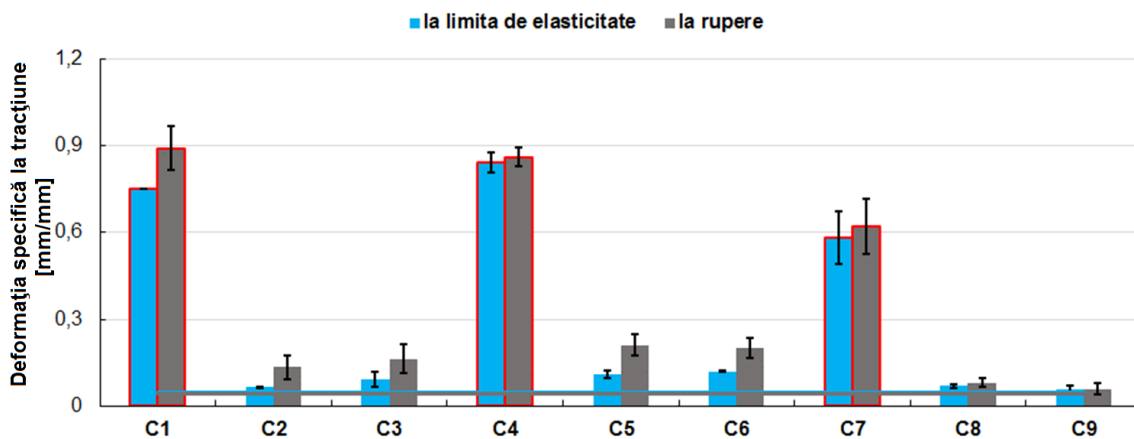

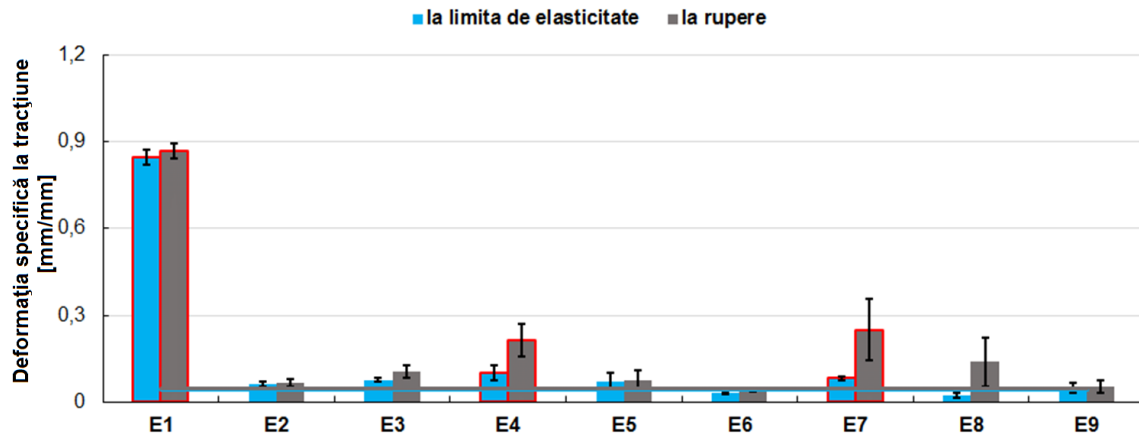*Figure 57. Specific deformation under tension for type C materials.*

Figure 58. Specific deformation under tension for type E materials.

For Epiphen epoxy resin only N,N dimethyl formamide causes a drastic softening of the polymer. For any of the three resins, the use of starch or glucose solutions rebrings the studied parameter to values comparable with those of the polymer specific deformation under tension (in this case too the specific deformation under tension at the elastic limit and upon fracture have similar values).
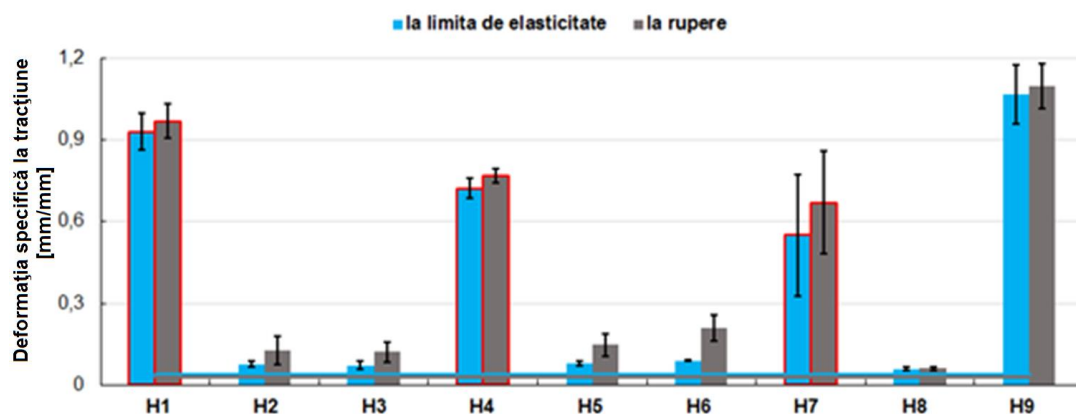

Figure 59. Specific deformation under tension for type H materials.

Concerning deformation under tension at the elastic limit and, respectively, upon fracture, according to figures 57, 58, 59, we notice that the highest values are reached for the materials to which solvents are added, respectively, C1, C4, C7, E1, E7, H1, H4, H7. The only material modified with solution (NMP with glucose) which behaves differently is H9, which, in fact, records the highest value of the specific deformation from all the materials formed with H epoxy resin.

The analysis of the unit stress under tension (also, at the elastic limit and upon fracture) - figures 60, 61, 62 – reveals the fact that only for three modified materials the value of this parameter is superior to the unit stress at the elastic limit and these are H5, H6 and H8, materials modified with solutions (1-4 Dioxane and starch for H5, 1-4 Dioxane and glucose for H6 and 1 methyl– 2 pyrrolidone for E8).

All the other modified materials do not present values of the unit stress at the elastic limit inferior to the value corresponding to the polymer. Concerning the unit stress upon fracture, in the case of materials based on E and H resin, those modified with starch solutions have higher values of the parameter than those of the basic polymer. For C resin, there is no material which reaches the performances of the basic polymer, but the materials modified with starch or glucose solutions in 1 methyl– 2 pyrrolidone have better performances.
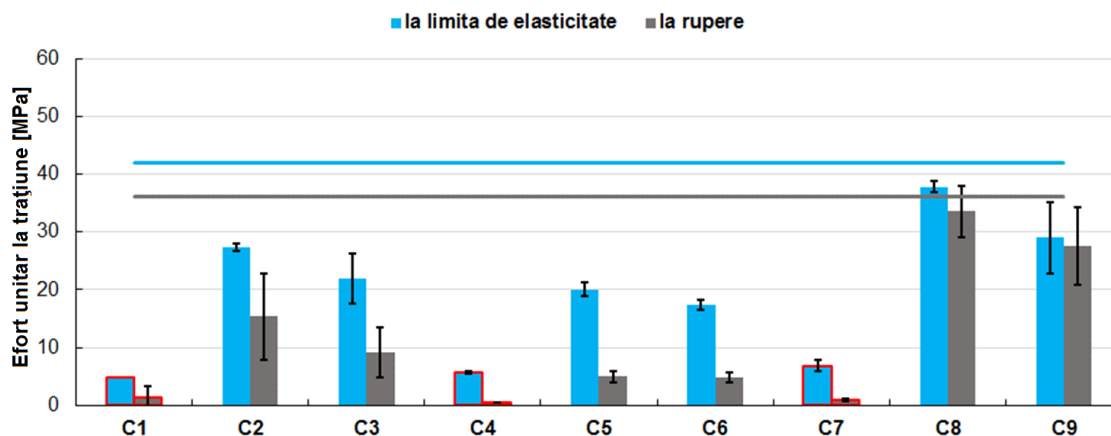
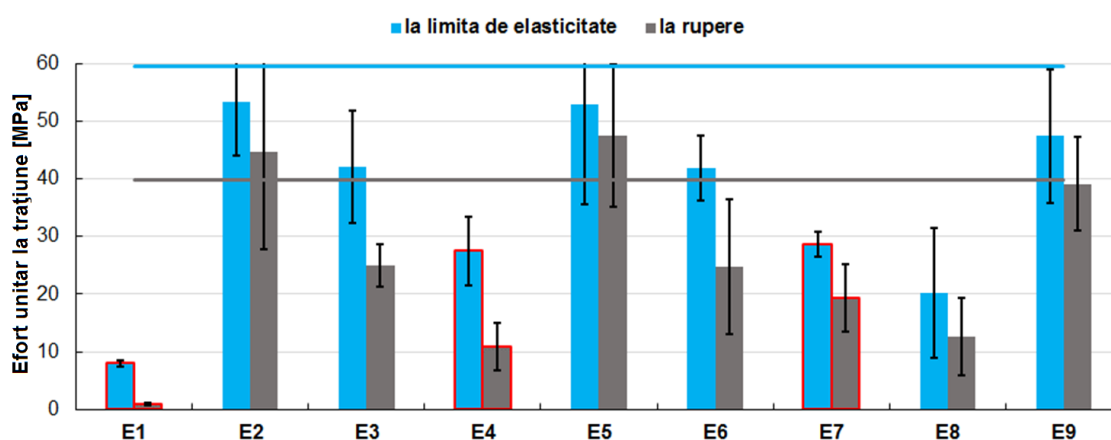Figure 60. Unit stress under tension for type C materials.

Figure 61. Unit stress under tension for type E materials.
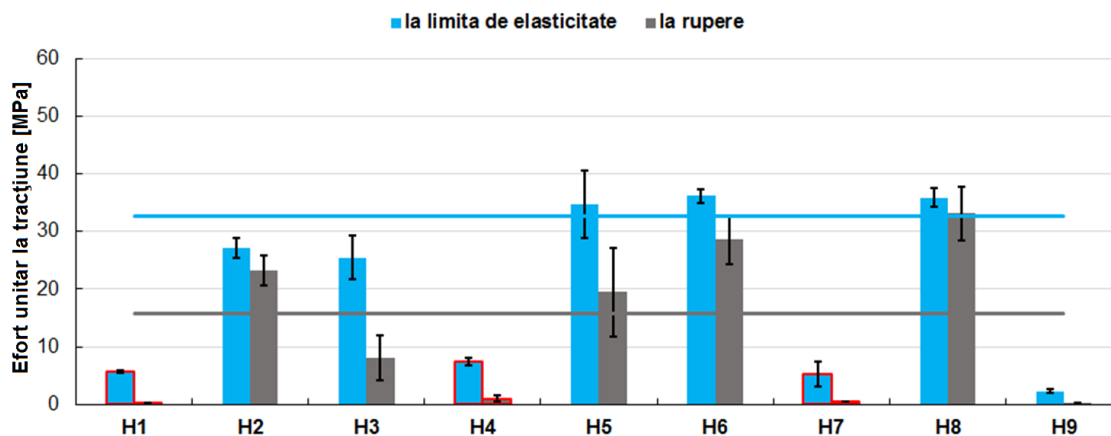
Figure 62. Unit stress under tension for type H materials.

The data concerning the tensile modulus of elasticity of the studied materials are rendered in figures 63, 64 and 65. Normally, given that the materials are obtained through the homogenisation of the solvent or of the organic agent solution in the pre-polymer mixture, the materials should be homogenous and isotropic and, in this case, the tensile moduli of elasticity would be numerically equal with the compressive moduli of elasticity. The first remark concerns the fact that, in the case of polymers, the values of the tensile modulus are roughly twice smaller than those of the compressive modulus of elasticity.

For C and H resins, solvents determine the softening of the material (1 methyl– 2 pyrrolidone the least), the differences between the values of the tensile modulus of elasticity of

these materials and the values of the same parameter for the basic polymers being almost two orders of magnitude.
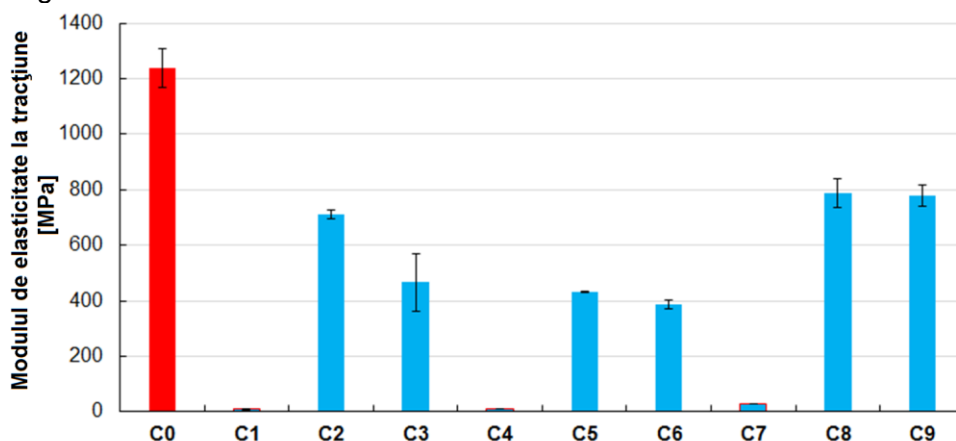

Figure 63. Tensile modulus of elasticity for type C materials.
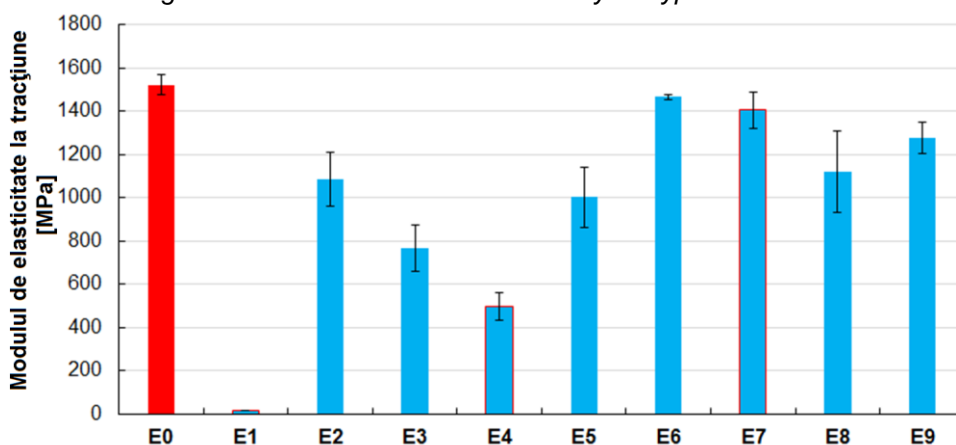
Figure 64. Tensile modulus of elasticity for type E materials.
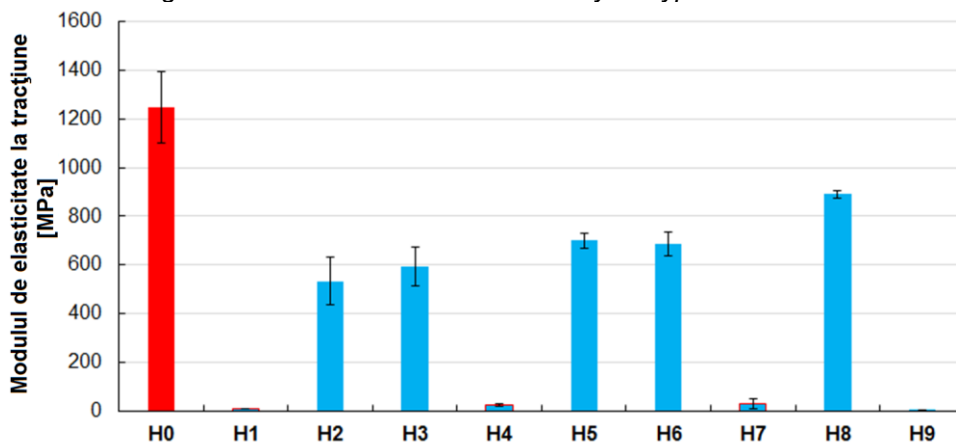
Figure 65. Tensile modulus of elasticity for type H materials.

For C and H resins, the materials modified with solutions present higher elastic moduli than the diluted materials. For E resin, only N,N dimethyl formamide leads to an extremely low value of the module, while 1 methyl– 2 pyrrolidone leads to the forming of a material with an elastic modulus comparable with that of the basic polymer. As in the case of C and H resins, starch and glucose solutions in N,N dimethyl formamide and 1-4 Dioxane determine, in the case of E resin as well, increases of the tensile modulus of elasticity, but, in the case of solvent NMP, the solutions lead to the decrease of the elastic modulus compared to the diluted polymer.

Another parameter monitored during the tension tests was breakage energy. This parameter could be used to describe, in mechanical terms, the cohesion between the different

components of the materials (or how the presence of solvents or solutions reduces the cohesion of the polymer networks). What's important to notice in figures 66, 67 and 68 is the fact that, generally, (softer) modified materials have higher breakage energies than those of unmodified polymers. The highest value, in this respect, is encountered in the case of material H6. There are two exceptions from this type of evolution, namely, materials E6 (1-4 Dioxane and glucose) and E8 (1 methyl– 2 pyrrolidone and starch).

For Epiphen RE4020 – DE4020 epoxy resin, it is visible the fact that the breakage energy is higher for the diluted material as compared to any of the materials modified with starch or glucose solution in the same diluting medium. In the case of C and H resins, higher values of the breakage energy for the material modified with solution are encountered only when using 1-4 Dioxane as solvent.
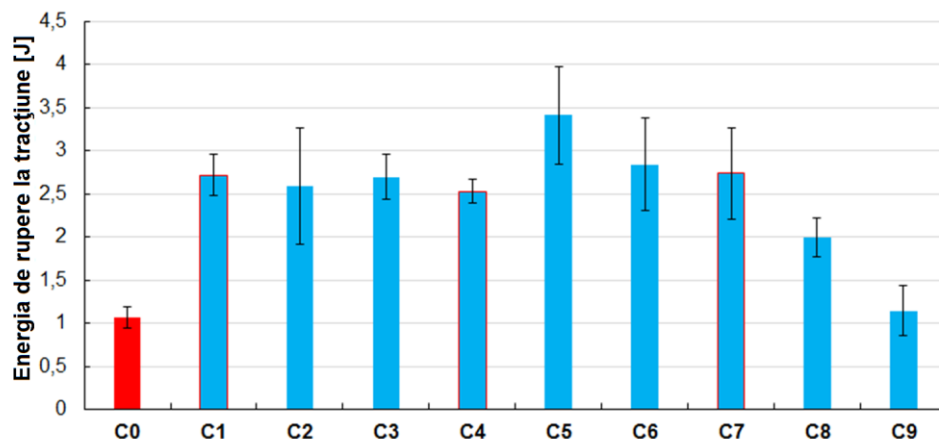
Figure 66. Breakage energy under tension for type C materials.
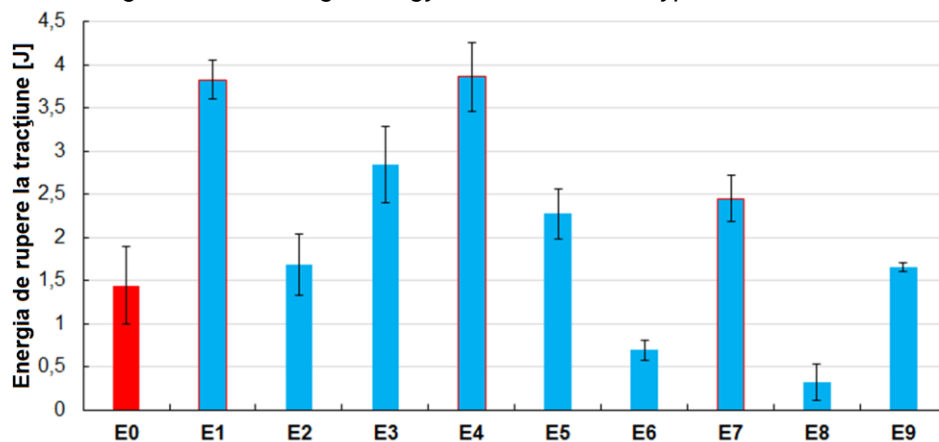
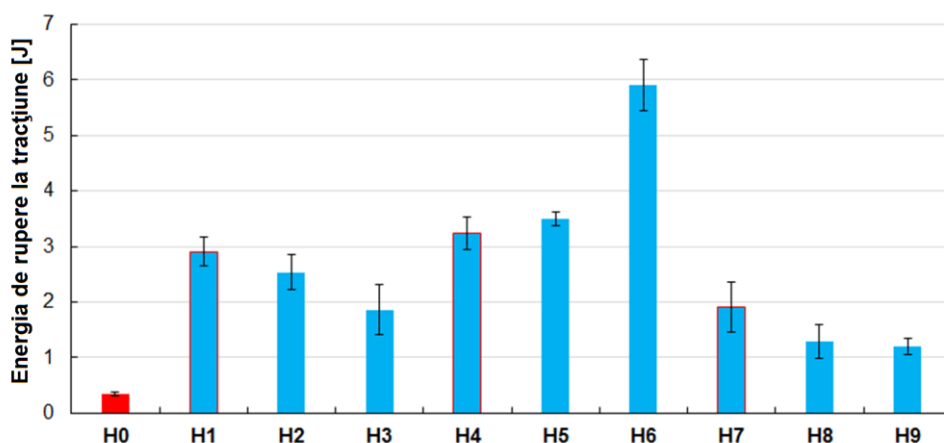Figure 67. Breakage energy under tension for type E materials.

Figure 68. Breakage energy under tension for type H materials.

The breakage energy of the formed materials is significantly higher than of the reference materials, therefore, we may conclude that the materials chosen to modify the three epoxy resins, C, E and H, improved this parameter. The only materials with values below the reference material are E6 and E8.

Figures 69, 70, 71 illustrate the values for the maximum load, all the obtained and tested materials (each value representing the average value based on the statistical analysis of the obtained data). For Epiphen RE4020 – DE4020 epoxy resin, we can see that the maximum tensile strength corresponds to the basic polymer, while the smallest values correspond to the diluted polymer. For each material obtained through the modification of the basic resin with starch or glucose solutions, the values of the parameter are higher than those corresponding to the polymer diluted with the solvent in which the starch or glucose solution was made.

For C epoxy resin, the situation is similar, the only exception being the fact that material C8 (modified with starch solution in 1 methyl– 2 pyrrolidone) has a better strength even than the basic polymer. For H resin, the values of the tensile strength of the solution-modified materials are, generally, higher than the value of the tensile strength of the basic polymer (with the exception of H3, modified with N, N dimethyl formamide and glucose and H9 modified with 1 methyl– 2 pyrrolidone and glucose and which is, as already pointed out, the softest of the formed materials).
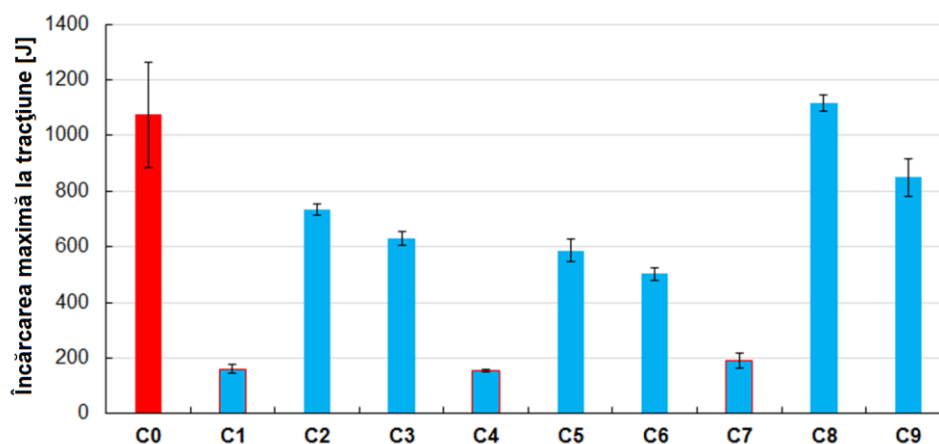
Figure 69. Maximum load during tension tests for type C materials.
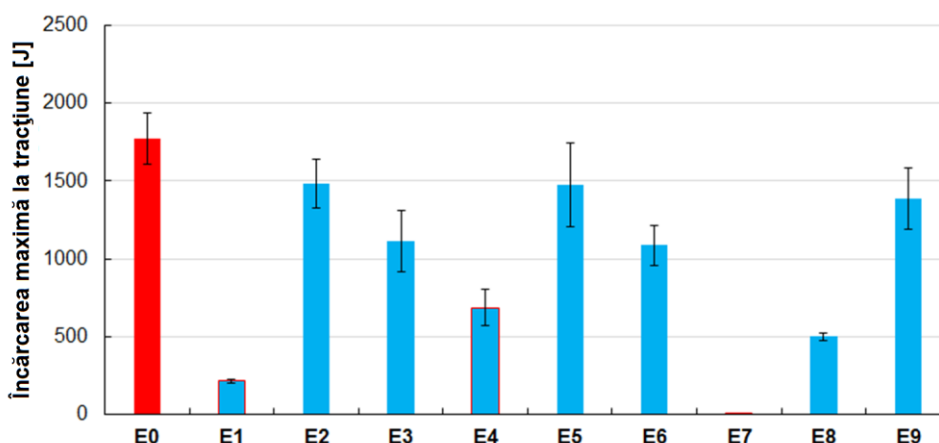
Figure 70. Maximum load during tension tests for type E materials.
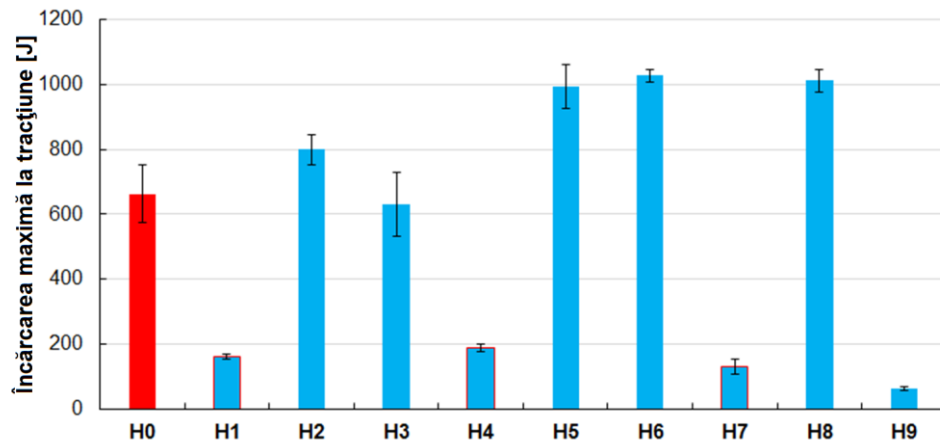
Figure 71. Maximum load during tension tests for type H materials.

6.4. Electromagnetic properties of the composite materials modified with organic agents

The first analysed parameter is the volume electrical permittivity of the materials which was performed on three different values of the frequency of the measuring signal (measurement taking place through the equilibration of a bridge in sinusoidal regime). For type C materials, we notice an increase of the surface permittivity value along with the measuring frequency. For type E materials, the value of the parameter does not seem to depend on the value of the measuring frequency (even if there are small variations which may be attributed to the non-flatness of the tested specimens). For type H materials, the data indicate a slight decrease along with the frequency of dielectric permittivity (figures 72 - 74).
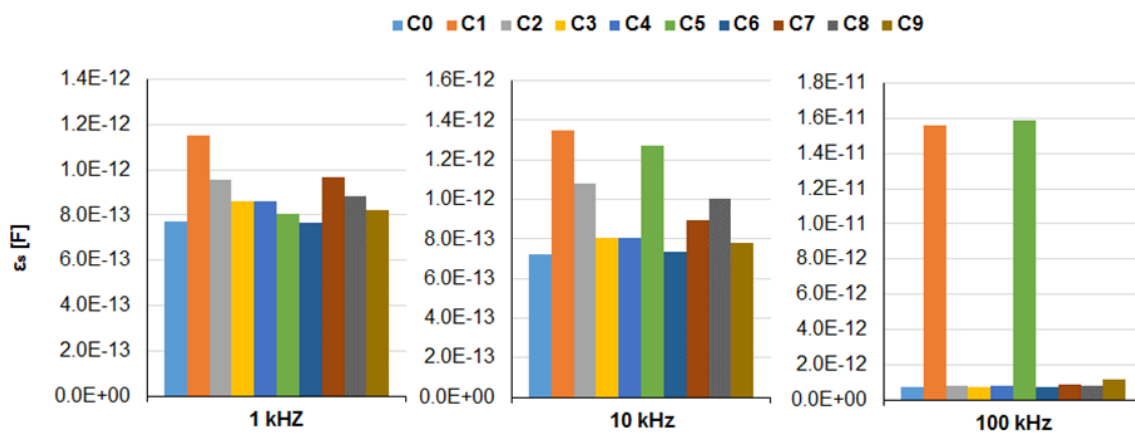
Figure 72. Surface dielectric permettivity for type C materials.
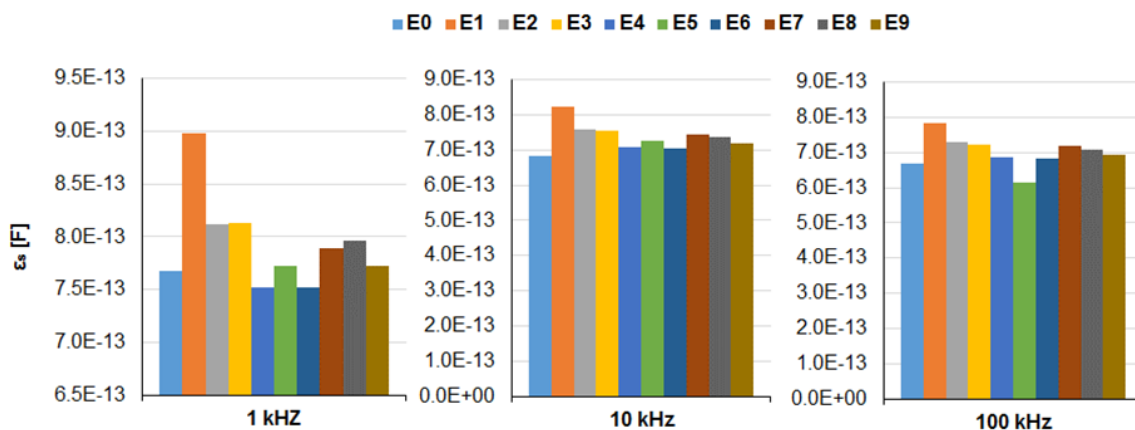
Figure 73. Surface dielectric permettivity for type E materials.
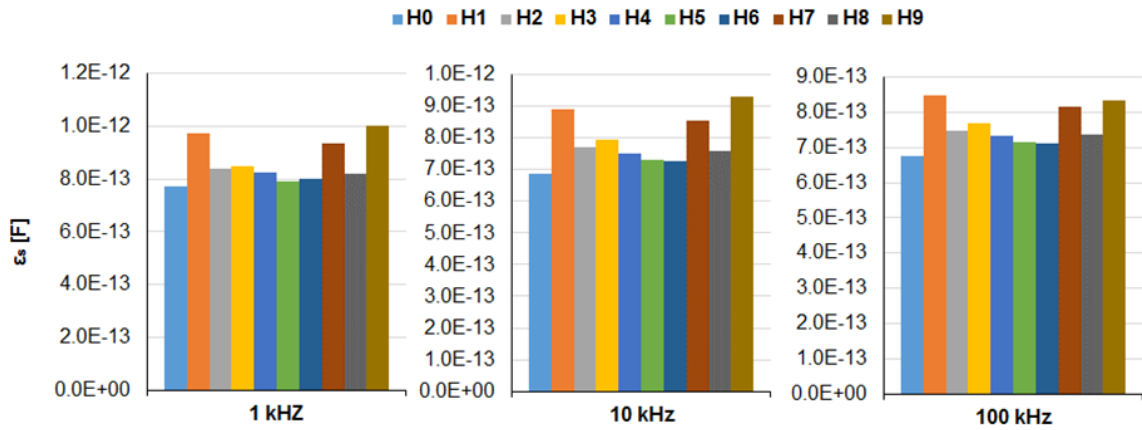
Figura 74. Surface dielectric permettivity for type H materials.

For surface conductivity (figures 114 -116), we can notice a negative conductivity type of behaviour (in two of the measuring frequencies) of some of the type C materials. For type E and H materials, we notice slight increases of surface conductivity at the same time with the increase of the measuring frequency. The obtained results impose the performance of more controlled analyses, with more input data (even if for each parameter, there were over two thousand automatic records of the data during the measurements). Some of the effects might be due to the impurities on the specimen surfaces or to the non-flatness of the specimens or of the measurement system components (figures 75 – 77).
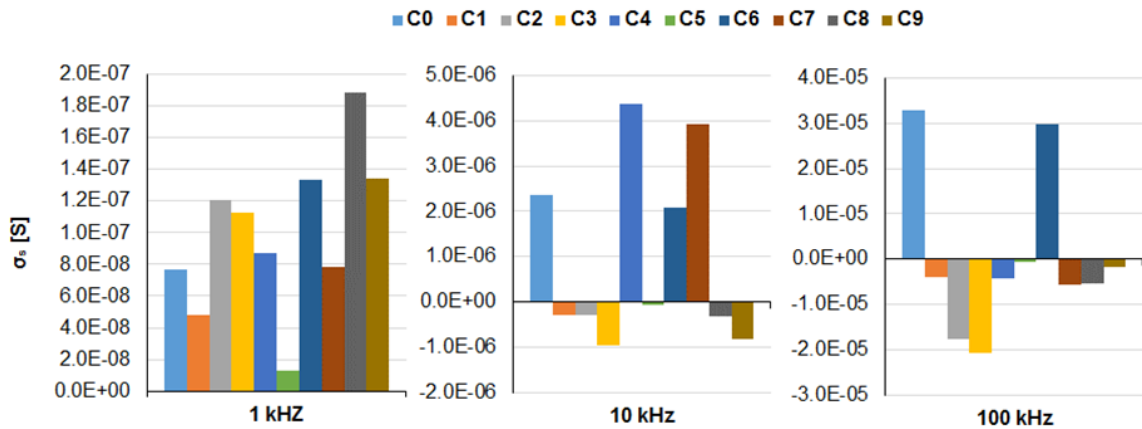
Figure 75. Surface conductivity for type C materials.
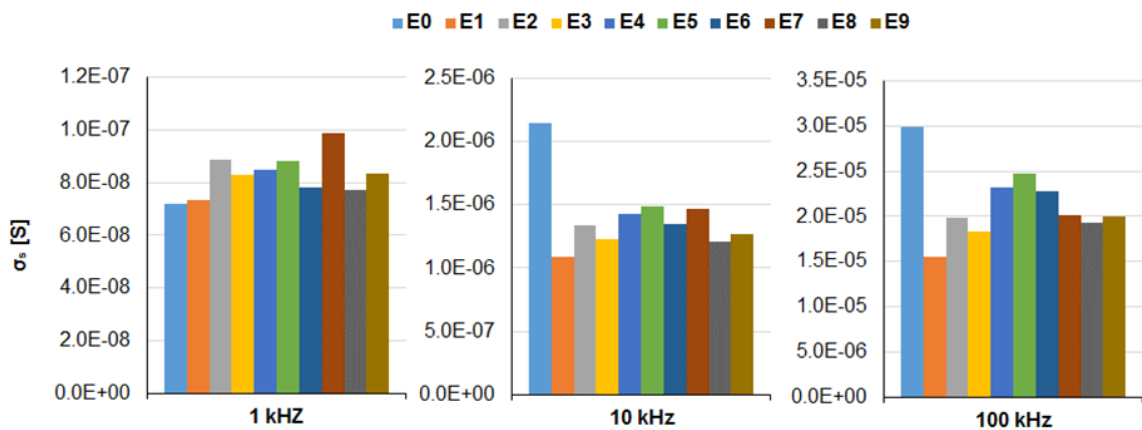
Figure 76. Surface conductivity for type E materials.
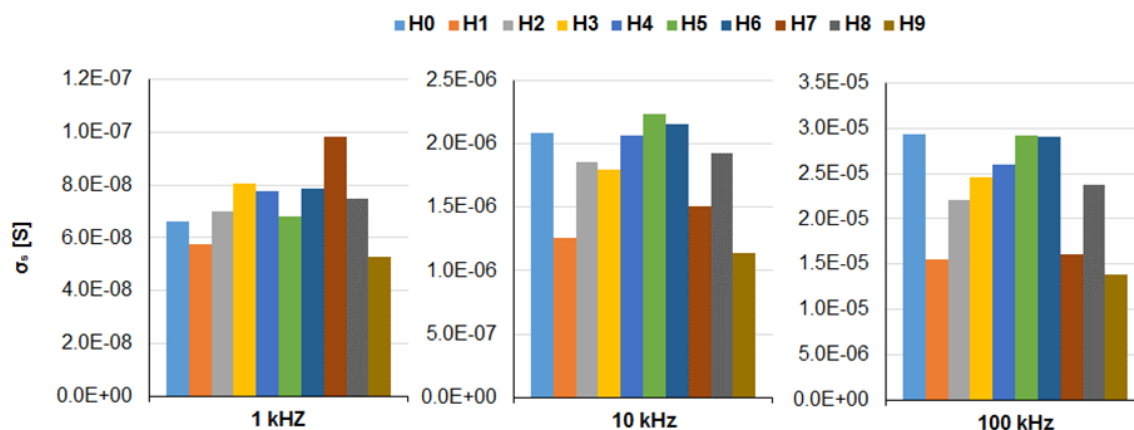
Figure 77. Surface conductivity for type H materials.

From the obtained data, illustrated in figures 75, 76, 77 for the surface electrical conductivity of the materials, we note the following:

- for materials E, the modifiers decrease the electrical conductivity of the materials in relation to the reference material;

- for materials C, the same, the value of conductivity decreased as compared to the reference material and all the formed materials get below 0, except C6;

- for materials H, for most of the performed tests, conductivity decreases, except for three materials, where we notice an increase, H4, H5 și H6, therefore, we can state that solvent 1,4-D increases the value of electrical conductivity, which is higher even than that of the basic polymer (at any of the measuring frequencies).

Concerning the volume dielectric permittivity of the formed materials (figures 78, 79, 80), we notice a decrease of the value of this parameter according to the measuring frequency, more accentuated for materials H and C. At the same time, we notice that, generally, the highest values of the parameter are attained by the polymers diluted with N, N dimethyl formamide.
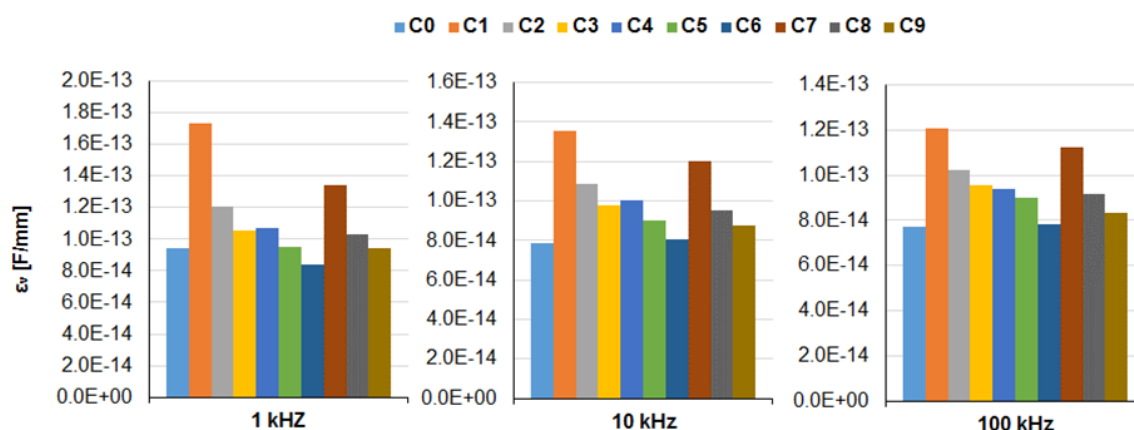
Figure 78. Dielectric volume permittivity for type C materials.
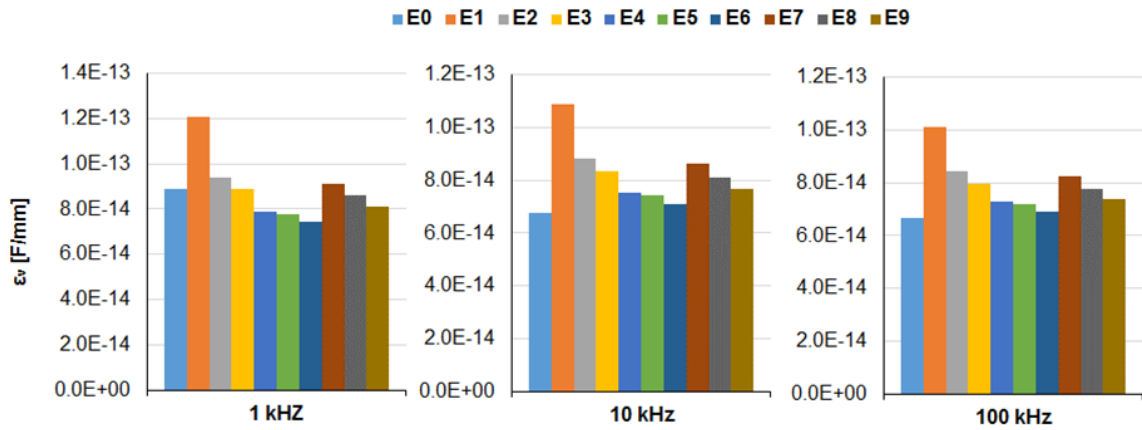
Figure 79. Dielectric volume permittivity for type E materials
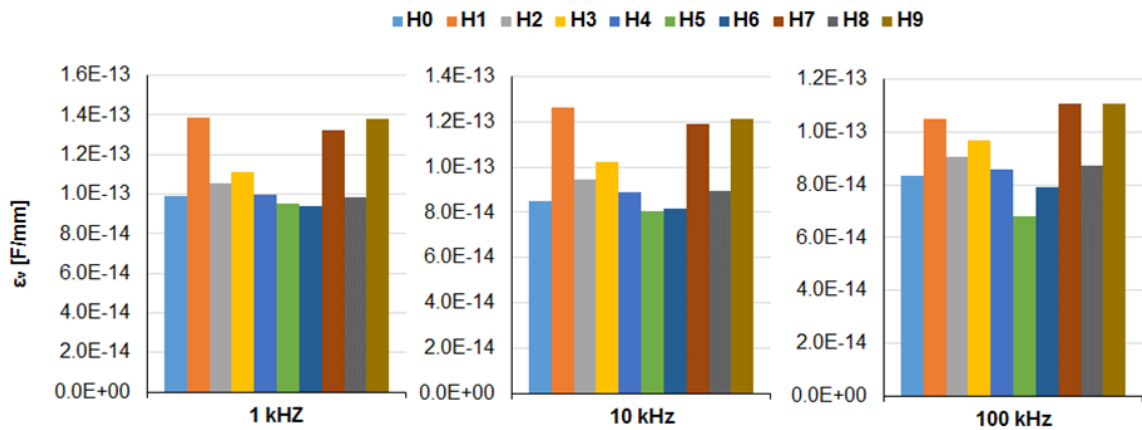
Figure 80. Dielectric volume permittivity for type H materials.

Relatively high values, compared to the other materials, are also noticed in the case in which each of the analysed polymers was diluted with NMP and even, for HT epoxy resin, with glucose solution in 1 methyl– 2 pyrrolidone.

Based on the electrotechnical method for the determination of the electromagnetic parameters of the materials, the magnetic permeability of the materials (figures 81 – 83) was also evaluated and we notice that the obtained values are negative. The electrotechnical method does not guarantee, however, the validity of the data, but only provides an overall image of the behaviour of the material, as if it were a circuit element. The negative values – if they are confirmed – shall represent a starting point for the potential creation of some metamaterials.
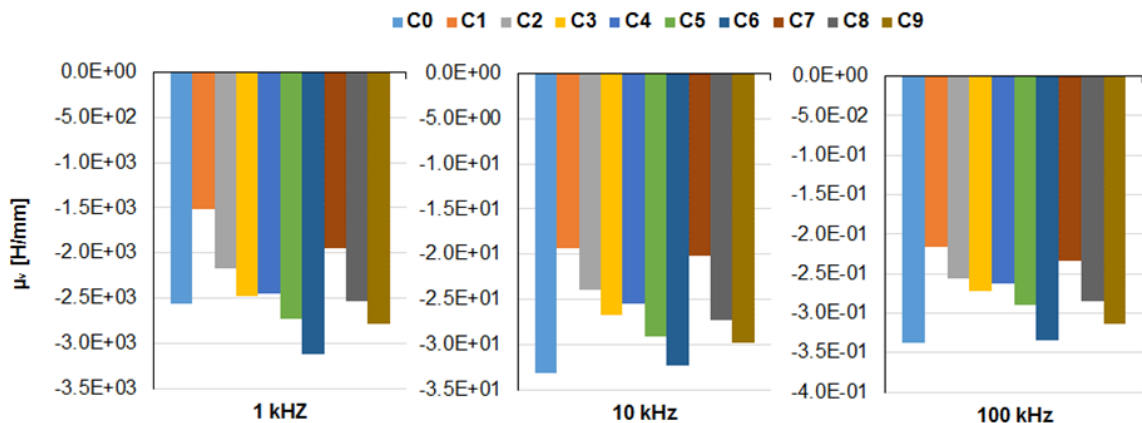
Figure 81. Magnetic volume permeability for type C materials.

E0 ■E1 ■E2 ■E3 ■E4 ■E5 ■E6 ■E7 ■E8 ■E9
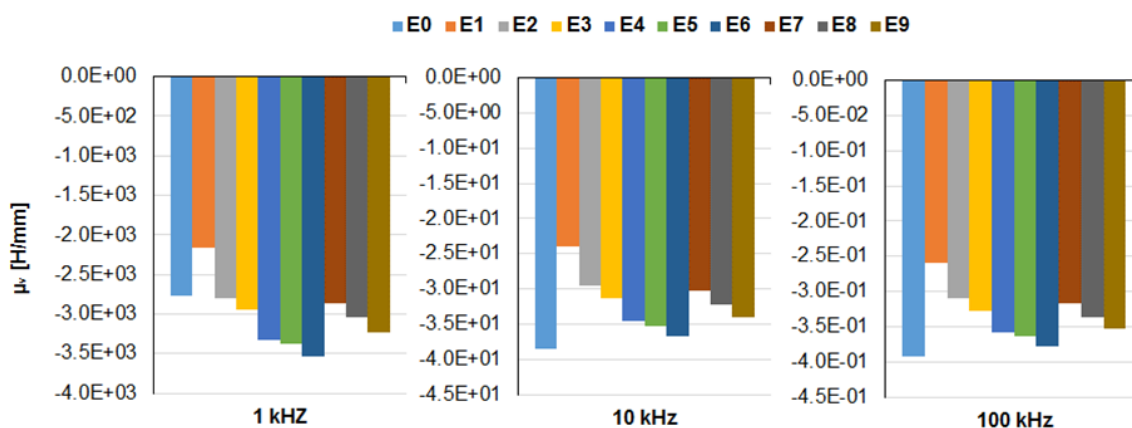
Figure 82. Magnetic volume permeability for type E materials.

H0 ■H1 ■H2 ■H3 ■H4 ■H5 ■H6 ■H7 ■H8 ■H9
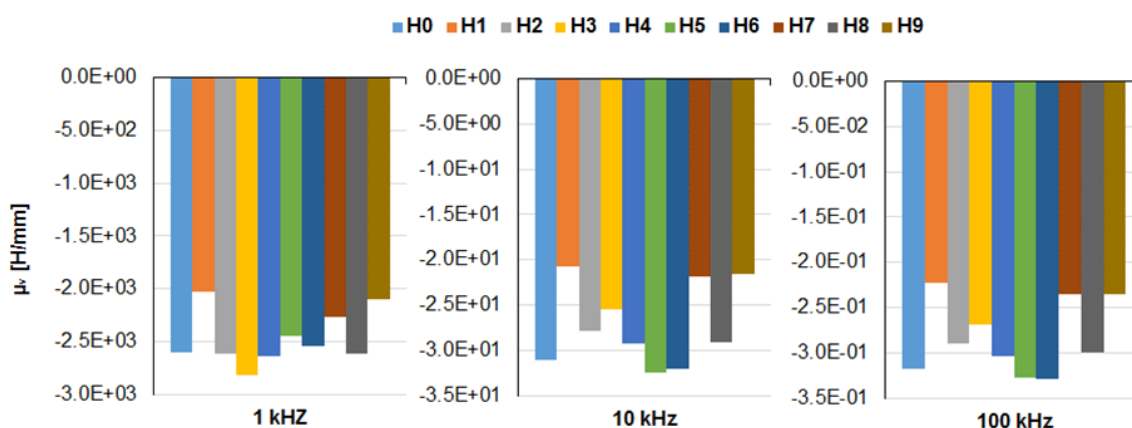
Figure 83. Magnetic volume permeability for type H materials.

The electrical volume conductance of the materials follows – to a certain extent – the evolution of the surface conductivity presented above. We notice that for some of the type C materials (figure 84), negative values of electrical conductance are obtained. Increases of the electrical volume conductance with the value of the measuring frequency are also detectable in the case of type E and H materials, the maximum values of conductance corresponding to the unmodified polymers (figures 85 and 86).

C0 ■C1 ■C2 ■C3 ■C4 ■C5 ■C6 ■C7 ■C8 ■C9

Figure 84. Electrical volume conductante for type C materials.

Figure 85. Electrical volume conductante for type E materials.

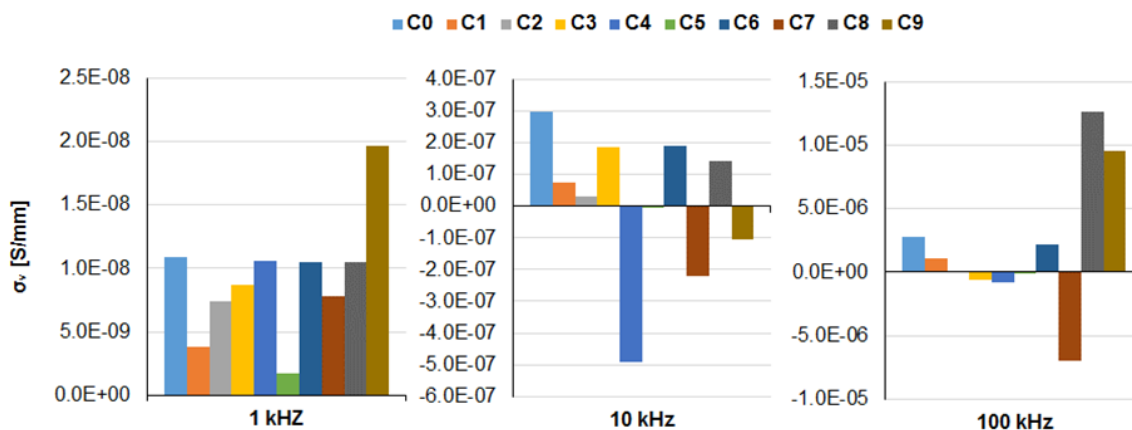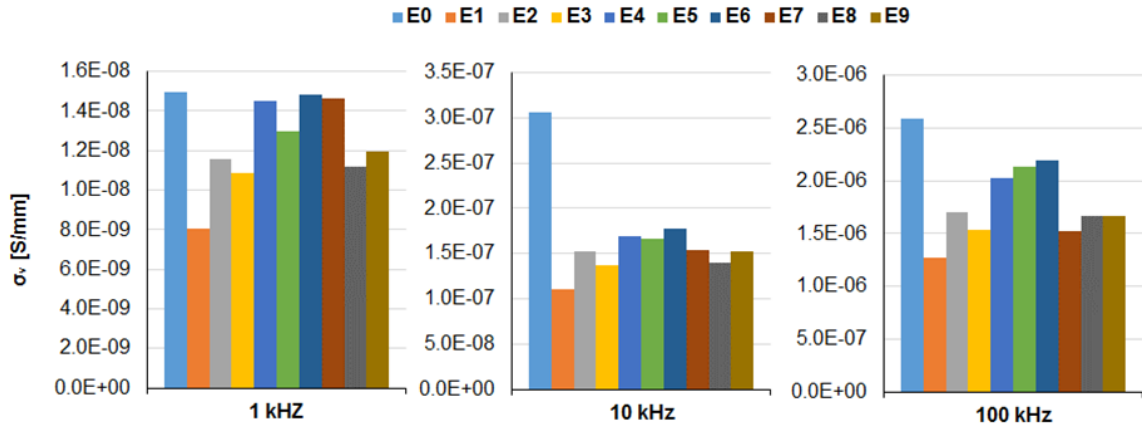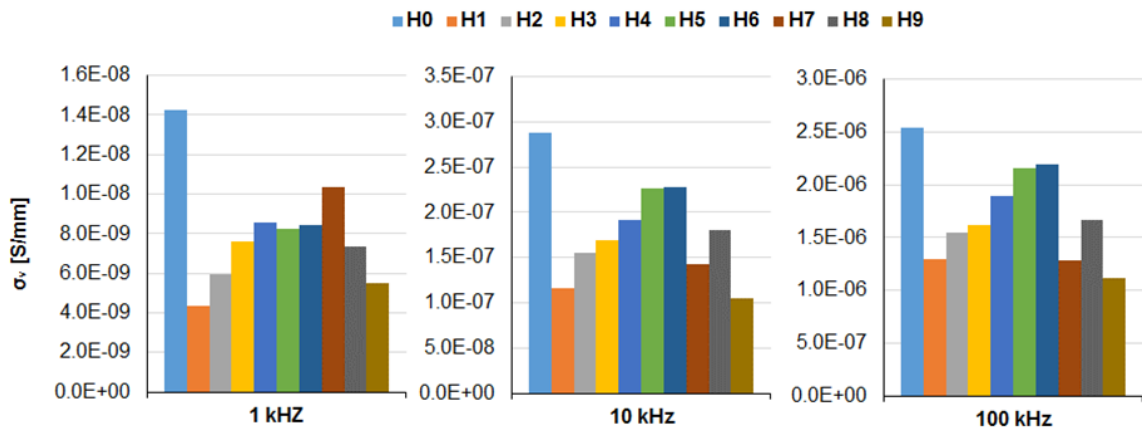*Figure 86. Electrical volume conductante for type H materials.*

7. Conclusions and directions for research

This study started from the basic idea, namely, to form composite material with the help of the three epoxy systems existing in the laboratory, Epiphen, HT2 and C, by modifying them with inorganic and organic solvents in order to obtain materials with improved mechanical and electromagnetic properties.

To modify the properties of a material, when forming it we must use another material or accumulation of materials which can be introduce in the polymer volume and which contributes to the improvement of the mechanical and electromagnetic properties of the new material.

In order to obtain relevant data, in keeping with the goal of the study, we analysed the physical-chemical characteristics of the additives and solvents used for forming the new materials.

Thus, for the improvement of the mechanical and electromagnetic properties of the new materials, we chose two types of modifier:

- inorganic - a mixture of nickel, nickel oxide, nickel nitrate, zinc and lithium hydroxide and a second mixture of iron and iron oxide powder;

- organic – starch, glucose and three solvents DMF, 1,4-D and NMP.

With the inorganic modifiers, we formed six composite materials, using the three epoxy systems, C, H and E as matrix.

For the organic modifiers, we performed tests for the solubility of additives in solvents and established the adequate quantities for improving the desired properties, thus, for the experimental tests, we formed 27 materials, each of them in two plates, measuring 140mm x 140mm and six cylindrical specimens with the diameter of 8 mm.

The properties of the formed composite materials were subject to the following tests:

- thermal tests (heat expansion coefficient, specific heat) for the materials modified with inorganic agents;

- characterisation of the SEM images of the composite materials formed with inorganic agents;

- compression tests (compression stress in the linear area, deformation upon compression in the linear area, tensile stress, deformation upon breakage and modulus of elasticity);

- bend tests (maximum bend stress, modulus of elasticity)

- tensile tests (specific tensile deformation in the linear area, tensile unit stress in the linear area, tensile specific deformation upon breakage, tensile unit stress upon breakage, breakage energy, maximum load upon breakage);

- tribological tests (friction coefficient and wear rate);

- electromagnetic tests (dielectric permittivity on surface and volume, surface conductivity on surface and volume and magnetic permeability).

Based on the tests, we have arrived at the conclusions below:

1. The thermomechanical analysis performed for determining the linear expansion coefficient of the composite materials obtained through the modification of the three types of resins with iron and iron oxide, respectively, nickel, nickel oxide, nickel nitrate, zinc and lithium hydroxide revealed the following:

- generally, the expansion coefficient of the polymer used as matrix has higher values than the expansion coefficient of the modified materials;

- the first thermal cycle of the method used for determining the expansion coefficient may be interpreted as a material reinforcement treatment;

- polymers display, on the first heating segment, at 60-70°C, critical points which disappear after heating at 180°C;

- the critical points appear on the first heating segment for the nickel-modified materials as well but they are shifted to the right (towards the 70-80$^{°}$C temperature range);

- iron and iron oxide modified polymer matrices manifest – on the first heating segments – different behaviour as compared to the polymer matrices and the nickel-modified materials which may lead to the conclusion that chemical interactions occur between the components of the epoxy systems (most probable Bishpenol A) and dispersed powders;

- the values of the expansion coefficients (final determinations – the last cooling segment) do not follow any rule given that in the case of resins C and E the highest expansion coefficient is presented by the nickel-modified materials and, in the case of resin HT, the iron-modified materials;

- the modification of the three epoxy systems, C, E and H with inorganic agents led to the modification of the expansion coefficient of the materials in relation to the reference material, therefore, we may say that C and E epoxy matrices, modified with nickel powder, compressed by 13%, respectively 40% more, and the maximum expansion of the H epoxy matrix modified with nickel powder falls within the 80 - 140°C temperature range.

- the combination and amount of inorganic powders selected for modifying materials with type C epoxy matrix is beneficial. For E and H epoxy matrices, only the mixture of the nickel, nickel oxide, nickel nitrate, zinc and lithium hydroxide powders increases the value of specific heat;

2.   The DSC analysis of the materials proposed to be used as electrodes of the structural batteries, compared with the polymers used as matrix revealed the following aspects:

- the values of the specific heat parameter are higher on the first cycle of the test than on the second cycle, for each polymer;

- generally, polymers, present a slow linear dependency of the specific heat on the value of the temperature at which it is determined;

- iron and iron oxide modified materials have lower values of the specific heat than those of the basic polymer which, on the one hand, may be explained based on the existence of certain chemical reactions between the agents used for the modification of properties and polymers in the dispersion phase of these agents and, on the other hand, confirm the fact that in this case the mixture rule cannot be applied;

- nickel, nickel oxide, zinc and lithium hydroxide modified materials have the highest values of the specific heat;

- we should perform detailed chemical analyses to be able to identify the chemical reactions which take place at the dispersion of iron and iron oxide in the pre-polymer mixture of epoxy systems.

3.   The SEM structural analysis of the materials modified with inorganic agents reveals the fact that the agents used for modifying the polymer properties cause changes which affect the behaviour of matrices under mechanical stress, leading to different morphologies of the fracture areas, outlining the aspects below:

- for the materials modified with nickel, nickel oxide, nickel nitrate, zinc and lithium hydroxide, we notice agglomerations of the agents and their organisation in coral like formations;

- for the materials which contain iron and iron oxide powder, the connection between the epoxy matrix and the modifier is not good, noticing powder agglomerations, which might affect the tribological and electrical properties;

4.   The tribological analysis carried on the three epoxy resins modified with solvents and, respectively, starch and glucose solutions, revealed the following:

- the transitional regime takes place (for each tested material and for each regime) over the first four meters of sliding, at most;

- the values of the friction coefficient upon sliding among the pins made by the unmodified epoxy resins on the steel disk are practically constant for each type of polymer and for each regime of the tribological regime;

- adding the solvents or the starch or glucose solutions in the three solvents in the polymer matrices leads to the softening of the matrices with effects on the evolution of the friction coefficients between the tested material and steel;

- for the materials made based on E epoxy resin (Epiphen RE4020-DE4020), the profiles of the evolutions of the friction coefficients are almost identical and are more grouped for regime R1 than in the case of the two other resins;

- for all the tested materials, it is found that in the regimes with a high loading force and low sliding speed, there are great dispersions of the friction coefficient values;

- in the case of C epoxy resins, N,N dimethyl formamide modifies the least the tribological behaviour of materials;

- 1-4 Dioxane produces the greatest changes to the tribological behaviour of Epiphen RE4020-DE4020 epoxy resin, as in the case of HT epoxy resin;

- the lowest friction wear rates are noticeable in the case of materials based on E resin, followed by those on H resin and, at last, the materials based on C resin.

5. The results of the compression test can be summarised as follows:

- the elastic moduli on compression of the modified polymer materials have lower values as compared to the basic polymers and the highest values correspond to Epiphen RE4020 - DE4020 epoxy resin;

- the unit stresses at the elastic limit of the diluted materials are higher than those of the basic resin for E resin, but for C and H resins they have the same value for the materials diluted with N,N dimethyl formamide, for these two resins, the only diluted systems with higher values of the parameter being H4 (diluted with 1-4 Dioxane) and C7 (diluted with 1 methyl – 2 pyrrolidone);

- for some of the tested materials we noticed the tendency to return to their original shape (even if the specimens are cracked and, in some cases, cracks extend up to the edge of the specimen);

- the dilution of polymers or their modification with starch and glucose solution increases the deformability level;

- the compressive modulus of elasticity has low values for the modified materials as compared to the elastic modulus on compression of the basic polymer and the highest values correspond to Epiphen RE4020 – DE4020 epoxy resin.

6. Three point bend tests revealed the following:

- polymer dilution leads, without exception, to the drastic reduction of the compressive modulus of elasticity;

- for C epoxy resin, the materials formed by modifying the basic solution with starch or glucose solution determine a three to five times increase of the bending modulus of elasticity as compared to the value of the parameter recorded for the unmodified polymer;

- for the other two polymers, dilution leads to the reduction of the bending modulus of elasticity as well, but the use of starch or glucose solutions do not cause the effects which appear in the case of C epoxy resin;

- in terms of the three point bend test, C resin is more vulnerable to 1-4 Dioxane (the most drastic reduction of the elastic modulus), while the other two resins are more vulnerable to N,N dimethyl formamide;

- as in the case of compression, material H9 is too soft to be tested in the experimental conditions set for the analyses;

- as the materials present a load characteristic on bending which has a maximum point which coincides with the elastic limit, the values of the unit stress and, respectively, of the polymer specific deformations have equal values for each polymer (whether it is measurement at the elastic limit or maximum load), so that in the representations of those parameters for the modified materials, there is only one line which corresponds to the parameter for the polymer;

- as with compression (but this time there are no cracks of the specimens), there are materials which regain their initial shape after a certain period of time (the factors which influence recovery speed have not been analysed).

7. Tensile tests revealed the following:
- the modification of C and E epoxy resins with a solvent or solution did not increase the value of the tensile unit stress in the linear area; materials which undergo an improvement as compared to the reference material H0 are H5, H6, H8;
- the graphic illustration of the data obtained for the tensile stress on breakage outlines that for the materials formed only with solvents the value of this parameter decreased for all the three resins, the only materials which exceeded the value of the reference material being E2, E5, H2, H5, H6 and H8. Thus we can say that an improvement of this parameter is due to the solutions made of DMP with starch, 1,4–D with starch and glucose, and the solution made of NMP with starch only reacts well when H epoxy resin is used as matrix. Given that improved values are obtained only in the materials which contain starch and glucose, we may conclude that the two additives modify the basic property of the materials;
- the breakage energy of the formed materials is significantly higher than of the reference materials, therefore, the materials selected to be added to the three resins improved this parameter. The only materials with values below the reference material are E6 and E8.

8. The electromagnetic tests revealed the following:
- according to the data presented for the dielectric permittivity of materials, we may say that the effect of additives increases the value of this parameter at all frequencies and for all the materials, as compared to the reference material.
- surface conductivity: for materials E, C, the value of conductivity decreases, as compared to the reference material, below 0, in all the materials, except for C6, therefore, they have become better insulators than the reference material. Regarding materials H, for most of the performed tests conductivity decreases, except for three materials which record an increase, H4, H5 and H6, therefore, we can say that solvent 1,4-D increases the value of conductivity;
- dielectric permittivity on volume of the composites materials increased in the case of materials E, C and H only for 10 and 100 Hz frequencies, and decreases at 1Hz frequency for materials E4, E5, E6 and E9, C6, H5 and H6;
- magnetic permeability on volume of the composite materials preserves the basic property of diamagnetic material of the resin, although, according to the values obtained for the modified values, we notice an increase of the values;
- the only formed and tested materials which experience a significant increase of conductivity are materials C8 and C9.

In the light of the conclusions afferent to each parameter studied in this thesis we may conclude that the goals of the research have been reached and the corresponding materials are the following:
- material C5 – negative electrical resistivity on volume at 100 Hz – better insulator than the reference material and, implicitly, than silver $1,5 *10^{-8}$ or copper $1,7 * 10^{-8}$, increased bending modulus of elasticity, therefore, it may be used as separator between cathode and anode in batteries;
- H2, H5, H6, due to the high tensile unit stress un breakage;
- the shape-memory materials;
- after the electrical load tests of the materials modified with inorganic agents, cast as plates, given that they were not activated, we infer that no electrolyte absorption occurred in the composite material as it is not porous enough, therefore, the test failed;

In subsequent studies, we shall focus on:
- analyses for the identification of the chemical reactions which occur between the epoxy resins and the mixture of iron and iron oxide
- the determination of the heat expansion coefficient of the materials modified with organic solvents using the TMA device;

- the determination of the specific heat of the materials modified with organic solvents using the DSC device;
- dynamic tests of the materials modified with organic solvents which regain their initial shape;
- the forming of new composite materials with the help of a new type of epoxy matrix (type L), with the organic solvents used in this study;
- the characterisation of the mechanical, tribological and electromagnetic properties of the composite materials formed with L epoxy matrix.

8. List of works published and presented at national and international conferences

Articles ISI :

- G. Mihu, I. Mihalache, M. Bodor, O. Mircea, I. Graur, Tribological characterization of modified epoxy systems, Mater. Plast., vol. 53, no. 2, 2016**,** ISSN: 00255289

Articles BDI :

- I.G. Bîrsan, M. Bunea, **G. Mihu**, A. Cîrciumaru, The electromagnetic proprieties of hibrid composites, Nr. 2 al revistei The Annals of '' Dunarea de Jos" University of Galati, fascicle IX, Metallurgy and Materials Science, ISSN 1453 – 083x, 2015
- I. Graur, **G. Mihu**, V. Bria, A. Cîrciumaru, I.G. Bîrsan, Compressive Behavior of Ultra-sonicated Starch/Carbon black/Epoxy Composites, Nr. 2 al revistei The Annals of '' Dunarea de Jos" University of Galaţi, fascicle IX, Metallurgy and Materials Science, ISSN 1453 – 083x, 2015

Conference presentations:

- M.Bunea, C. Munteniţă, A. Căpăţînă, **G. Mihu**, A. Cîrciumaru, I.G. Bîrsan, The termal behaivour of hibrid composites, Conferinţa Internaţională TEME, 21-23 octombrie 2015 Galaţi. (poster)
- M. Bunea, C. Munteniță, A. Căpăţînă, **G. Mihu**, A. Cîrciumaru, I. G. Bîrsan, THE THERMAL BEHAIVIOR OF HIBRID COMPOSITES, International Conference of Young researchers, New trends In environmental and materials engineering, of '' Dunarea de Jos" , 2015, Galati
- I. Bosoancu, R. Bosoancu, **G. Mihu**, M. Bodor, C. Muntenita**,** I. Mihalache, I. Graur, C. Ungureanu, A. Circiumaru, V. Bria, *TRIBOLOGICAL BEHAVIOUR OF IN SITU NANOSTRUCTURED POLYMERS,* VIII International conference BALTTRIB' 2015, 26-27 November 2015, Akademija, Kaunas, Lithuania, (poster)
- M. Bunea, I. Bosoancu, R. Bosoancu, **G. Mihu**, M. Bodor, C. Muntenita, I. Graur, C. Ungureanu, A. Circiumaru, V. Bria, *TRIBOLOGICAL BEHAVIOUR OF STRATIFIED COMPOSITES,* VIII International conference BALTTRIB' 2015, 26-27 November 2015, Akademija, Kaunas, Lithuania, (poster)
- **G. Mihu**, I. Mihalache, I. Graur, C. Ungureanu, V. Bria, Comparative study regarding friction coefficient for three epoxy resins, ROTRIB'16, The 13th International Conference on Tribology, September 22-24, 2016 – Galați, ROMANIA

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