IOSUD – „DUNĂREA DE JOS" UNIVERSITY OF GALAȚI

Doctoral School of Mechanical and Industrial Engineering

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ABSTRACT

DOCTORAL THESIS

Research on the methods and techniques for controlling the electrical conductivity of polymers and their effects on the mechanical properties of the formed materials

Doctoral student,

Eng. Gabriel SĂRACU

Scientific coordinator,

Prof. dr. habil. Adrian CÎRCIUMARU

Series I6 Mechanical Engineering No. 76

GALAȚI

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Research on the methods and techniques for controlling the electrical conductivity of polymers and their effects on the mechanical properties of the formed materials

Ph.D. Candidate,

Eng. Gabriel SĂRACU

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Series I6 Mechanical Engineering No. 76

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Thanks

As the quote above tells us, we have come to the position of living those unique and special moments in which I can say, with great emotion, that I look behind me and find that I have evolved at the most appropriate pace, safe and healthy, steadfast and wise.

The completion and support of this doctoral thesis is the time when I close an important stage of my vocational training and is the result of a sustained effort over five years of intensive studies and research. This moment, the crown of my professional route, is due to those who helped me, stood besides me and with whom I formed a team at professional level and not only.

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More than mere thanks I address to my family, my wife and my little boy for their endless understanding, patience to endure my absence, their unconditional help, for the fact that they constantly cheered me and supported me during these years of study.

Galați, 12th of November 2023
Gabriel SĂRACU, Ph. D. Candidate

Content

List of figures
Pg.

10

List of tables

Introduction

In the course of time, the level of technology has enhanced swiftly, almost exponentially, over the years, impelling the levels of science and research to much higher standards, impossible to anticipate half a century ago. It is also the case of finding, in the context of the current crisis of energy and raw materials, new solutions to solve old problems (for which solutions already exist, but they are more and more difficult to implement in the context of the mentioned crises). The best example of this is found in the consumer (or industrial) electronics industry – televisions, telephones, computers, where new materials are increasingly being used to replace the famous silicon chips. An extraordinary role as concerns this undertaking was played by a new type of understanding of the mechanisms of electrical (actually, electronic) conductivity, much more subtle than that on which silicon- and germanium-based electronics were based. Coming from solid-state physics, an example to this extent is represented by the CMOS devices.

The current world is already oriented, at the level of fundamental research, towards the development of quantum computers - faster, more reliable - but this development also implies the existence of basic materials.

From another viewpoint, everything around us is based on the chemistry of polymers – from packages for food, to domestic appliance casings and from aircraft parts to car components, polymers are part of life in modern society due to the fact that they are cheap and have remarkable properties of chemical, dimensional and thermal stability along with mechanical properties adequate for those applications – tensile strength, impact strength. A step further in this field was made along with the development of composites – that is, materials made by the interfingering of two phases – one called the matrix and the other traditionally called the reinforcement. Undoubtedly, composites have solved, at a low price, many problems that tangled the use of devices or equipment as common as possible (televisions - from the wooden case to the polymer or composite case). The same situation is found in all industries producing means of transport because decreasing the mass of the vehicle means boosting its economic efficiency. Unfortunately, the vast majority of polymers are derivatives of fossil fuels (crisis again).

Perhaps the greatest advantage of using polymers (despite their huge polluting potential) is related to their low density combined with the remarkable properties mentioned above. The question is whether, while keeping the mechanical properties, a polymer can be modified so that it can perform at least one other function (besides the protective one). The first, and the most accessible, was to ensure the appearance (interior design) by adding various additives to the polymer matrix to change the external appearance (generally polymers are white or have various shades of yellow).

The current energy crisis has generated another burgeoning industry that uses polymers (this time with high transparency and high hydrophobicity) – the production of solar panels – active elements that convert light energy into electricity. Similarly, the wind generator industry uses polymers in the form of protective paints (offshore) and polymer matrix composites (blades). For all these applications, one, at the very most, two properties of polymers are definitive.

The design of composites reached another level when the research required the use of the same reinforcement element in order to solve two functional problems. For example, carbon fiber solves, at the same time, problems related to the mechanical strength of composite structures (essentially by the way in which carbon fibers are distributed in the matrix) but also problems related to the electrical conductivity of the composite (at least in

the longitudinal direction of the fiber), given that these fibers have a very high electrical conductivity in this direction (being anisotropic, in the transverse direction, the value of electrical conductivity is diminished). Thus appears the idea of multifunctional composite materials, materials that allow solving not only mechanical strength problems, but also other problems in relation to the electrical or magnetic responses of the material, to the dimensional thermal stability or thermal stability of the mechanical parameters (see the on-board elements of commercial cars).

Most polymers used to form various composites with properties of this kind are thermosetting polymers. These polymers cannot be reused, recycled. Once formed they are very stable chemically, thermally (reason for which they are appreciated and used in industry) and cannot be neutralized, contributing to environmental pollution. It is a huge problem for the current society to neutralize this type of waste (resins). One of the solutions to reduce the impact on the environment is to extend the life of landmarks made of thermosetting polymers or composites with thermosetting matrices. Here things are more intricate since all polymers are (more or less) hydrophilic and the combination of atomic factors (temperature, humidity, pressure) and their alternations (day/night and seasonal) cause polymer aging and, consequently, diminish the values of the characteristic parameters. In the case of composites, the effects may be more serious because the mentioned factors may lead to a decline in the quality of the polymer-arming element interphase, with terminal consequences on the use of that landmark.

The current research is aimed at finding new resources for the polymer industry (especially made of materials considered as having little use value – vegetable residues, first of all) so that this industry becomes sustainable in the long term, in the absence of fossil sources (gas and crude oil). One of the most researched organic substances is chitosan, a natural polymer extracted from the keratinous tissue of some crustaceans or insects. It is also working on getting polymers from substances known as: starch, agar, amino acids that could be neutralized by metabolic-type mechanisms. Polylactic acid (PLA) is a thermoplastic polymer obtained by polymerizing (under certain conditions) lactic acid coming from the fermentation of corn or sugar cane.

Paradoxically, the extraordinary properties of polymers sometimes cause a lack of efficiency of their use for certain applications. One of these remarkable properties is that all polymers are electrical insulators with high values of dielectric permittivity. This is the main reason why one of the most important applications of polymers is to make insulating jackets of various conductive cables of all sizes. Adding various dyes to the polymer does not change their insulating properties, and there is the possibility of making variously-colored insulated conductors (for example FTP cables), ensuring an enhanced comfort in use.

For other applications, however, this property is a hindrance because static electrical charge accumulates on insulating surfaces and electrical discharges (which cannot be controlled) have very serious (sometimes devastating) effects. Boat fuel tanks are also made of plastic, but they are *grounded* (actually, watered) to ensure discharge of electrical charge accumulated on the surface. In the case of a much more expensive application - helicopter rotor blades - there have been reported accidents with very serious consequences due to the accidental discharge of the electric charge on them and a cloud (equivalent to a thunderbolt striking the blade), causing the material penetration (composite reinforced with carbon fibers) and having the immediate effect of breaking the bonds at the interphase level. Once these links are destroyed, the mechanical integrity of the structure is lost and it yields to the efforts to which it is subjected.

A cheap polymer, with high electrical conductivity, would allow the electric charge to drain into the ambient air and would considerably lower the risk of occurring an accident such

as the one described above. There are various studies confirming that the use of structures (as modifying agents) contributes to improving the electrical conductivity of polymers (or of some polymers), these structures, most often nanometric in size, being allotropic forms of carbon – nanotubes, fullerenes, graphene, nano-graphite, etc. Nevertheless, not always dispersal of these powders in the polymeric matrix is a successful one since once in a liquid medium (mixture of liquids or melt), these nanometric structures tend to agglomerate and form *defects* of polymer network, with consequences on mechanical properties.

There are many experimental studies confirming that uniform dispersions can be obtained up to a maximum of 2% (mass fraction) concentration of these polymer structures (the concentration also depends on the nature of the polymer and the dispersion conditions), but such a concentration is small enough not to cause a significant increase in the electrical conductivity of the formed composite. Furthermore, all these composites get a black color due to the presence of the mentioned structures and thus cannot be used in any applications where transparency or semi-transparency would be required.

Another approach to the problem of enhancing the electrical conductivity of polymers was that of the dispersion of metallic nano-structures (silver, zinc, iron, gold, platinum). The shortcomings, in this case, are related to the high costs of making metallic nano-structures (although powder metallurgy is spreadingly used).

Ultimately, the study of semiconducting ceramics brought another breath to the research concerning the electrical conductivity of polymers. Nanoscale ceramic structures are extremely stable and have pronounced semiconducting behavior. Unlike the modifying agents mentioned above, they have the advantage (some of them) of being transparent and, therefore, do not affect the polymer transparency. Unfortunately, even in this case, getting uniform dispersions is still a challenge. Moreover, the fact that the nanostructures cannot be aligned in certain directions in the polymer (directions that would be in accordance with the crystallization structures) leads to an attenuation in transparency.

A solution in this regard could be the creation of a very thin ceramic network over which a thin layer of polymer can be placed. The solution is being used for some models of TVs or phones.

At the Research-Development Center for Composites with Thermosetting Matrices (RDCCTM) of the *Dunărea de Jos* University in Galați, there have been carried out studies regarding polymers modified with carbon nanostructures (CNT, carbon black) by Adrian Cîrciumaru (doctoral thesis - *Contributions to the study of the electrical and mechanical properties of composites reinforced with fabrics and matrixes from additive epoxy*, Galati, 2009 – for CNT), Marina Bunea (Doctoral Thesis – *Contributions to the study of impact strengths of fabric-reinforced epoxy matrix composites*, Galați, 2015 – carbon black). Another study, conducted by Iulia Păduraru-Graur, intended to dope an epoxy resin with alkaline ions so that they contribute to enhancing the electrical conductivity of the obtained material (Doctoral Thesis - *Study of the mechanical properties of epoxy materials doped with ionic substances through dispersion strategies based on the use of ultrasound*, Galați, 2015). Mihaela-Claudia Gorovei (Doctoral Thesis - *Research on the nano structuring of polymers through electrochemical methods and the effect of nano structuring on the mechanical properties of polymers*, Galați, 2021) carried out research concerning getting ceramic nanostructures by developing local chemical reactions in the volume of the polymer (found in liquid phase).

As an electrical engineer, the field of conductive materials is obviously familiar to me, but I had no knowledge of polymers with high electrical conductivity. This is the reason why I felt attracted to this research, even though along the way I had to learn more and more in order to understand the complexity of the (electrical) conduction mechanisms of polymers.

As clearly as possible, I started with a bibliographic study for which I benefited from the access provided by the Dunărea *de Jos* University in international databases. I had moments of weakness, when it seemed to me that I would not have enough time to cover at least a part of the vastness of the field, when I had the feeling that I could not understand a certain mechanism or a certain theory. I managed to overcome these moments and discovered that the formation of materials is not a game either and certain rigors must be observed. Like any other PhD student, I wished things to develop more swiftly. I realized, by making electrical conductivity measurements through various methods and under various conditions, that speed of execution is not what defines the work of research. When I did the mechanical tests, it felt like I was flying, compared to the electrical tests carried out.

The research whose results I bring you forward here began with the assumption that the presence (in the polymer network) of some d-type metals (transitional metals, as they are also called) could have an influence on the electrical conductivity of modified polymer materials, due to the existence of a large number of free energy levels in these atoms. Of course, in the case of compounds, these energy levels are somehow blocked by the presence of oxygen through dative (coordinative) bonds, in which oxygen binds pairs of electrons to the free energy levels.

For improving electrical conductivity, the method proved effective. Unfortunately, the materials obtained were so soft that the question of their mechanical testing could not be raised. This occurred due to the presence of the solvent used to solvate the d-type metal salts. The amounts of solvent used were too high and, as the solvent is a known plasticizer, the final material was far from a modified epoxy resin. The effect of the presence of the solvent in the epoxy resin was not unknown to me since, also at CCDCOMT, it was carried out research in this direction by Georgel Mihu (Doctoral Thesis - *Study of the properties of epoxy systems modified with organic solvents*, Galaţi, 2017).

The second approach was similar to the one followed by Mihaela-Claudia Gorovei and targeted to possibly grow electrical conductivity through the formation of nanostructures following chemical reactions developed in the polymer volume. We did not use the same precursors and used a different strategy of producing materials. The results acquired are encouraging as concerns the electrical properties of the materials, but somewhat disappointing in terms of their mechanical properties.

Chapter 1

Electroconductive Polymers – Current Directions

Polymers are being used on a large scale in industry and our daily life, due to their diverse functionality, low density, low cost, and excellent chemical stability [1]. Considerable progress has been made in the previous decade in the development of high-performance polymers thanks to the structure and ionic character of their bonds [2]

Polymer-based materials are extensively applied in various scientific and engineering applications, such as industrial production, agricultural science and technology, petrochemicals, marine technology, automotive, aeronautics and astronautics industry. In practical and industrial applications, polymer-based materials are often subjected to differentr types of environmental factors, such as ultra-high and low temperature and pressure [3].

Conductive polymers have come into prominence in the interdisciplinary scientific research concerning the modern aspects of organic synthesis, electrochemistry, catalysis, solid body physics and thin layer physics with applications in the field of state-of-the-art unconventional technologies. Applied research targeted microelectronics, electrochemistry, catalysis, energy and information storage, due to the specific properties of these materials and the functions they can achieve: transport and storage of electrical charges, activation of electrochemical processes, selective permeability and ion transport [4], [5].

Conductive polymers are organic polymers with high intrinsic electrical conductivities. These got more and more attention with the essential contribution of Heeger, Mac Diarmid and Shirakawa, who jointly received the Nobel Prize in Chemistry in 2000 [6], [7], [8], [9], [10].

Although they were initially investigated as substitutes for metals, their range of applications quickly expanded to covering several research fields (Fig.1.1), such as electrocatalysis, energy storage [6], [11], or more often encountered applications, in the field of sensors, transistors, data storage devices, photovoltaic cells, transparent conductive materials, electrochemical devices, actuators, surface protection as well as substitutes for carbon materials [12], [13], [14].
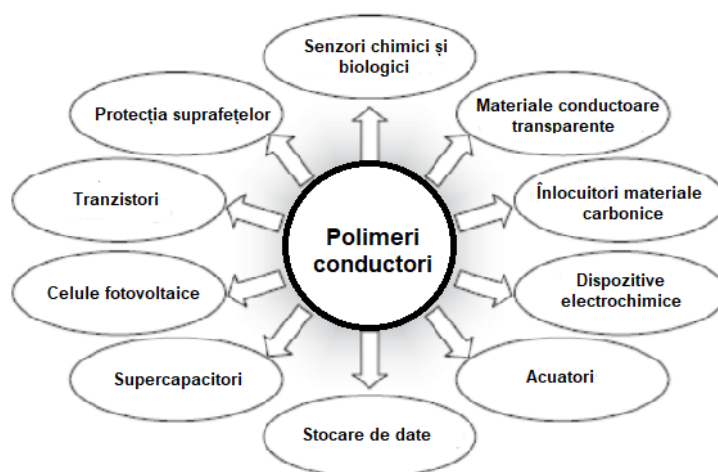
Fig.1.1. Areas of use of conducting polymers [12].

A lot of interesting studies in the field of conductive polymers are mainly based on polypyrrole, polythiophene, polyaniline and poly(3,4-ethylenedioxythiophene) derivatives, **Fig.1.2.**
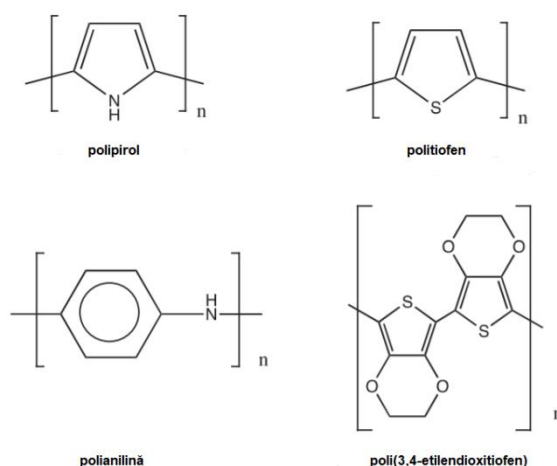
Fig.1.2. The most common conducting polymers in undoped form [6].

The electrical properties of polymers are usually related to dielectric permittivity and electrical conductivity. The addition of various conductive nanomaterials to polymer matrices determines some interesting electrical properties to polymers. The incorporation of graphene nanophones can offer more possibilities for electron transfer in the nanocomposite, which makes it electrically conductive [15], [16].

Electropolymerization is a relatively new and efficient method to make graphene-polymer composites for conductive applications. This method is easy to do, saves time and is ecological. The finished products acquired by this method are generally applied for electrochemical sensing and energy storage, such as supercapacitors and batteries. The most common electropolymerized composite is based on polyaniline (PANI) and graphene [17].

Thanks to its thermal and chemical stability, simple polymerization process, easy protonation doping, and low cost, PANI has been intensively investigated as a conductive polymer and has conductive, as well as insulating properties, depending on its oxidation state and the proton species used during the doping process [18], [19], [20], [21].

In the source of information [22], the authors present the characterization of the composite material formed by reduced graphene oxide (rGO) and PANI, used as material for pseudocapacitor electrodes. The technique used to properly coat rGO over PANI is *in situ* polymerization. This aspect determines a very good conductivity of the acquired composite and, therefore, it can be used as an electrode in a supercapacitor offering a high capacity, up to 600F/g.
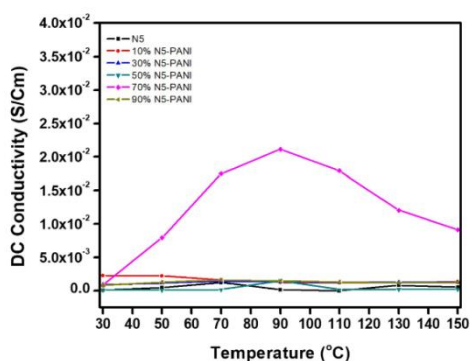
Fig.1.3. Electrical conductivity as a function of temperature for the NiO-PANI composite [31].

Another conducting polymer very often used in research, due to its high conductivity and excellent mechanical properties, is polypyrrole (Ppy) [23], [24]. It is already used as an electrode for rechargeable batteries, as an electromagnetic shield in electronic equipment, in printed circuit boards and many other diversified applications [25], [26], [27], [28], [29].

Another polymer that has come into notice lately due to its promising conductivity, which can be accustomed from the insulator, to semiconductor, and then to the metal range, by doping, is polythiophene (PTh) [30], [31].Thanks to its conductive aspect, it can be used in a wide range of applications, such as: batteries, smart windows, anti-static coatings and various types of sensors. PTh with a semiconductor domain of electrical conductivity is found in applications such as light emitting diodes (LEDs), field effect transistors (FETs) and photovoltaic cells [32], [33], [34], [35], [36].

Unfortunately, after injection molding, it was discovered that the process ensured a poor CNT-to-matrix contact and low electrical conductivity. Starting from this, in the study [37], it was an made an attempt to improve this characteristic in CNT-modified and injection-moulded polycarbonate (PC) composites, using both types of CNTs, namely, single-walled and multiple-walled carbon nanotubes (SWCNTs and MWCNTs, respectively). Nevertheless, electrically conductive CNT networks have been readjusted by annealing (post-processing) at high temperatures. For example, the SWCNT conductivity (1% - mass percent)-PC was enhanced 10^{12} times after annealing. Here, the electrical network of SWCNT-based polymer composites transformed after annealing was investigated in detail for the first time. Polarized Raman testing clearly proved the transition from aligned, unconnected CNTs before annealing to a randomly oriented interconnected network after annealing. As a result, the response of the composite to electromagnetic waves changed from absorption to reflection, and the conductivity improved. A 3% concentration of SWCNT-PC percentage by mass, displayed the highest electrical conductivity and, in addition, it provided the highest electromagnetic interference (EMI) shielding efficiency of 46.7÷51.1dB, giving an extremely interersting direction of application – electromagnetic shielding, as can be also seen in Fig.1.9, shown below.
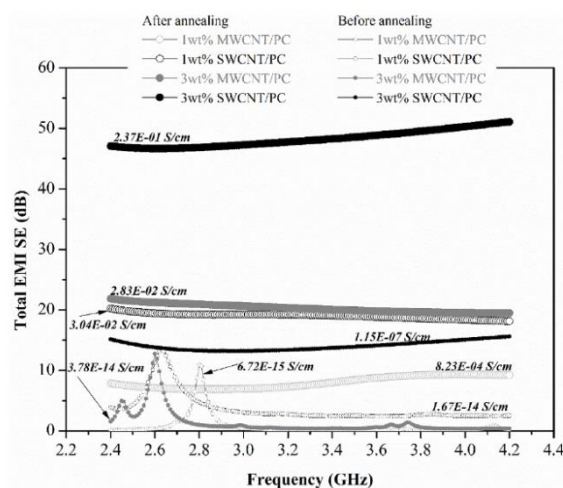
Fig.1.9. Measured total S-band EMI and electrical conductivity at 1% and 3% mass fractions of SWCNT-PC, before and after baking [115].

There is an increasing interest in conducting polymer composites (CPCs), especially in several application areas, such as static charge dissipation [38], [39], actuators [40], [41], shielding for electromagnetic interferences [42], [43] and so on, due to low cost, easy and adjustable processability, as well as high electrical conductivity [44], [45], [46]. Notwithstanding,

the most common method of manufacturing in industry, melt blending, could cause CPCs to encounter high percolation thresholds, resulting in high costs and densities, poor mechanical and processing properties [47], [48]. Up until now, the measures that have been proposed in order to get rid of this dillema have focused on the structural design of solid CPCs [49], [50], [51], [52], [53], [54]. The formation of a doubly percolated structure is one of the most effective ways to reduce the percolation threshold and to enhance the electrical conductivity of composites [55].

On the basis of these narratives, in study [56], the produced Ag-Cu nanoparticles were used as conductive filler and epoxy resin as polymer in order to make Ag-Cu epoxy composites. There have been added conductive fillers with different concentrations (1%, 2%, 3%, 4%, 5%, and 10% by percentages by mass) into epoxy resin to investigate the electrical properties of Ag-Cu-based epoxy composites. The XRD pattern of the fcc phase made of Ag-Cu alloy with Miller indices (0 0 2), (1 1 1) and (2 0 0).
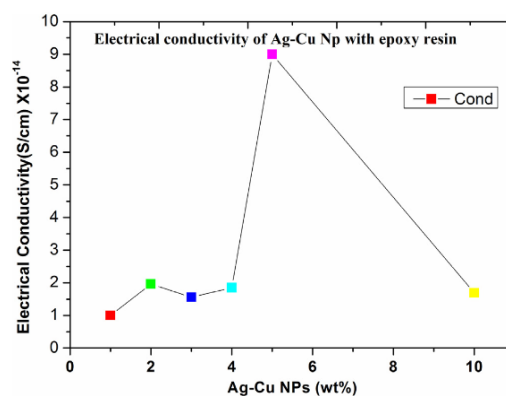
Fig.1.12. Electrical conductivity at different percentages by mass of Ag-Cu NPs with epoxy resin film [173].

There is a wide variety of nano-sized metal oxides (NPs), such as silicon, aluminum, copper and iron oxides, which have been used in order to better the epoxy performance [57]. It has also been recommended the application of silver NPs as a filler for epoxy polymer due to their ecological, antibacterial and anticorrosive properties [58], [59]. At the same time, magnesium oxide (MgO) was used as a modifying agent since it enhanced the thermal conductivity of the epoxy [60], [61]. Copper oxide (CuO) is an environmentally friendly material, as it is non-toxic and antibacterial/antimicrobial when doped with Ag [62].
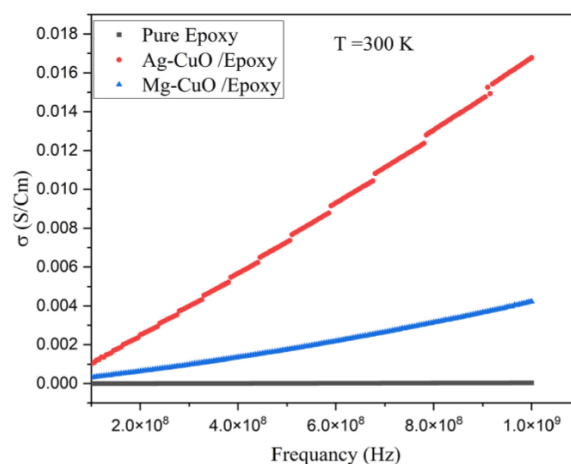
Fig.1.15. The electrical conductivity of pure epoxy, (Ag-CuO)-Epoxid and (Mg-CuO)-Epoxid [189]

Chapter 2

Objectives of the research

Polymer-based composite materials are more and more often used in growing fieds, a reason for which is why getting a polymer composite material is a process that must take into account every possibility, with a view to reaching the proposed goals.

The main purpose of this study was to highlight the effect of modifying a polymer matrix (epoxy resin) with inorganic compounds.

The introduction of inorganic compounds into the polymer matrix obviously leads to the modification of the polymer properties, the changes targeted by this research being the electrical properties and the effects on the mechanical properties of the obtained materials, thus being reguired to study several properties of the newly formed materials.

In order to be able to have a complete answer and analysis, we set, in this study, a number of tests and analyzes on the newly formed materials, as follows:

- establishing the optimum solvation condition for each type of inorganic substance used;
- setting the strategy of uniform distribution of the solution in the epoxy resin;
- determining the way of blending epoxy resin mixtures with solutions of inorganic substances so as to ensure the possible local chemical interaction;
- establishing the manner of casting and the shape of the mold to ensure the need for test specimens required for the characterization of the formed materials;
- formation of witness materials [63], [64];
- the formation of the epoxy material modified with the 1-Methyl 2-Pyrrolidinone solvent;
- formation of epoxy composites modified with inorganic agents;
- carrying out solubility tests;
- determining the degree of solubility of each inorganic agent in 1-methyl 2-pyrrolidinone and, respectively, in N-N dimethylformamide;
- acquiring solutions of inorganic agents;
- determining stoichiometric coefficients of inorganic agents;
- NH_4VO_3, $(NH_4)_2MoO_4$, $MnCl_2$ in 1- methyl 2-pyrrolidinone;
- $BaCl_2$, $CuCl_2$, $YCl_3 \cdot 6H_2O$ in N-N dimethylformamide;
- determining the volumes of solutions to be added to the epoxy resin to achieve the designed inorganic substance concentrations;
- formation of materials with a solution of inorganic agents in N-N dimethylformamide;
- formation of materials modified by applying an electric field;
- formation of materials modified by applying a magnetic field;
- strengthening the materials by applying a thermal treatment;
- extracting the test specimens necessary to carry out the mechanical tests;
- carrying out mechanical tests;
- interpretation of mechanical test results;
- carrying out tests for determining the electrical conductivity of materials under conditions of electromagnetic exposure at different wavelengths of radiation (for materials modified with a solution in 1-methyl 2-pyrrolidinone);
- interpretation of experimental electrical conductivity data according to wavelength;
- conducting tests to determine the electrical conductivity of materials under conditions of electromagnetic exposure at different wavelengths of radiation (for materials modified with N-N dimethylformamide solution);

- interpretation of experimental data, electrical conductivity depending on the wavelength;
- analysis of the effects of applying the electric field;
- analysis of the effects of applying the magnetic field;
- performing tests for determining the electrical conductivity of materials depending on temperature (for materials modified with N-N dimethylformamide solution);
- carrying out DSC tests to determine specific heat (for materials modified with 1-methyl 2-pyrrolidinone solution);
- analysis of specific heat values;
- executing DSC tests in order to determine specific heat (for materials modified with N-N dimethylformamide solution);
- analysis of the results of tests carried out for the specific heat evaluation;
- dissemination of results.

Chapter 3.

Material Formation

For the purpose of performing this study, it was used Epiphen RE 4020 – DE4020 type epoxy resin, made by R&G Gmb Waldenbuch, due to its very low shrinkage coefficient during casting. The main goal of this study was to get a polymeric material with high electrical conductivity, but without adversely affecting the mechanical properties.

3.1. Used Substances

3.1.1. The Epoxy Resin

With a view to producing the polymer materials, we employed the Epiphen RE 4020 epoxy system, together with the DE 40-20 hardener.

The viscosity of RE4020 at a temperature of 25ºC is 2,200mPa·s, and the density, at the same temperature, is 1.15g/cm^3. The DE 4020 hardener, has a viscosity of 50mPa·s at 25ºC and a density of 0.98g/cm^3, at the same temperature. The viscosity of the mixture, made from well-defined volumes of the two components, varies relatively slowly over time, allowing the handling of the pre-polymeric liquid for approximately 45 minutes [65].

3.1.2. N-methyl pyrrolydidone Solvent

The N-methyl-2-pyrrolidinone (NMP) compound is a heterocyclic polar solvent with low volatility, thermal stability, high polarity and aprotic, non-corrosive properties. NMP is an organic solvent miscible with water. It is a hygroscopic, colorless liquid with a slight amine odour and used in many industrial fields, such as: the petrochemical industry, in the microelectronics manufacturing industry, in the plastics industry, but also in the manufacture of various compounds, including cosmetics, pigments, insecticides, herbicides and fungicides [66], [67].

3.1.3. N,N dimethylformamide Solvent

N-N dimethylformamide (DMF) is a neutral solvent as concerns hydrophobic and hydrophilic properties; these properties are almost subject to compensation. Thanks to the almost complete absence of structural effects in the pure state, such as the lack of hydrogen bonds [68], the DMF is a compound of particular interest as a solvent for a wide range of organic and inorganic compounds and can be used in the chemical industry, the pharmaceutical industry, the textile industry, in the field of pesticides and leather [69], [70].

3.1.4. Ammonium Metavanadate

Ammonium metavanadate is a mixed compound and has the chemical formula NH_4VO_3. It is a white solid, but due to the vanadium pentaoxide (V2O5) impurities, its samples are very often found and their color is yellow. NH_4VO_3 is prepared by adding ammonium salts to solutions of vanadate ions that are formed by dissolving vanadium pentoxide in basic aqueous solutions. The compound is obtained through a precipitation stage, which can be slow, in the form of a colorless solid. Ammonium metavanadate is used to prepare the *Mandelin* reagent, a qualitative test for alkaloids. [71], [72].

3.1.5. Ammonium Molibdate

Ammonium molibdate is an inorganic compound and has the chemical formula $(NH_4)_2MoO_4$. Similarly to ammonium metavanadate, it is a white solid that is prepared by

treating molybdenum trioxide (MoO_3) with aqueous ammonia. On heating these solutions, the ammonia is lost, in order to give ammonium heptamolybdate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$) [73], [74].

3.1.6. Manganese Chloride

Manganese chloride is an inorganic salt of manganese with hydrochloric acid and has the chemical formula $MnCl_2$. It is made up of Mn^{2+} and Cl^- ions in a 1:2 ratio, for each Mn^{2+} cation there are two Cl^- anions.

Manganese chloride can be used in the laboratory as a catalyst for the chlorination of organic compounds, but also in industry as a raw material for the production of additives for gasoline; welding material for non-ferrous metals; intermediate in the production of pigments; and linseed oil dryer; for printing and dyeing; in the production of various manganese salts, including methylcyclopentadiphenylmanganese tricarbonyl used as a dye for bricks; and in the production of dry electric cells [75], [76].

3.1.7. Barium Chloride

Barium chloride is an inorganic compound with the chemical formula $BaCl_2$. Like most other salts it has white color, it is toxic and gives a flame the yellow-green color.

Although having low cost, barium chloride is limited to laboratory and industrial applications due to its high toxicity. It is usually used in industry, for the solution purification in caustic chlorine plants and in the production of heat treatment salts [77], [78].

3.1.8. Copper Chloride

Copper chloride is an inorganic compound and is the copper salt of hydrochloric acid with the chemical formula $CuCl_2$. It has a bluish-green crystal appearance, and when tested with a flame, it is obtained a bright blue color. An aqueous solution of copper chloride with a low concentration may be blue-coloured, and when the copper chloride concentration is bigger, the color may be green. This compound is essentially acquired by synthesis and is hard to found it in nature [79], [80].

3.1.9. Yttrium Chloride

Yttrium chloride is an inorganic compound consisting of yttrium salt and chlorine with the chemical formula YCl3. It has a solid structure, is colorless, highly soluble in water and hygroscopic.

The molar mass of yttrium chloride is 303.36g/mol, the solubility in water 2.170g/100ml (20ºC) [81], [82].

3.2. Formation of Materials Containing D-type Elements

Following the discussions held with the PhD coordinator, we decided that, in a first stage, based on other research carried out at the Research and Development Center for Composites with Thermosetting Matrices (CCDCOMT) [193], [195], we should test the possibility of bringing up the electrical conductivity of the epoxy resin by introducing metal ions of type d elements into the polymer network. The hardener (DE 4020) is a blend of aliphatic amines modified in such a manner that it is assumed that it would not chemically interact with complex ammonium salts. For this reason we chose ammonium metavanadate and ammonium molybdate. Furthermore, we assumed that in the solution there could be a reaction between the $NH4^+$ and Cl^- ions that could lead to the occurrence of metavanadate, molybdate and manganese ions in the free state. The presence of oxygen in these latter ions could result in the formation of quaternary compounds of the $V_xMo_yMn_zO_t$ type, a ceramic

complex that could have semiconducting properties based on the fact that the atoms of the mentioned metals have many free energy levels in the d layer.

We have established stoichiometric amounts of the inorganic substances so as to obtain a quaternary compound of the $VMnMo_2O_x$ type.

3.2.1. Type A Materials Formation

For this stage of study we formed five materials, and the notation used to facilitate their identification and research is **A**, type A materials, thus:
- reference samples - A1;
- samples formed by direct casting – A2;
- samples formed by casting at 48 hours – A3;
- samples formed by casting at 96 hours – A4;
- samples formed by casting at 144 hours – A5.

In order to make A2, A3, A4 and A5 samples, I mixed 12g of the three substances (ammonium metavanadate, ammonium molybdate and manganese chloride) with 120ml of solvent (N-methyl-2-pyrrolidinone) and 12g of PMMA, the concentrations calculating being carried out according to the research [193]. I left the formed blend in the stirrer at a temperature of 60ºC with 500rot/min for 7 days, then I extracted 30ml of substance which I mixed with 100ml of epoxy resin and 33.34ml of hardener which I poured into molds, thus resulting sample A2. The left amount of substance was mixed for 48, 96 and 144 hours respectively on the stirrer, following the same amounts as in sample A2 and getting samples A3, A4 and A5, respectively. After obtaining all the samples, they were thermally treated in order to finish the epoxy matrix polymerization and to better the mechanical properties, and to be able to identify them easier, we added the "t" index to the notation (A1t, A2t, A3t, A4t and A5t), but some were left untreated thermally so as to be able to do a comparative analysis.

Fig.3.1. Samples acquired (from top to bottom) A1t, A2t, A3t, A4t, A5t on the left, and on the right the first and seventh days of the mixture in the stirrer

3.3. Formation of Materials with Metal Chlorides – type B Materials

The YBCO compound is a ceramic material recognized for electrical superconductivity at high temperature values. It is generally obtained by hot processing after which it is ground, purified and sintered with a view to producing testable materials. The theory of superconductivity of this ceramic compound is known as the Cooper electron pair theory. My colleague, Eng. Mihaela-Claudia Gorovei, Ph.D., in the research carried out during her doctoral studies (Mihaela-Claudia Gorovei, *op. cit.*), experimented getting the compound from inorganic precursors (the nitrates of the three metals) solvated in NMP. In my study, the YBCO formation is intended from chloride precursors (of the three metals)

solvated in DMF (N,N dimethylformamide). The idea is the same – to ensure the development of local chemical reactions, in the volume of the epoxy resin, which would result in the formation of nanometer-sized YBCO structures.

3.3.1. Getting Samples

In the second stage of the study, we used two types of molds, one of cylindrical type made of polypropylene with a 220mm length and 8mm diameter (already described when presenting the formation of type A materials), and the second, a flat mold made up of two sheets of glass separated through a rubber gasket (for sealing) with a thickness of 5mm.

With the purpose of producing the substances, I mixed 37.4g of the three chosen substances (12.4g of $BaCl_2$, 16g of $CuCl_2$ and 9g of $YCl_3 \cdot 6H_2O$) together with 623ml of N-N dimethylformamide solvent and left in the stirrer at 600rpm, 50ºC for seventy-two hours. After keeping it in the stirrer, 330ml of solvent volatilized, and the remaining substance was moved into three mixing recipients, each with 100ml of substance and 1325ml of epoxy resin (first I poured the resin and on top I added the solution of the precursors in DMF), which were then put on three stirrers at 200rpm with 30ºC, but due to the fact that the blend was not achieved, I enhanced the number of rotations and the temperature up to 1000rpm with 90ºC. The notation employed in order to simplify identification and research at this stage is **B**, type B materials.

After homogenizing the blend, I extracted for the first pouring from the first mixing recipient 375ml of mixture and added 116.6ml of hardener and mixed for twelve minutes at 450-650rpm, after which I poured the samples into cylindrical molds (required for carrying out the electrical conductivity tests) and in glass plate molds (required in order to carry out mechanical tests), one of them being simple and the other with magnetic foil affixed on the back, the notations used in this case being B11 and B11m respectively.

In the second mixing recipient, I followed the steps above, but before blending, I executed an electrolysis of the mixture for 40 minutes, with copper electrodes being at 4cm distance. The parameters at which we performed the electrolysis were: voltage U=23.8V, frequency f=25kHz and intensity I=1.4µA. Notations used B12 and B12m.

For the third mixing recipient, I followed the steps from the second mixing recipient, the only difference being the electrodes used, this time being made of graphite. The notations used are B13 and B13m.

The second casting took place at a distance of one month from the first one, I followed the same data as the first casting, the only difference being the duration of the electrolysis which increased to 60 minutes, the distances between the electrodes were set at 1cm and from the parameters I changed the voltage value at which the electrolysis U=28V was performed. The notations used at this stage were: B21, B21m, B22, B22m, B23, B23m.

The third casting took place one month later than the second, the same data as the second casting were observed, the only difference being the electrolysis duration, which went up to 90 minutes and, at parameters I changed the value of the voltage with which electrolysis U=25V was carried out. The notations used at this stage were: B31, B31m, B32, B32m, B33, B33m.

Fig.3.2. Mixture for sample formation with metal chlorides B, electrolysis with graphite electrodes, glass sheet mold and sample (left to right)

3.4. Formation of Materials with Metal Chlorides – type C Materials

Analyzing the results acquired in the case of type B materials, especially the casting behavior of the pre-polymer mixtures, but also the precursors solubility in DMF, for type C materials we enlarged the amounts of precursors so as to bring up the probability of developing local chemical reactions.

3.4.1. Getting Samples

For the first casting, I proceeded as follows:
- I extracted 25ml of substance from the mixing recipient and blended with 357ml of epoxy resin for 5 minutes, then added 119ml of hardener and mixed for 10 minutes, following which I poured into two flat molds, one plain and one with magnetic foil and two cylindrical molds; the materials formed at this stage are C11 and C11m;
- I took a double amount of solution from the mixing recipient - 50ml of substance and blended with 339ml of epoxy resin for 5 minutes, then added 113ml of hardener and mixed for 10 minutes, after which I made the casting under the same conditions as described above; formed materials are noted C12 and C12m;
- for the samples noted C13 and C13m I used 75ml of solution, 321ml of epoxy resin and 107ml of hardener respecting the same conditions as in the previous cases and forming the same types of materials for the samples.

After another seven days in which the mixture was left on the shaker at a temperature of 50ºC and 1500rpm, I did electrolysis again for 90 minutes, with graphite electrodes (the distance between the electrodes was 1cm), at a current with the intensity I=400mA, following which, complying with all the conditions described for the C1x materials, we formed the C31 and C31m; C32 and C32m; C33 and C33m materials. After casting, for the amount of solution left in the recipient, I carried out electrolysis for 60 minutes, with graphite electrodes (distance between electrodes of 1cm), and I=400mA.

After another seven days in which the mixture was left on the stirrer at a temperature of 50ºC and 1500rpm, I did electrolysis again for two hours, with graphite electrodes (distance between electrodes of 1cm), at a current of about I =400mA, after which, respecting all conditions described in the case of C1x materials, we formed the C41 and C41m, respectively C42 and C42m materials. The evaporation loss of the solvent did not allow also obtaining the last pair of materials C43 and C43m because the solution volume was insufficient. Once formed, the materials were left in the molds for 14 days (natural polymerization) after which they were reinforced by applying a heat treatment consisting of holding for eight hours at a temperature of 60ºC, four hours at 80ºC, ten hours at 90ºC and twenty-four for hours at 111ºC.

Fig.3.3. Mixture for sample formation with metal chlorides C in day 1, day 31, day 51
(from the left to the right)

The application of the alternating electric field (electrolysis) targeted to provide additional energy to the metal ions (but the anions were also affected) in order to destabilize them with the aim of favoring chemical reactions (assuming that in their evolution towards equilibrium they could perform more stable chemical configurations).
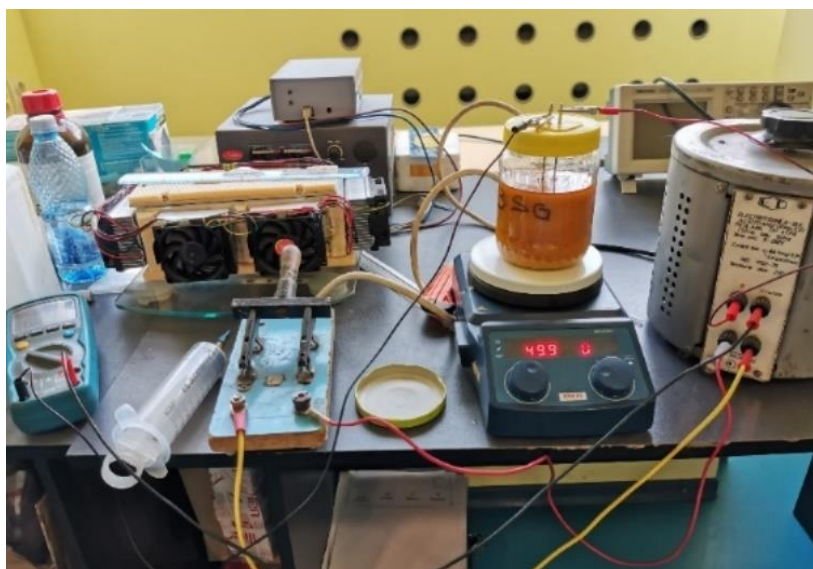
Fig.3.4. Sinusoidal electric field action

During the application of the alternating electric field, I also noticed gas bubbles in the neighbourhood of the electrodes, a sign that the electrolysis worked. If during this process atoms (of copper or carbon) were detached from the electrodes surface, they will be found in the final mixture, contributing to the enhancement of electrical conductivity.

We tried to acquire growing concentrations of inorganic agents in the epoxy matrix and, to a large extent, this is true, but we also have to take into account the fact that keeping it in a state of permanent agitation and at a fairly high temperature value favored the evaporation of the solvent (DMF) and then there may be small differences in concentration.

Chapter 4.

Characterization of Type A Materials

4.1. Electric Properties Analysis of type A Materials

After casting, there have been obtained more samples for each type of material, some of which were thermally treated and I noted them A1t, A2t, A3t, A4t and A5t, and the rest remained untreated, with the notation A1, A2, A3, A4 and A5.

During polymerization, the samples were maintained in a vertical position so that it was as natural as possible to take into account the electrical conductivity of the materials at the ends and in the middle of each tested sample (thus possibly highlighting the precipitation of the chemical agents used).

For each of the samples, the measurements intended to determine the electrical resistance in three regions – the lower part, the middle and the upper part (according to the position in which the materials were kept during polymerization). For each of these regions three measurements were executed, the final resistance being the average of the three recorded resistances. These measurements, as I specified, were performed in the dark and at each wavelength of electromagnetic radiation that we had available (from 405nm to 1070nm).

For each sample (as mentioned) there have been fixed three target areas – these three target areas are marked with i – lower; m – middle; s – superior, in what follows.
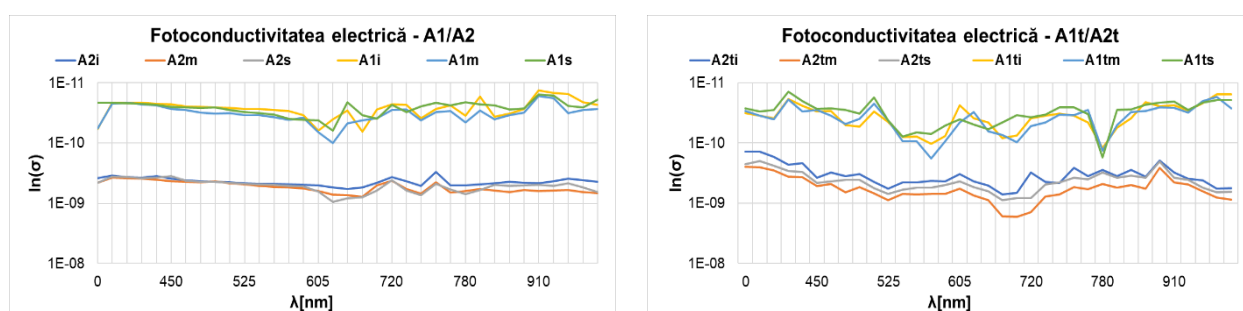
Fig.4.1. Photoconductivity - a comparison between A1 and A2

In Fig.4.1. are given the curves of the logarithm of electrical conductivity depending on the wavelength of the radiation used (0nm means dark). The effect of the presence of inorganic agents in the epoxy matrix is immediately perceivable and consists in increasing the electrical conductivity value by an order of magnitude (approximately) in the case of A2 materials. Following the application of the reinforcement treatment, the difference is no longer very large, which means that the reinforcement treatment leads to the formation of chemical bonds that block the conduction mechanisms.
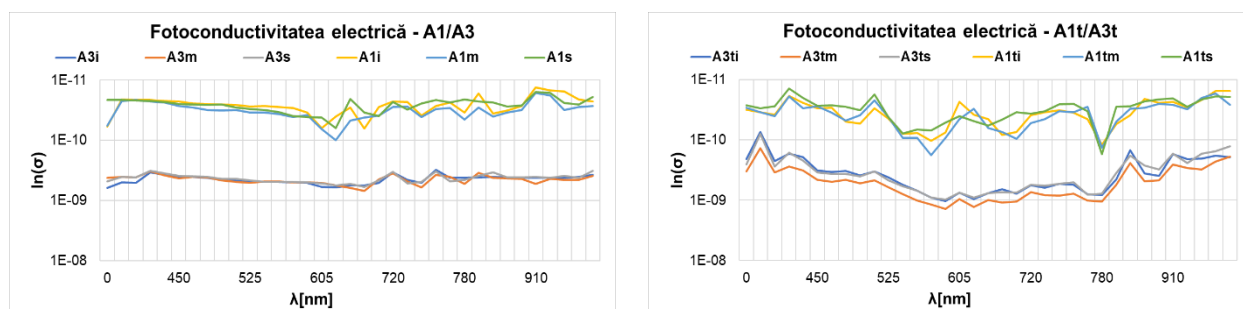
Fig.4.2. Photoconductivity - a comparison between A1 and A3

In Fig. 4.2. it is carried out, in a graphics form, the comparative analysis of the photoconductivity of the A3 material with the reference material (epoxy resin) A1. As I specified in the chapter dedicated to the formation of materials, between the time of forming material A2 and the time of forming material A3, the solution in NMP of the three inorganic compounds was stirred continuously (500rpm, 60°C) for 48 hours.
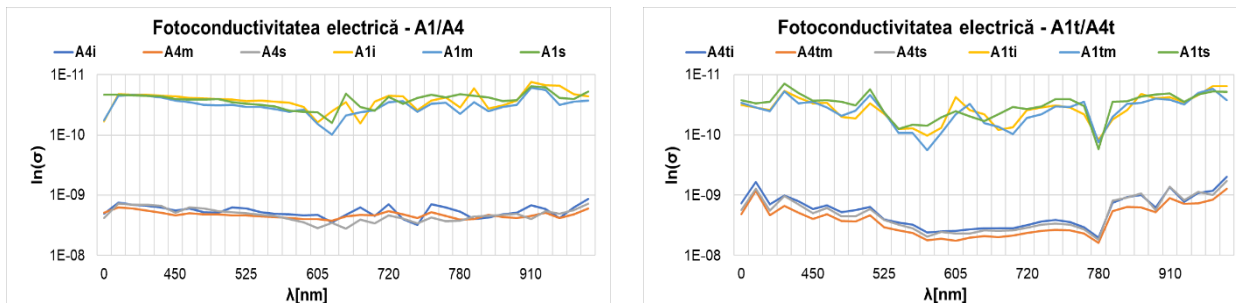
Fig.4.3. Photoconductivity - a comparison between A1 and A4

As concerns the A4 material – with a little higher concentration of inorganic agents than A3 (due to maintaining the aforementioned stirring conditions for another 48 hours), the results are shown in Fig.4.3. Similarly to the previous cases, the photoconductivity of the unconsolidated material is almost constant (the small, visible variations can be ascribed to some measurement errors – for example, the fact that the materials being soft allow the deeper penetration of measuring tongs teeth and, in this way, it is possible an error in evaluating the cross-sectional area of the sample).

In Fig. 4.4. is given the comparative analysis of A5 and A5t materials with the references (A1 and A1t) and what is surprising is that we witness the lowest value of electrical photoconductivity despite having the highest concentration of modifying agents. The situation is valid for both reinforced and unreinforced material. Moreover, the reinforced material has the same type of response (same curve profile) as the reinforced reference. Under these conditions, we should take into account the fact that a very important effect on the photoconductivity could have the solvent itself – NMP.
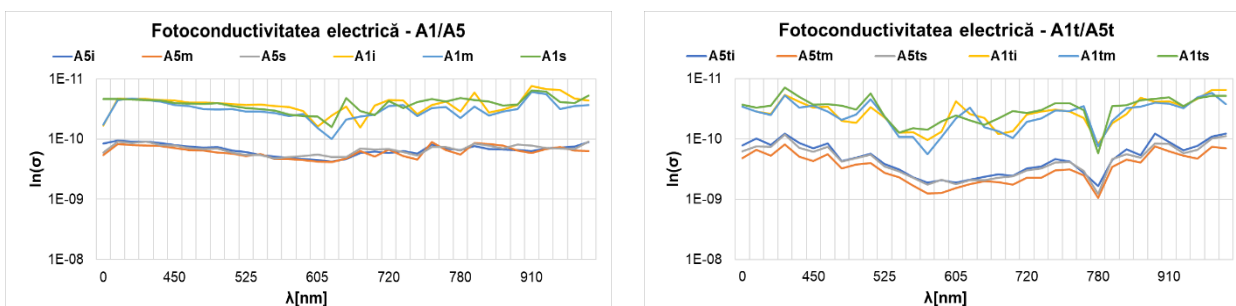
Fig.4.4. Photoconductivity - a comparison between A1 and A5

A consequence of using NMP, which in the chemical industry is used as a plasticizer, is that the samples acquired are very soft. Unfortunately, the amount of NMP used cannot be diminished because it is determined by the separate solvation of the three inorganic agents, the final blend being made after the complete solvation of all, by mixing the solutions.

4.1.1 Electric Properties Analysis of Type A Materials – Conclusions
- for all the modified materials, there are found increases in the electrical photoconductivity values are found, but these cannot be correlated with the duration of maintaining the mixed solution in NMP of the three inorganic agents, under specified stirring conditions, as long as

the largest increase is recorded in the A4 materials and goes down close to the reference value of A5 materials;
- for all non-thermally consolidated samples, the photoconductivity variations depending on the wavelength are very small while, for the thermally consolidated samples, these variations are significant, I am referring here to the distances among the curves corresponding to the three measurement points;
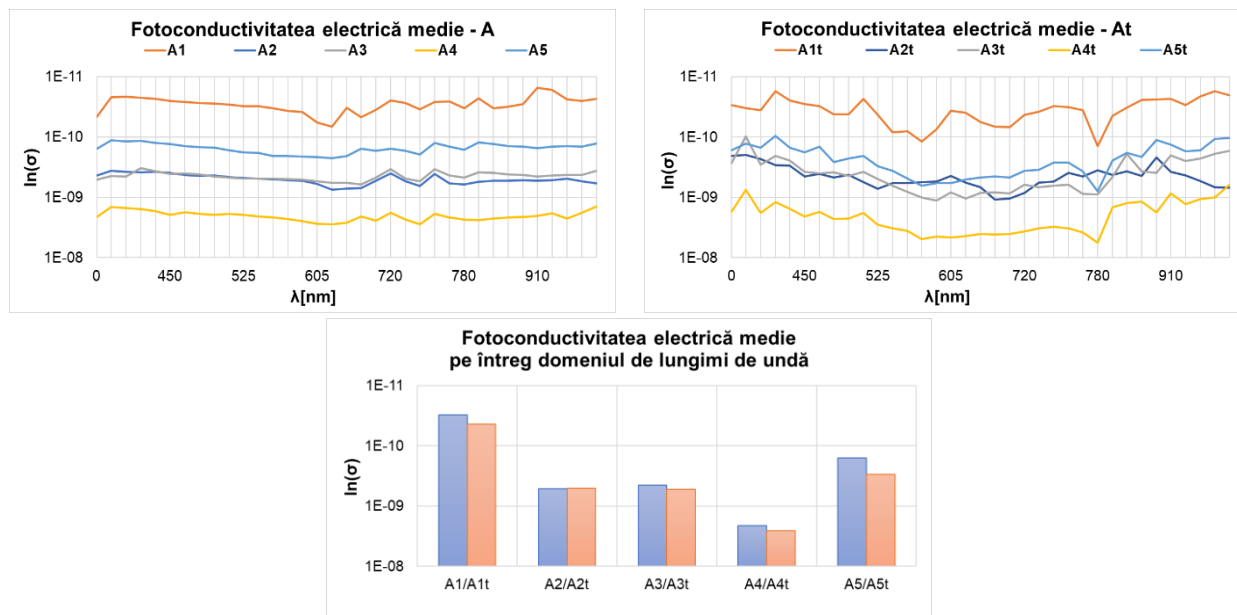
Fig.4.5. Averaged electric photoconductivity

- there can be observed competing mechanisms of electrical conductivity - in some cases - observable either by increasing the value of photoconductivity or by decreasing it, in areas where the behavior of the reference is known;
- certain variations (from one material to another) could be explained not so much by the concentration of inorganic agents, but by the reduction of the NMP presence in the epoxy matrix;
- it is worth analyzing the fact that the A4 material has the highest values of electrical photoconductivity - a hypothesis in this sense (but which must be verified) is that it is possible to establish a stoichiometric balance (absolutely at random) between the inorganic agents, the solvent and the two components of the epoxy system;
- in this case it is possible (again, a hypothesis to be investigated) to create mixed ceramic structures with special properties, by maintaining the specified stirring conditions, during the formation of the A5 material they are either destroyed or affected by the reduction of the amount of NMP.

4.2. Thermal Properties Analysis of Type A Materials

The analysis of the thermal properties, and I am referring here the determination of the specific heat value of the materials, can provide certain information related not necessarily to their heating behavior, but to the manner in which they structurally respond to heating beyond the limits of the reinforcement treatment.

The analysis method used for the thermal analysis of these samples was tested by my colleague Miss Mihaela-Claudia Gorovei (Research on the nanostructuring of polymers by electrochemical methods and the effect of nanostructuring on the mechanical properties of polymers, PhD thesis, Galați, 2021) and is the result of the tests succession of various

methods developed at CCDCOMT. The analysis program consists of several segments (eight): keeping the sample at 25°C for three minutes (S1); cooling the sample from 25°C to -45°C at a rate of 10°C/min (S2); maintaining the sample for three minutes at -45°C (S3); heating the sample from -45°C to 185°C at a rate of 10°C/min (S4); maintaining the sample for three minutes at 185°C (S5); cooling the sample from 185°C to -45°C at a rate of 10°C/min (S6); maintaining the sample for three minutes at -45°C (S7); returning to the starting temperature, 25°C, at a rate of 10°C/min.

Analyzing the curves shown in fig. 4.6., segment - S4 - heating (first line), it can be seen a certain difference between the behaviors of the materials. I recall that all materials were modified by the same amount of inorganic agent solution in NMP. A3 material shows (on the heating curves) the most different behavior in relation to the other materials analyzed – material A1 is epoxy resin. All other materials have a behavior similar to reference (A1), on the heating segments. On the cooling segments, although A3 has a different response, it is much closer to the other materials, including A1. How could such behavior be explained?

As it can be seen from Fig.4.7., the only material for which the evaluations led to a higher value of the specific heat on the cooling segment than on the heating one, is the A3 material, in all other cases the situation is reversed in each domain of temperature values. Material A3 has a slightly different behavior also on all cooling segments, as can be seen in fig.4.6., the second line. All other materials have specific heat evolutions close to those of epoxy resin. There is nothing surprising in this, since the mass fraction of the modifying agent (the solution of inorganic agents in NMP) is very small, and as from the law of mixtures, the specific heat of the modified material depends on the mass fractions of the matrix and the modifying agent, it is expected a small contribution of the specific heat of the modifier compared to the epoxy resin.
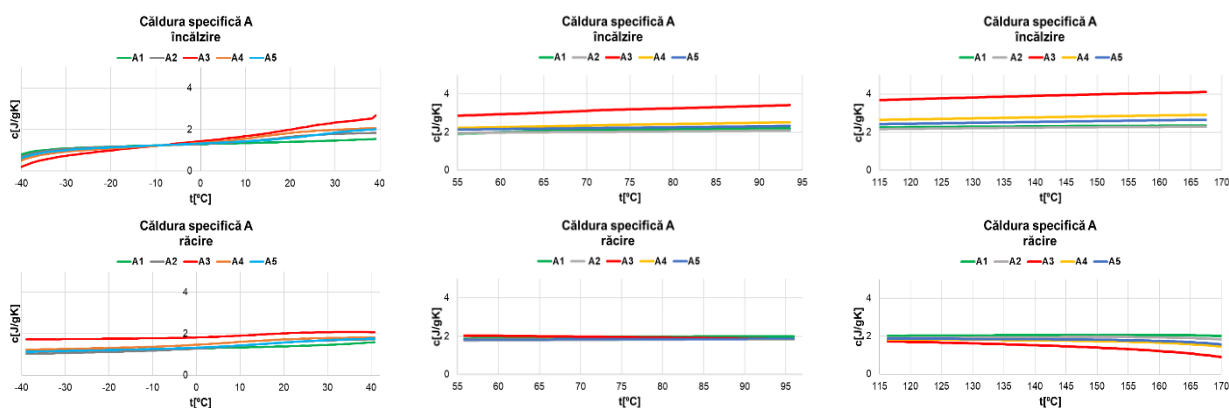
Fig.4.6. Specific heat for samples A, over the three chosen ranges

As I have already specified, in Fig. 4.7. there are given the average values of the specific heats of the materials over the ranges of temperature values, obviously for both heating and cooling segments. Again, the A3 material is the one that stands out due to the noticeably larger values of the parameter, compared to the other materials.
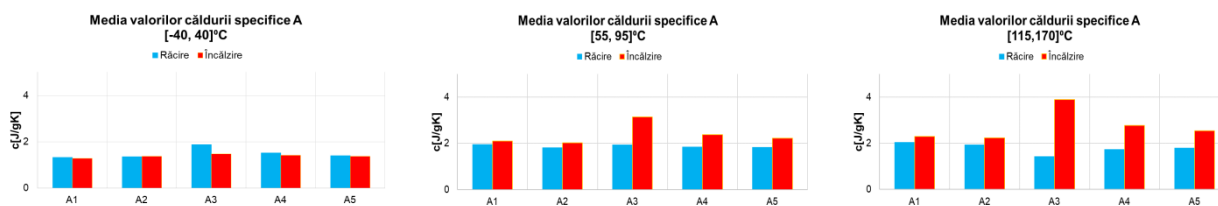
Fig.4.7. Average of specific heat values for samples A over the three chosen intervals

Carrying out the tests also involved, as I have shown before, the determination of mass losses during the tests. Given the fact that three samples were tested for each material, the mass loss values are the averages of the individual losses and they are presented in Table 1.

Table 1. Loss of substance of A-type materials during thermal analysis tests (DSC)

Material	A1	A2	A3	A4	A5
Δm [mg]	0.667	3.167	2.867	3.467	2.833

Epoxy resin is a stable material, and in the case of A1, the average mass loss has the lowest value. For the A2 material, formed instantely after making the solution of inorganic agents in NMP, the average mass loss is significantly higher (of around 4.75 times higher) and can easily be ascribed to the NMP vaporization . The high mass loss of the A4 material, which theoretically has less NMP, is likely to raise certain question marks, especially since A4 has the highest electrical conductivity of all the materials analyzed. The only hypothesis, but it needs to be verified, is related to a possible metastable state (obtained purely by chance). In this manner, the material is apparently stable, but once heated it goes into a disequilibrium state and evolves towards a stable state losing certain components (I assumed it was NMP, but it is possible, if the metastable state really exists, to also be about the hardening agent of the epoxy resin, for example).

Given the mass losses presented in Fig.4.7. we also made a correction of the average value of the specific heat on the reference ranges of the temperature values and the corrected values are shown in Fig.4.8.
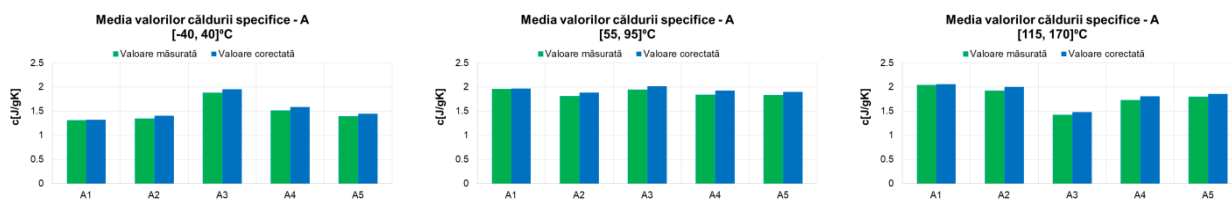
Fig.4.8. Average of specific heat values for samples A over the three chosen intervals

The A2 material has values of the specific heat close to the values of the specific heat of the epoxy resin (on all three ranges of temperature values), as A2 is formed immediately after making the solution of inorganic agents, we could get a picture of what is the effect of the presence of the solution in the epoxy matrix – practically insignificant.

In Fig. 4.9. it is shpwn the evolution of the specific heat as a function of temperature for the five analyzed materials.
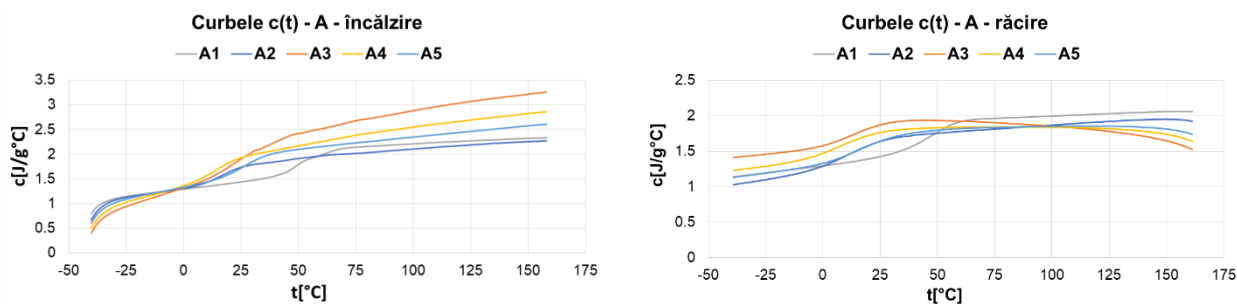
Fig.4.9. Dependence of specific heat on temperature

The specific heat is a physical quantity that strongly depends on the temperature (water, for example) and the jumps in its values give information about possible phase

transitions. What can be observed, from the graphs presented, is the glass transition of the resin – the shoulder of the curve around the temperature value of 70°C – for all modified materials, this shoulder is shifted towards the value of 25°C.

4.2.1. Thermal Properties Analysis of Type A Materials – Conclusions
- there are seen small variations of the specific heat values - certainly due to the presence of the solution of inorganic agents in the epoxy matrix;
- a migration of the glass transition temperature of the epoxy resin from 70°C to 25°C is observed in the case of the modified epoxy resin.

4.3.1. Thermomechanical Analysis of Type A Materials
The sample, enclosed in an oven, is heated in a controlled manner from 30°C to 170°C, at a rate of 10°C and, then, naturally cooled from 170°C to 30°C. Such a measurement is long-lasting due to the fact that the cooling is natural – the heating takes 14 minutes, while the cooling can take 30 minutes (depending on the conditions in the laboratory).

The results achieved for the values of this parameter, shown in Fig.4.10., are obtained as the arithmetic mean of three determinations (three samples) for each material.
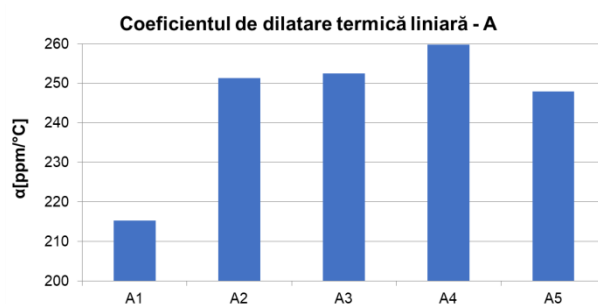
Fig.4.10. The coefficient of linear thermal expansion - A materials

The unit of measurement used is ppm/°C which, in the International System of Quantities and Units, translates to µm/m°C. It is obvious that the values displayed in Fig.4.10. provide a very good thermal dimensional stability of the epoxy resin. For materials modified with a solution of inorganic agents in NMP, the values of the coefficient of linear thermal expansion are larger. What is most interesting is the fact that the A4 material shows the highest value of the coefficient of linear thermal expansion, and apparently this is related to the highest value of electrical conductivity of this material.

4.3.2. Thermomechanical Analysis of Type A Materials – Conclusions
- all materials modified with a solution in NMP of inorganic agents have values of the of linear thermal expansion coefficient higher than the value of the epoxy resin – normal if we take into account that NMP is used as a plasticizer in the polymer industry;
- A2 and A3materials have close values of the coefficient of linear thermal expansion; the 48 hours of difference between the formations of the two materials is not enough to produce essential changes in the structure of the polymer (chemical bonds);
- the lowest value of the linear thermal expansion coefficient of for the modified materials, corresponds to A5 material – the lowest value of the NMP concentration in the epoxy resin (due to the solvent evaporation).

4.4.1. Tensile Tests of Type A Materials

The results of the stretching tests are shown in Fig. 4.11. and I chose to present both the stress/deformation curves for each tested specimen (five for each material), as well as details of these curves in the area of small deformations (elastic response). As expected, the presence of NMP in the epoxy matrix caused a material softening effect and practically all four modified materials have almost identical mechanical responses (as profile).
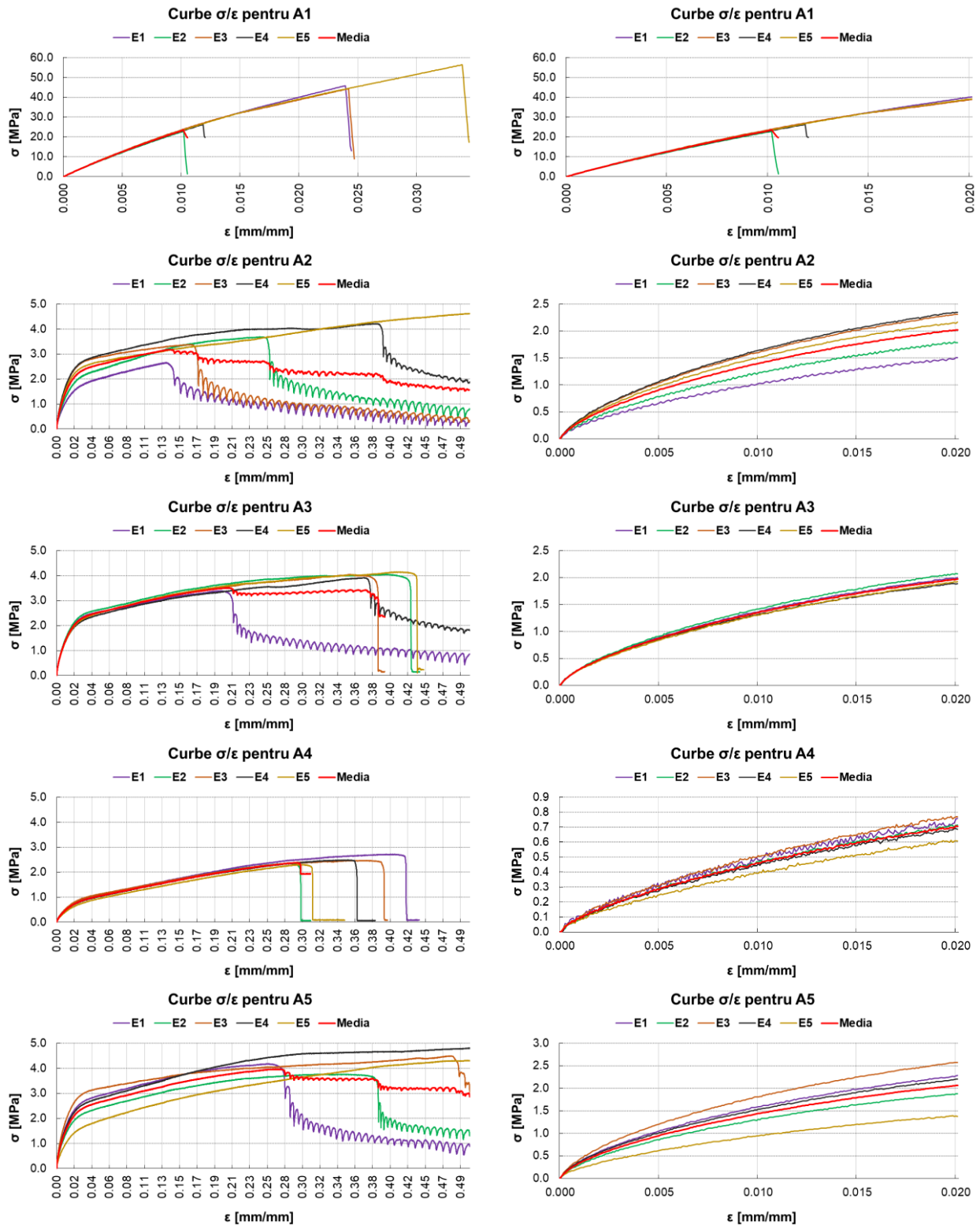
Fig.4.11. σ/ε curves – A-type materials. On the right side a detail of curves on the domain of small deformations

What is important to note is that the epoxy resin (A1) has a linear (tensile) response to stretch, up to breaking. It can also be observed that not all the samples break at the same relative deformation (or at the same tension), this aspect being related to the inhomogeneities of the materials formation – the occurrence of defects such as gaseous intrusions, or the fact that, during the polymerization, given the fact that chemical reactions are accompanied by the release of heat, a deformation of the polypropylene tube may occur (due to the increase in temperature) with consequences on the shape of the sample (deviations from cylindricity).

The dispersion of the individual curves could be explained, in the case of A2, by the fact that the modifying agent (solution of inorganic agents in NMP) is not yet stable and its constituents interact with the substances in the epoxy resin formulation, leading to inhomogeneous samples. As the modifying mixture matures (A3 and A4), the dispersion of the curves is smaller, so that, in the case of A5, it becomes significant again (I specified when analyzing the results of previous tests that this could be an effect of a smaller amount of NMP).
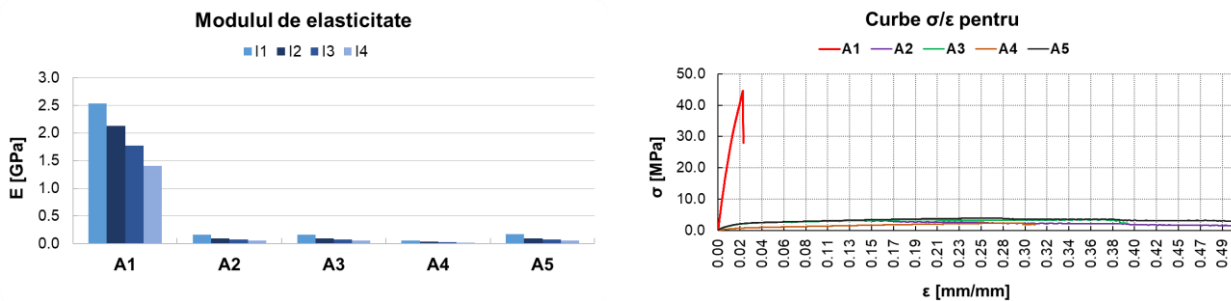
Fig.4.12. Tensile modulus of elasticity and average tensile behavior - A

The weakest response is that of the A4 material, that is precisely the material that has the largest value of electrical conductivity and the highest value of the coefficient of linear thermal expansion. Assuming solvent vaporization (while maintaining the solution of inorganic agents in NMP under stirring conditions), the amount of NMP in A4 should be between that of A3 and that of A5. In this sense, the average tensile behavior of A4 should be between the average behavior of A3 and that of A5, which is obviously not true. In order to elucidate this situation, it would be required a separate study of mixtures of A3, A4, A5 type with the emphasis on A4, changing the time intervals between the sample formations.

In fig. 4.12. the values of the tensile modulus of elasticity of the materials are shown - calculated on four ranges of variation of the specific deformation (it is about the average behaviors - presented in the graphic representation on the right): (0, 0.005), (0.005, 0.01), (0.01, 0.015) și (0.015, 0.02) noted, in this order, I1, I2, I3 și I4.

4.4.2. Tensile Tests of Type A Materials – Conclusions

- all modified materials have a mechanical behavior in tension completely different from that of epoxy resin;
- as the tension grows, in the case of modified materials, some portions of the material caught in the threading dies are engaged and, when they escape from the grip, there occur significant jumps in the specific deformation at very small variations in the tension and the wavy appearance of some curves appears;
- this aspect does not appear, obviously, in all curves but, probably, only in those that were not very well tightened in the tanks (tightening is manual and it is difficult to control its level);
- the values of the elasticity modulus of the modified materials are much lower than the value

of the elasticity modulus of the epoxy resin;

- A4 material, the one with the highest value of electrical conductivity, has the lowest value of the modulus of elasticity when stretching;

- contrary to expectations, the analysis of the elasticity modulus variation on specific deformation ranges, shows that also in the case of modified materials, the value of the parameter drops.

4.4.3. The Bending Tests of Type A Materials

We now know that A-type materials (except A1) are soft materials. It is only to be expected that the responses to inflection should be much lower than the epoxy resin response. As I reminded, the tests were executed on cylindrical samples with a length (generator) of 100mm placed in a balanced manner, on cylindrical holders with a diameter of 8mm, spaced 70mm apart with the punch acting in the middle of the sample and having a circular profile with 8mm diameter.
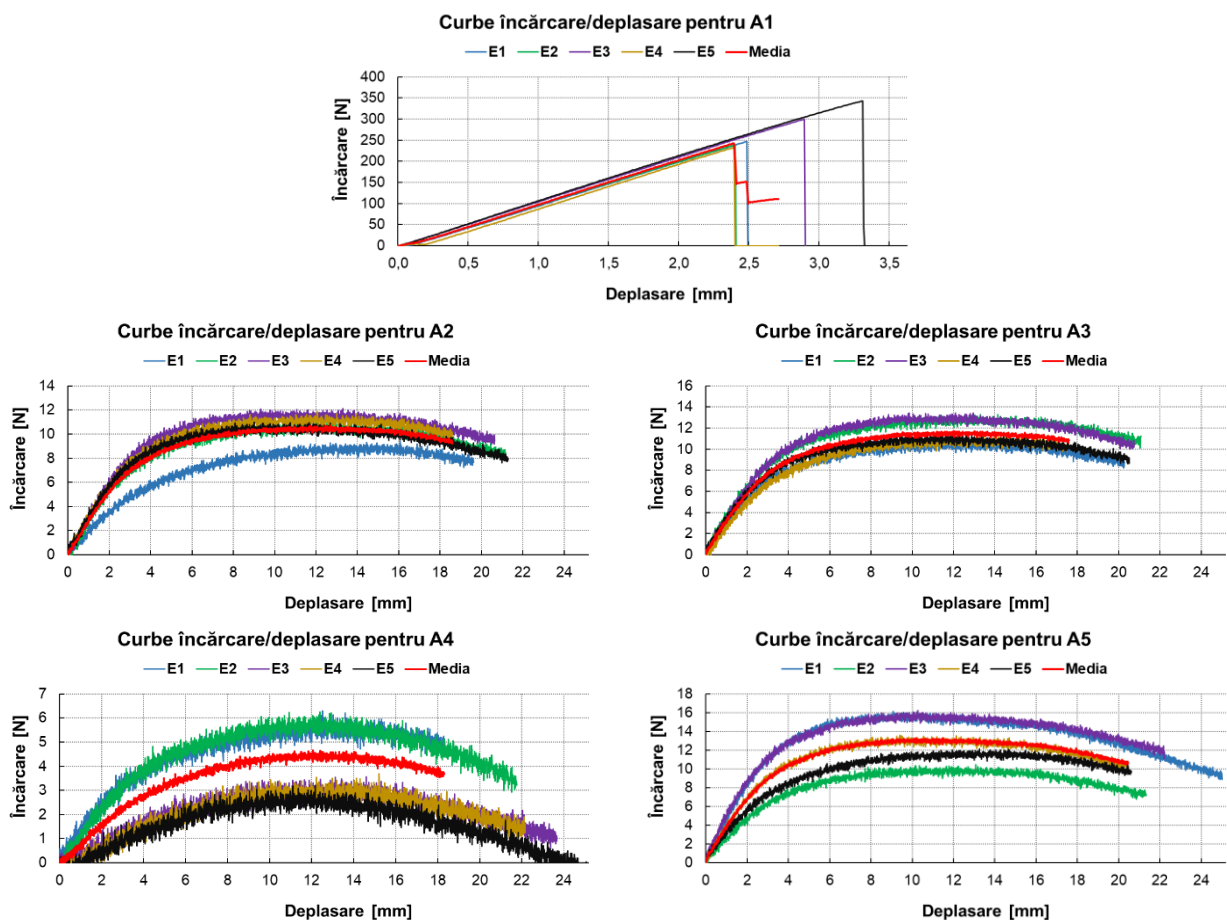
Fig.4.13. Load/displacement curves, three point bending tests A-type materials

These specifications are necessary since, the materials being soft, as the load enhances, the samples reset on the holders. In this manner, as can be noticed in Fig.4.13. the appearance of the curves (except for the curves corresponding to the epoxy resin – A1) is, again, shakily.

It can easily be noticed that A4 is the softest material (deformation of the samples occurs at very low loads). An elastic response of the modified materials (a linear passage of the load/displacement curve) can be observed, even though it is not very long – analyzing the length of this region on the mean curve is simpler, as can be seen in the plots above. I

should also mention that for A2-A5 materials, the samples did not break and the tests were generally stopped when the punch displacement exceeded 22mm.

I previously stated that this constant - k - is proportional to the modulus of elasticity of the material, the proportionality coefficient being dependent on the geometric dimensions of the sample. To conclude, the evaluation of the constant k, from the plots, is equivalent to the determination of the modulus of elasticity.

Table 2. End points coordinates and the values of k constant

A1		A2		A3		A4		A5	
(x*, F*)	k[kN/m]	(x, F)	k[kN/m]	(x, F)	k[kN/m]	(x, F)	k[kN/m]	(x, F)	k[kN/m]
(2.8, 248)	88.57	(2, 5)	2.5	(2, 6)	3.0	(2, 1.5)	0.75	(2, 6.5)	3.25

* x[mm]; F[N]

It is quite obvious that the elastic constant values of the modified materials are much lower than the elastic constant value of the epoxy resin.

4.4.4. The Bending Tests of Type A Materials – Conclusions
- all materials tested in three-point bending show much lower values of the elasticity modulus compared to the value of the modulus of elasticity of the epoxy resin;
- A4 material is, similarly to the case of the tensile tests, the softest material and, except for it, it can be noticed a slight growth in the value of the elasticity modulus with the increase in the duration of keeping the stirring of the polymerizable mixture (i.e., the diminishing of the amount of NMP by vaporization);
- the invariability of laboratory conditions cannot be guaranteed so that it is possible that the A4 material is different from the others, nevertheless, the fact that the A5 material observes the rule and this contradicts the assumprion of an accident caused by the laboratory conditions.

4.5. Characterization of Type A Materials – Conclusions
- materials modified with the inorganic agents solution (ammonium metavanadate, ammonium molybdate and manganese chloride in NMP) have electrical photoconductivities a little higher than the photoconductivity of epoxy resin;
- the evaluation of the photoconductivity in three different points of the tested sample (*s, m, i*) did not reveal effects due to the precipitation of inorganic agents;
- in the case of consolidated materials, the electrical photoconductivity is higher than in the case of non-consolidated homologous materials;
- the largest increase in photoconductivity corresponds to material A4, formed after 96 hours from the creation of the polymerizable blend;
- as concerns the specific heat of the analyzed materials, it can be said generally that there are not very large differences compared to the specific heat of epoxy resin, nor are the variation curves of this parameter with temperature very different;
- the mass losses recorded during the DSC analysis, calculated as the average of the mass loss values of the three samples analyzed from each material, are proportional to the NMP content, with the exception of the A4 material and, obviously, with the exception of the epoxy resin;
- the mass losses consist, besides the vaporization of volatile substances (including atmospheric water) from the surfaces of the samples also in the NMP vaporization, in the case of epoxy resin samples modified with the solution of inorganic agents in NMP;
- the material with the most different thermal behavior, compared to the epoxy resin, is the A3 material;
- the material with the highest value of the coefficient of linear thermal expansion is A4.

Chapter 5.

Characterization of Type B Materials

As specified, the A-type materials represented a way of testing an assumption - that of the possible growth of the electrical conductivity of the epoxy resin due to the presence of some d-type elements in the epoxy matrix. At the same time, the formation and characterization of type A materials meant, for me, an absolutely necessary training for the development of the research topic, both from a practical and a theoretical point of view. In addition, the tests conducted for the characterization of type A materials gave me the opportunity to accomodate to the equipment used and the way of processing and interpreting the experimental data.

For the B-type materials, following discussions with the PhD coordinator and members of the guidance committee, I resumed a researched topic, proposed by Mihaela-Claudia Gorovei (*op. cit.*), regarding the possibility of getting certain nanostructures through the development of local chemical reactions in the epoxy resin volume. For this purpose, Mihaela Gorovei used the solutions in NMP, stabilized with PVP, of yttrium, copper and barium nitrates.

For this research, by testing the metal chlorides solubility, I found that N,N-dimethylformamide is an effective solvent and a complex solution could be used in order to modify an epoxy resin. In Chapter 3, there were presented the quantities of substances used and it was described the working method used to get the materials.

For samples B1x – the polymerizable mixture formation was performed immediately after the homogenization of the blend of resin and solution of inorganic agents in DMF by adding the required amounts of hardener of the epoxy system. The exact volumes have already been presented in Chapter Three. Thus, B1 represents the materials formed in this manner. The x variable (with the values 1, 2 or 3) is an indicator of the special conditions applied before making the polymerizable mixture – 1 without special conditions, 2 – the application of a sinusoidal electric field, in the volume of the blend of resin and solution of inorganic precursors in DMF, by means of two copper electrodes, 3 – application of a sinusoidal electric field, in the volume of the mixture of resin and solution of inorganic precursors in DMF, through two carbon electrodes. For the B12 and B13 materials the sinusoidal alternating field was generated by a source with the voltage and frequency mentioned in Chapter 3, and the current through the mixture had the intensity also specified in Chapter 3.

After applying the sinusoidal electric field, in each case, it was added the required amount of epoxy system hardener to the mixture and the procedure described in the formation of material B1.1 was followed.

The B.2.x and B.3.x materials were formed after 31 and 61 days, respectively, of keeping the mixtures of resin and solution of inorganic agents in DMF (under the conditions described in Chapter 3), but following the same steps as in the case of B1x materials.

5.1. Electric Properties Analysis of Type B Materials

In the case of these materials, due to the fact that the compound YBCO is a superconductor, there were also executed analyzes of the temperature dependence of the electrical conductivity of the analyzed materials. The measurements were made in the dark – the samples were closed in an enclosure, with the electrodes positioned for measurement – and at temperatures corresponding to domestic values: - 19°C – the temperature in the household freezer; 3°C – the usual temperature in a household refrigerator; 21°C – the ambient temperature in a home.

In Fig. 5.1. are given the electrical conductivities of B-type materials as a function of temperature. The determinations were made, as previously stated, at temperatures of –19°C, 3°C and 21°C, respectively. In conditions where, inside the freezer or refrigerator, the relative

humidity cannot be controlled, it is very likely to have a layer of condensation on the surfaces of the tested samples. The measurements were carried out after the samples were cleaned with isopropanol and kept for 24 hours under the conditions in which the electrical determinations were made. Moreover, the measurements were made with a TerraOhmMeter, with short-circuit protection (the applied voltage values being 5kV) and, in none of the measurements, we had any incidents of uncontrolled electric discharge.
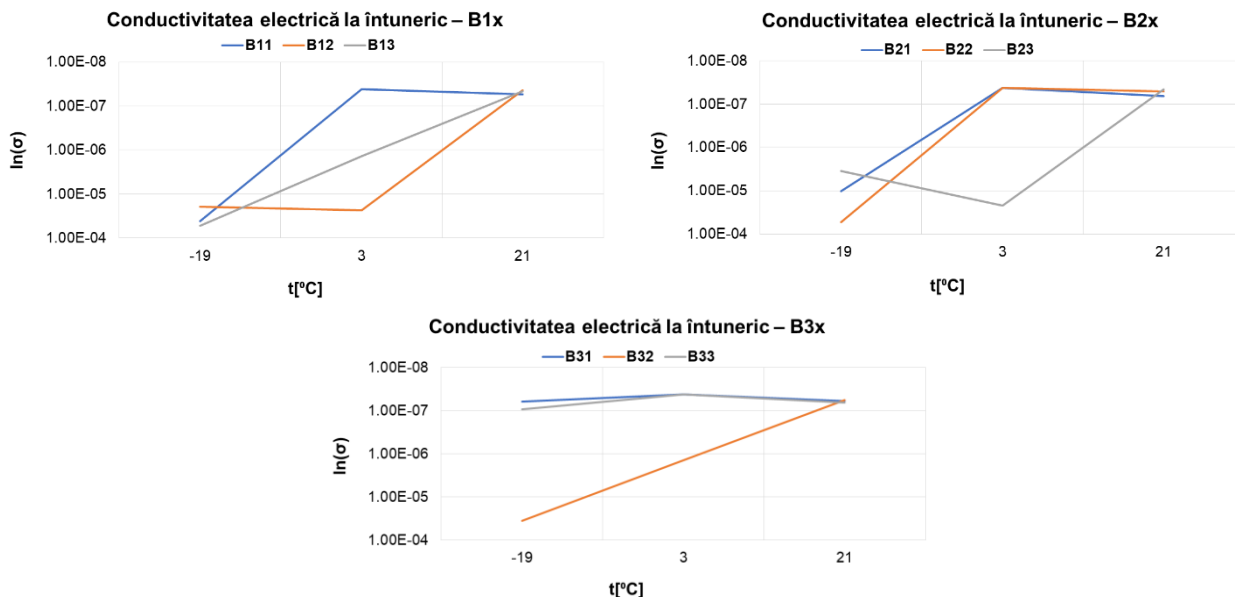
Fig.5.1. Temperature dependence of electric conductivity – B-type materials

In the case of the materials formed after 61 days, there can be noticed the identical behavior of the B31 and B33 materials – temperature - independent electrical conductivity and the different behavior of the B23 material – unstabled by the application of the sinusoidal alternating electric field through the copper electrodes. A strong enough explanation (also mentioned by Mihaela Gorovei, *op. cit.*) is that of the creation of complex, stable structures, during mixing in controlled conditions for long periods of time the inorganic agents solution. The fact that only the B32 material has a different behavior would be due, in this case, only to the presence of copper in the mentioned complex structures.
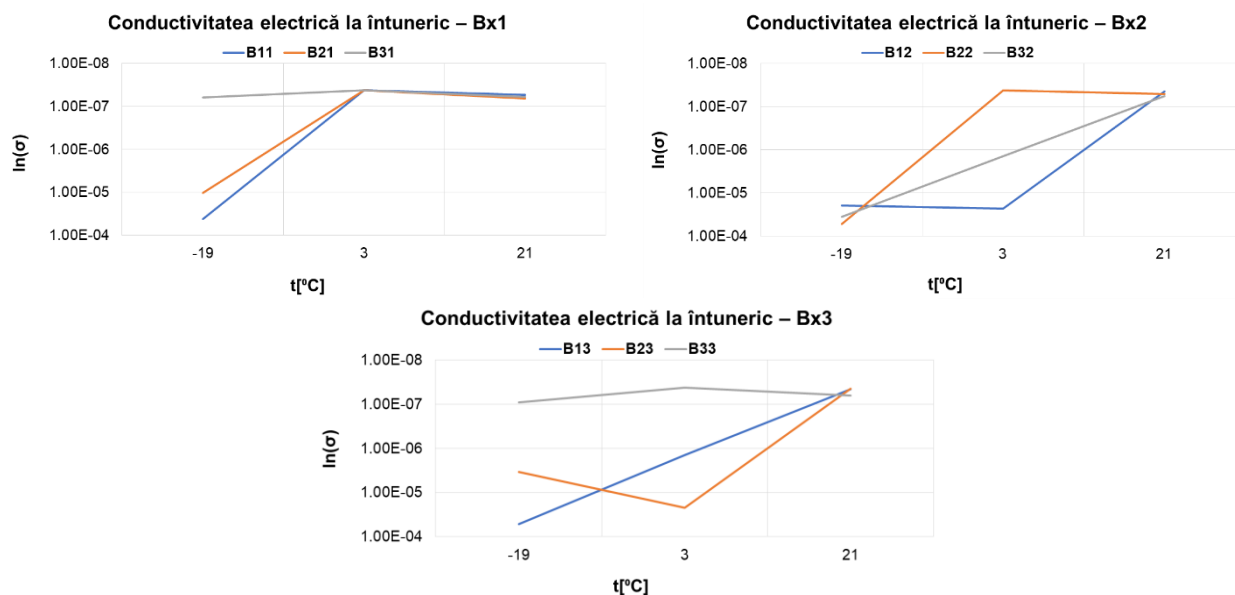
Fig.5.2. Electrical conductivities for samples B – according to pre-cast conditions

In Fig. 5.2. are shown the temperature dependences of the electrical conductivities of type B materials, depending on the conditions applied (or not – Bx1) to the blend of epoxy resin and solution of inorganic agents in DMF. It can be noted that the B31 material (made directly, without special conditions, but after a 61-day maturation of the mixture of epoxy resin and DMF solution of inorganic agents) does not show dependence of electrical conductivity on temperature, but compared to epoxy resin, has an electrical conductivity with four orders of magnitude higher. The other two materials seem to have the same behavior, although the B21 material has an electrical conductivity twice smaller than that of the B11 material.

In Fig. 5.3. are (as in the case of the dependence of electrical conductivity on temperature) the photoconductivities of materials B depending on the duration of keeping the blend of epoxy resin and solution in DMF of inorganic agents under controlled mixing conditions – B1 immediate casting, B2 – casting after 30 days, B3 – casting after 61 days.
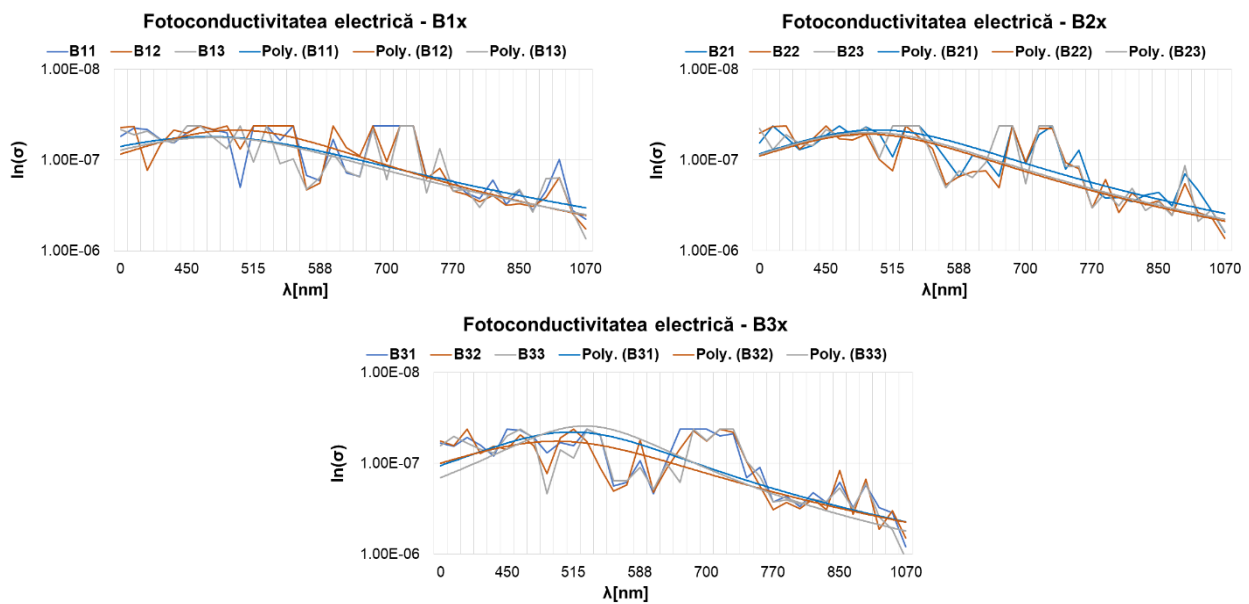
Fig.5.3. Electric photoconductivity of B-type materials depending on the duration of preparation

As in the case of the analysis of the dependence of electrical conductivity on temperature, in Fig. 5.4. is presented the photoconductivity of the materials depending on the application (or not) of the sinusoidal electric field by means of copper electrodes (Bx2) or carbon electrodes (Bx3).
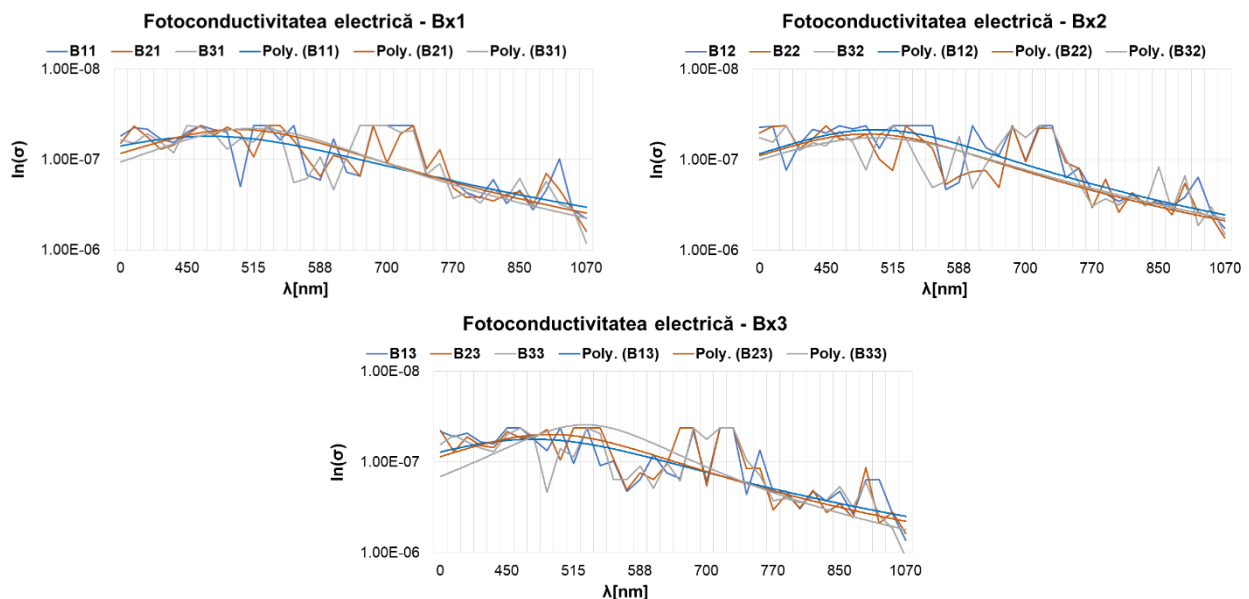
Fig.5.4. Electric photoconductivity depending on the pre-forming conditions

Data analysis shows that, when no sinusoidal electric field is applied, the materials behave almost identically. There is however a slight difference between B11 (immediately formed) and B12 and B13 respectively. The photoconductivity in the visible range of electromagnetic radiation seems to be dependent on the time of preparing the materials before casting. In the case of the materials formed following the application of the sinusoidal electric field through the copper electrodes, the higher values of conductivity in the visible range coincide for the materials with a long preparation time, while the photoconductivity of the immediately cast material is lower than that of the homologous material for which no the electric field was applied.

It is also noticeable that the average photoconductivities of B 1 and B21 materials (without an electric field, but formed one immediately and the other after 31 days) are not very different. In the case of the materials formed after 31 days, the effect of applying the electric field through the copper electrodes is the greatest. In the case of materials to which the sinusoidal electric field is applied by means of carbon electrodes, the effect depends on the time of the preparation.
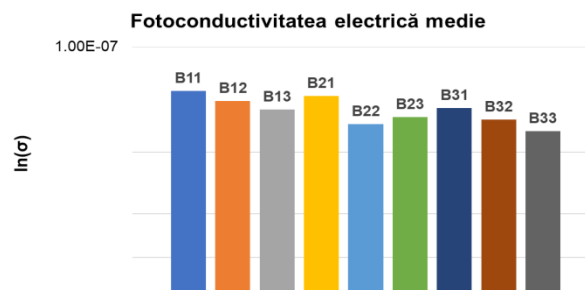
Fig.5.5. Averaged electrical photoconductivity

5.1.1. Electric properties analysis of type B materials – conclusions
- analysis of the variation of electrical conductivity of B materials B shows an advance of four to six orders of magnitude of this parameter compared to epoxy resin;
- in the case of the analyzing the variation of conductivity with temperature, two materials (B13 and B32) indicate an increase in conductivity with temperature, which means a metallic type behavior;
- the application of the sinusoidal electric field, before pouring the polymerizable mixtures into the molds, causes effects on the photoconductivity of the analyzed materials, both when it is applied by means of copper electrodes and when it is applied by means of carbon electrodes (graphite);
- the smallest effect of applying the sinusoidal field occurs in the case of the materials formed after the application of the field through the copper electrodes and regardless of the time of the preparation;
- for the materials with the longest preparation time, B31 (directly formed) and B33 (formed folowing the application of the electric field through the carbon electrodes) there is no dependence of the electrical conductivity on the temperature (on the analyzed temperature range);
- the photoconductivity of materials diminishes when they are irradiated with radiation with wavelengths in the visible range and goes up when they are irradiated with electromagnetic radiation in the IR range;
• a study on the conductivity and photoconductivity of thin films made of these materials could be performed under better conditions (much more accurate determination methods using low values of voltages and currents) could give an answer with regard to the use of these materials for applications in photovoltaics - unfortunately so far I have not been able to acquire thin films

(attempts made at CCDCOMT were also unsuccessful regardless of the method used to get the films).

5.2. Thermal Properties Analysis of Type B Materials

As I specified in Chapter 3, for class B materials I intended to check if the application of a magnetic field during the materials polymerization has any influence on their properties. The magnetic field was applied through self-adhesive, magnetic foils placed on the face of one of the two sheets of glass that make up a mold in which a sheet of material is formed.

In Fig. 5.6. are given the temperature dependences of the specific heats of the materials cast without being applied a sinusoidal electric field depending on the duration of maintaining the blending conditions of the mixture of epoxy resin and solution of inorganic agents, namely B1x and B1xm materials.

Fig.5.6. Specific heat evolution and averaged specific heat – Bx1 and Bx1m
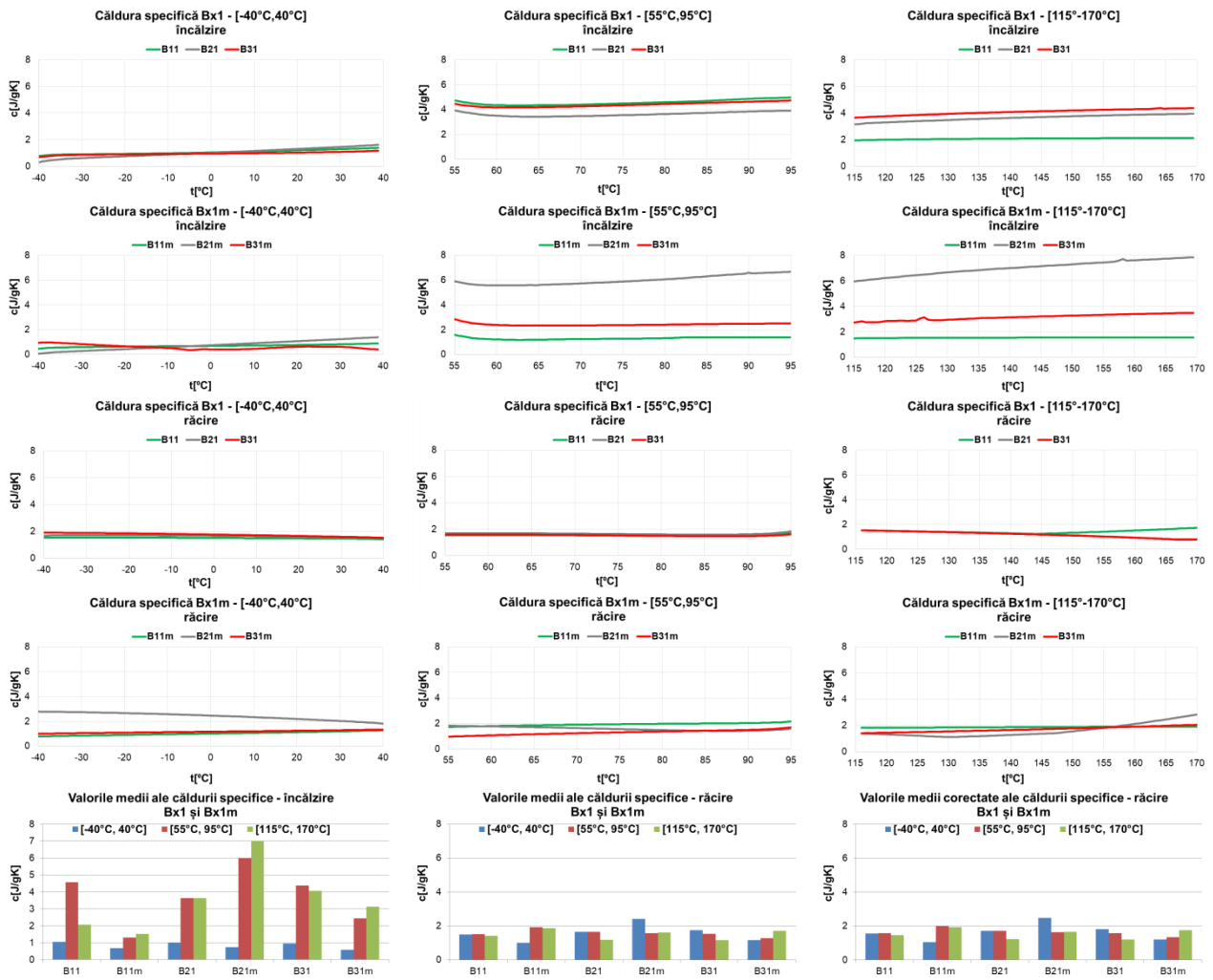
What can be easily noticed is the very high value of the specific heat of the B21m material over the temperature ranges corresponding to heating, but not, over the same range, in the case of cooling. This means that during heating are still caused structural changes to the material, even though it has already been thermally reinforced.

Table 3. Mass losses of Bx1 and Bx1m materials during DSC tests

Material	B11	B11m	B21	B21m	B31	B31m
Δm[mg]	1.13	1.0	1.17	1.23	1.2	1.23
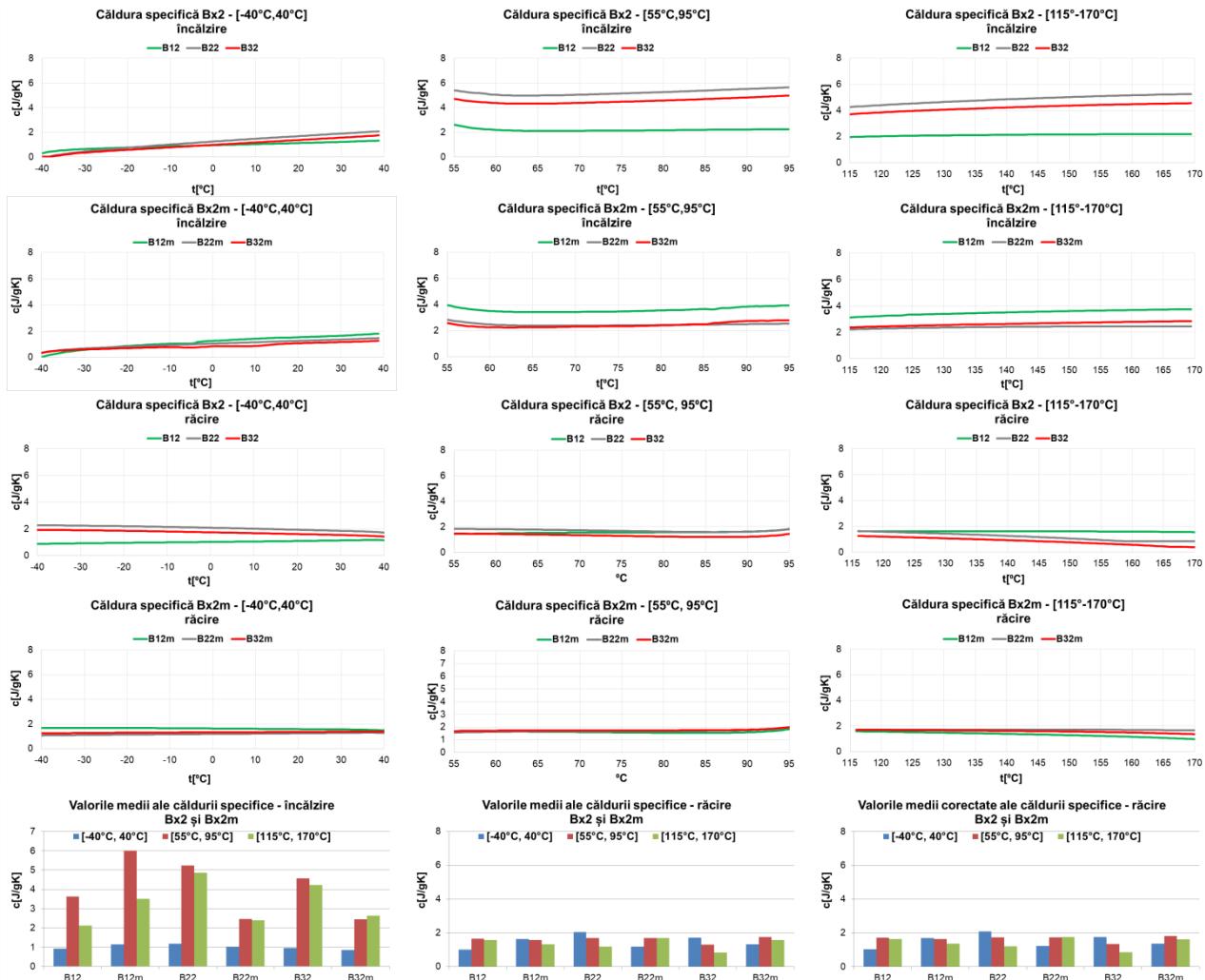
Fig.5.7. Specific heat of modified polymer B-type materials with copper electrodes applied sinusoidal electric field

In Fig. 5.7 are shown the curves describing the dependence of the specific heat value on the temperature value, on the three analysis ranges, both on the heating and cooling segments. Similarly to Bx1 and Bx1m materials, the values of specific heats (on heating segments) are much higher than the values of specific heats on cooling, which signals structural changes in the material. The highest values correspond to the B22 and B23 materials, but after the magnetic field application, these values are decreased and the B22m and B23m materials have values of the specific heat lower than the corresponding value for the B21m material.

Table 4 also displays the mass losses recorded during the tests carried out in order to determine the specific heat of the materials.

Table 4. Mass losses of Bx1 and Bx1m materials during DSC tests

material	B12	B12m	B22	B22m	B32	B32m
Δm[mg]	0.9	0.93	1.0	1.0	1.23	1.2

The data indicate, again, substance losses smaller than in the case of Class A materials (analyzed in the previous Chapter), but comparable to those of Bx1 and Bx1m type materials.

In Fig. 5.8. are shown the results of the thermal tests carried out on the materials achieved by applying the sinusoidal electric field by means of the graphite (carbon) electrodes, that is, the Bx3 and Bx3m type materials.

Once again, it can be seen that B23 and B23m materials have the highest values of specific heat (in the ranges corresponding to positive values of temperature) meaning that the time of preparing the blend is what matters.
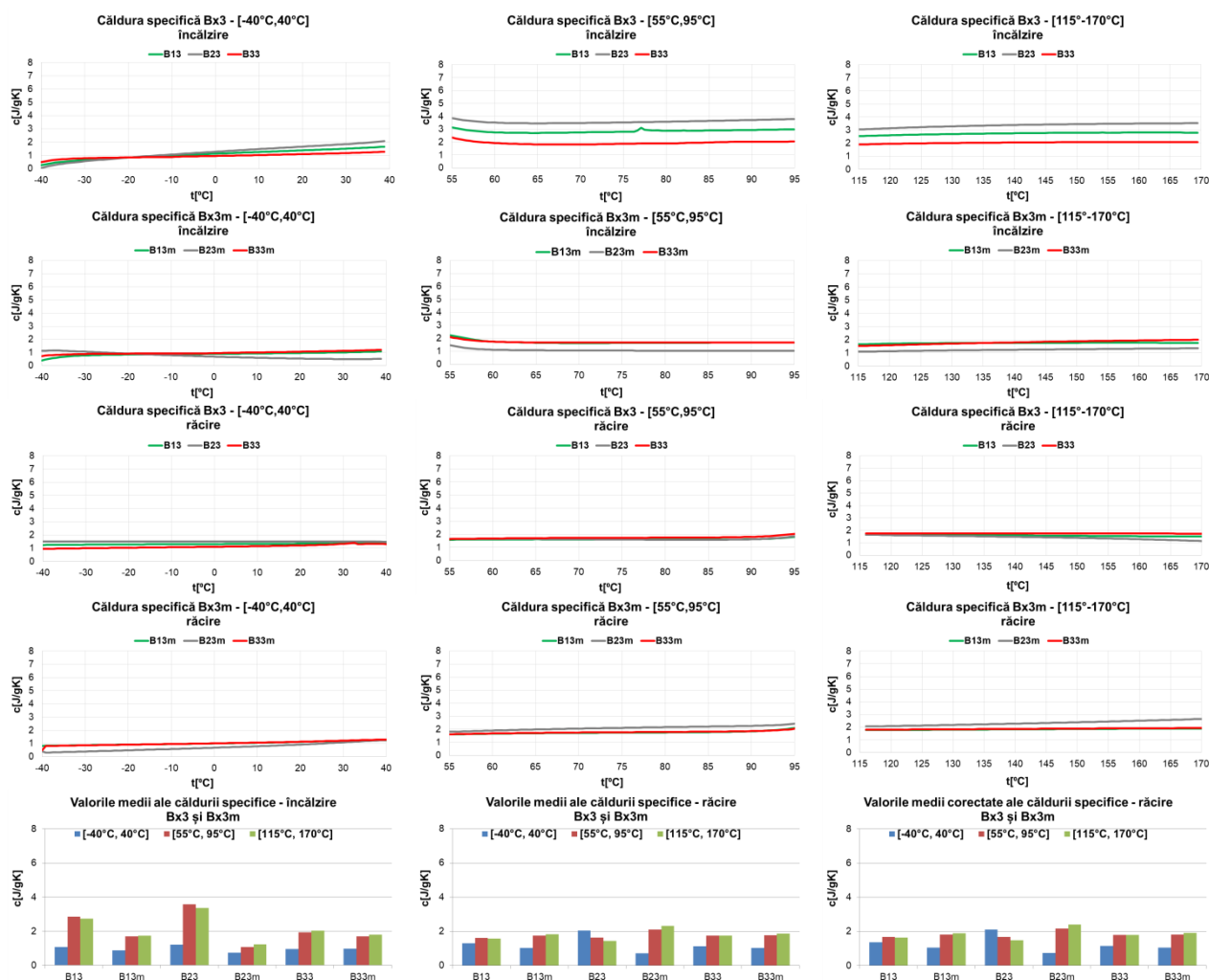
Fig.5.8. Specific heat of the modified polymer B-type materials with sinusoidal electric field applied through graphite electrodes

As with the other materials in the same class, during the DSC tests performance, it has been also monitored the loss of substance (the results were used to correct the value of the specific heat on cooling). The results are rendered in table 5.

Table 5. Mass losses of Bx3 and Bx3m materials during DSC tests

material	B13	B13m	B23	B23m	B33	B33m
Δm[mg]	1.3	1.13	1.27	1.13	1.17	1.07

5.2.1. Thermal Properties Analysis of Type B Materials – Conclusions

- it can be remarked the special thermal behavior of B21m and B31m materials, characterized by very high specific heat values (on the heating segments), but this behavior is no longer observable on the cooling segments;
- another outstanding behavior is that of the B32 material which shows higher specific heat values on the cooling segments compared to the values on the heating segments;
- in the case of the materials formed after the longest preparation time (Bx3), the mass losses of the materials formed in the presence of the magnetic field are smaller than the substance losses of the homologous materials formed without the magnetic field presence;

- relatively high specific heat values (on the heating segments and on the two domains of positive temperature values) can also be noted in the case of Bx2 materials (B22 and B32), but they are not as high as those recorded in the case of B21 and B31 materials;

5.3. Mechanical Properties Analysis of Type B Materials
5.3.1. Tensile Tests of Type B Samples

Similarly to the case of the Class A materials, Class B materials were mechanically tested in both tension and three-point bending. In the case of Class A materials, I saw that they behaved differently from epoxy resin (transition from rigid to elasto-plastic behavior), regardless of the duration of preparing the blend for forming.

In Fig. 5.9. are given the individual curves of the five samples tested for tension for each material of Bx1 type (formed soon after making the modified polymerizable mixtures).
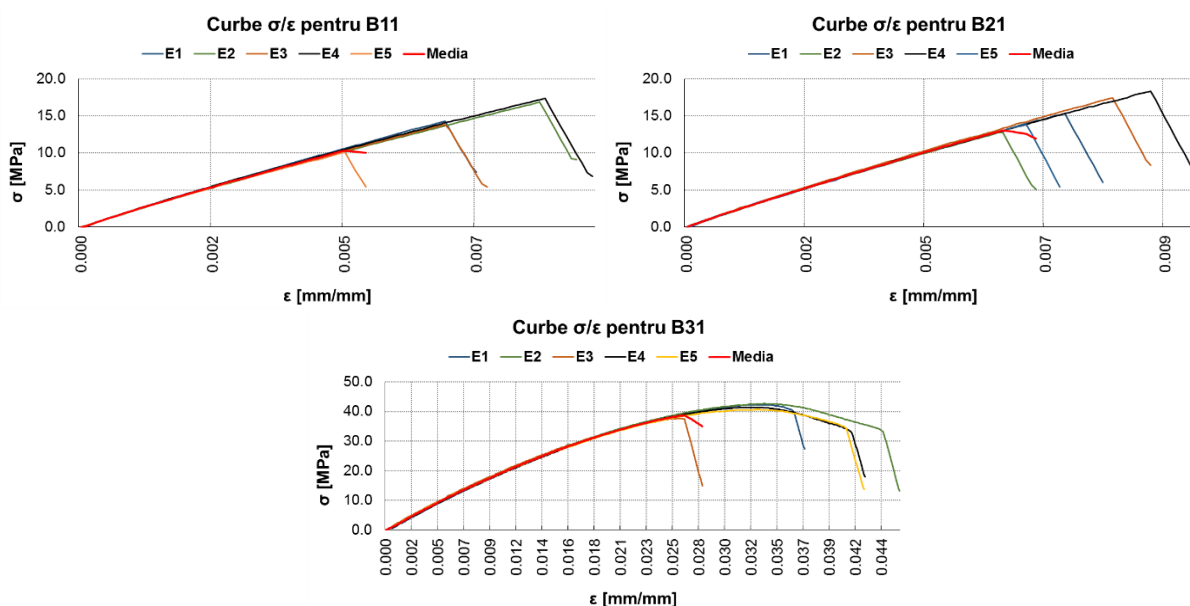
Fig.5.9. Tension/deformation curves of the materials formed after the realisation of epoxy resin/inorganic agents solution in DMF

It can be noticed that the B11 and B12 materials have, practically, the same behavior, of rigid type. The B13 material has a slightly different behavior (the slight curvature of the average curve can be noted), meaning that the application of the sinusoidal electric field through the graphite electrodes causes qualitative changes in the formed material.

The specific deformation at break also seems to depend on whether or not the sinusoidal electric field is applied. Thus, in the case of material B11 (without electric field), the specific deformation at break (first sample) has the value of 0.005. In the case of B21 material (sinusoidal electric field applied through copper electrodes) the value of this parameter is approximately 0.0065. For the material achieved applying the sinusoidal electric field through the graphite electrodes – B31 – the specific deformation at the break of the first sample is around 0.026 (four-five times larger than in the case of the other two analyzed materials).

The curves shown in red in the representations above are the average curves, which describe the behavior of each material as a whole. These are calculated up to the break of first sample and are representations of average values of tension vs. average values of specific deformation (average values are calculated as arithmetic means).
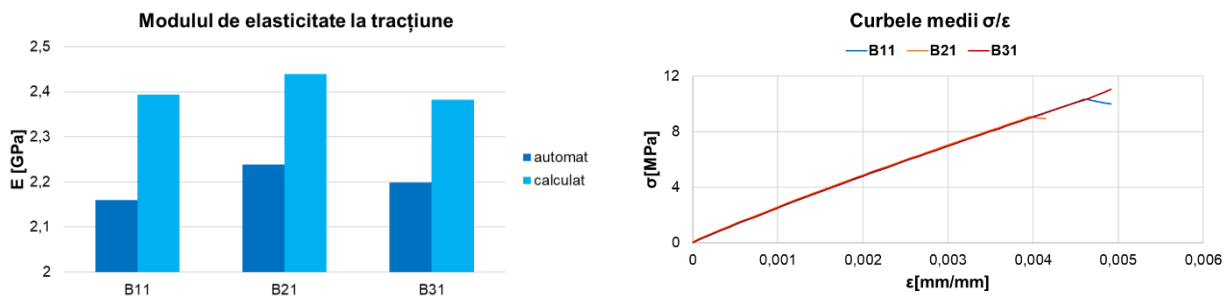
Fig.5.10. Moduli of elasticity and average evolutions of Bx1 materials

In Fig. 5.10. are rendered the elastic moduli and average specific tension/deformation curves of the Bx1 materials. The automatically determined elastic moduli are those provided by the software application that controls the testing machine and allows the determination of the values of certain parameters of interest. These average values are determined as the arithmetic mean of the values of the of elasticity moduli measured for each individual sample. In addition, these individual values are determined for the length of the entire individual curve.

The calculated values - also plotted in Fig.5.10. – are determined according to the fundamental law of elasticity on the average curves corresponding to each material and on the range of specific deformations [0.000, 0.003].

It should be noted that, for all three materials, the calculated moduli of elasticity are comparable to the value of the elasticity modulus calculated for the epoxy resin (fig. 4.12.). This result is expected because the concentration of inorganic agents solution in DMF is very low in the formed material.
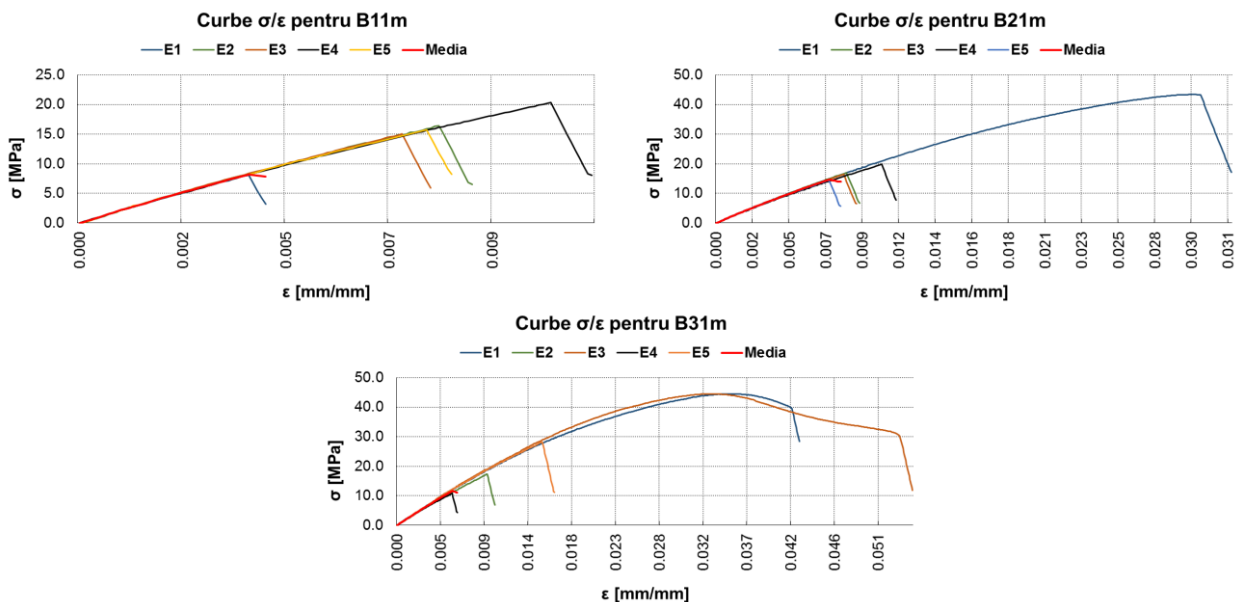
Fig.5.11. Tension/deformation curves of the materials formed after making the epoxy resin/inorganic agents solution in DMF and polymerized in external magnetic field

In fig. 5.11. are displayed the individual specific tension/deformation curves for the tested samples (five each) of the Bx1m materials, that is, polymerized in the presence of the external magnetic field.

It can be noted that for each individual case there is at least one sample whose tensile response is different from the others. E4 for B11m, E1 for B21m and E1 and E3 for B31m respectively.

An analysis of this kind is not, however, one that allows the detection of conclusions like the ones above. The fact that there are those samples with different behavior is a signal related to the inhomogeneity of the materials (due to the external magnetic field applied during polymerization) so that the data shown above, related to the breaking strength, are not representative of the materials analysis.
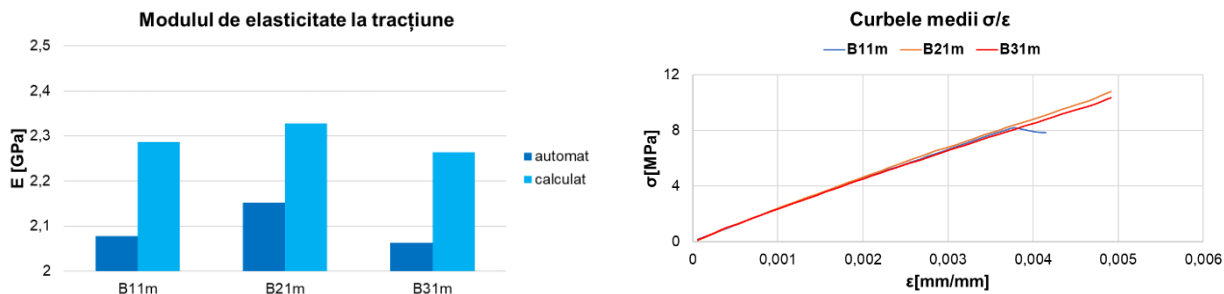
Fig.5.12. Elastic moduli and averaged evolutions of Bx1m materials

In Fig. 5.12. are given the tensile modulus values and the average behaviors (average specific deformation/tensile curves) of the Bx1m materials, namely materials formed immediately after the preparation of the epoxy resin blend and solution of inorganic agents in DMF.

A comparative analysis of the information presented in Fig.5.10. and Fig. 5.12. leads to the conclusion that applying the external magnetic field during the polymerization produces a fall in the values of the tensile elastic moduli, both as concerns the automatically determined values and those evaluated on the average curves.
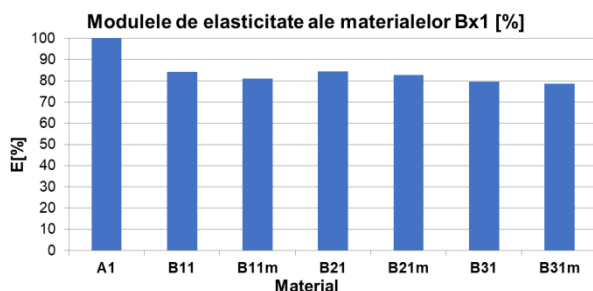
Fig.5.13. Percentage reduction of elastic modulus values with respect to the epoxy resin –Bx1y materials

In fig. 5.13. are shown the percentage values (relative to the modulus of elasticity value of the epoxy resin) of the Bx1 and Bx1m materials. As we have shown above, there are decreases in the values of the elastic moduli of the analyzed materials, due to the addition of inorganic precursors solution in DMF. These decreases are larger in the case of materials polymerized in an external magnetic field. For each pair of materials, it can be found that the difference between the percentage values of the elasticity modules is: 3.18 for the pair B11, B11m; 1.78 for the pair B21, B21m; 0.87 for the pair B31, B31m.

In Fig. 5.14. are given the individual curves (curves corresponding to each sample) for the materials formed 31 days after making the epoxy resin/inorganic agent solution blend in DMF, that is, the Bx2 materials. I remind that x=1 represents the material formed without any other intervention; x=2 the material formed after applying, for 30 minutes, a sinusoidal electric field through the copper electrodes; x=3 the material formed after applying, for 30 minutes, a sinusoidal electric field through the graphite electrodes. Sinusoidal electric fields were applied to the epoxy resin/inorganic agent solution mixture in DMF and then the required amount of hardener was added.
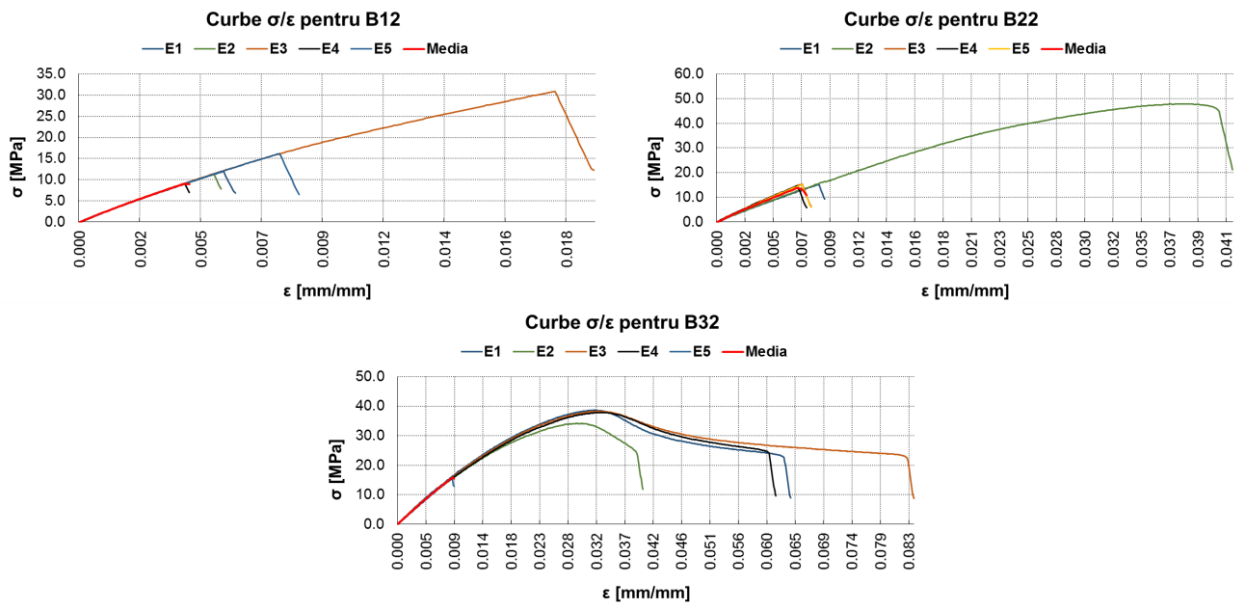
Fig.5.14. Curbele tensiune/deformație ale materialelor formate la 31 de zile după realizarea amestecului rășină epoxidică/soluție de agenți anorganici în DMF

Keeping the mixture of epoxy resin and solution of inorganic agents in DMF for 31 days under mechanical stirring determines the achievement of softer materials. In this case, the reductions in tensile strength go up together with the application of the sinusoidal electric field. The effect is more pronounced in the case of applying the field through the graphite electrodes. This time I also mention the fact that the breaking of first sample does not represent a significant event for the material analysis, but is only an indicator of inhomogeneity or an indicator of the presence of defects in the material formed.
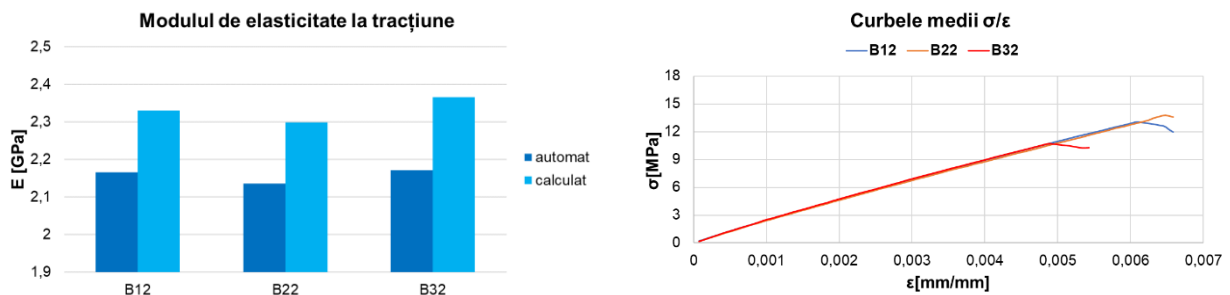
Fig.5.15. Moduli of elasticity and average evolutions of Bx2 materials

In Fig. 5.15. are shown the values of the modulus of elasticity of the Bx2 materials and the average curves describing the global stretching behavior of these materials, in the area of small deformations (elastic area). The values of the elasticity moduli are slightly reduced compared to those corresponding to Bx1 materials (Fig. 5.10.).

In Fig. 5.16. are given individual specific tensile/deformation curves for samples of Bx2m materials, i.e. counterparts of Bx2 materials, but polymerized in the presence of external magnetic field. One can note the relatively large dispersion of the experimental data for the B22m material. It can be also seen a decrease in the tensile strength of this material compared to its counterpart – B22.

Fig.5.16. Tension/deformation curves of the materials formed at 31 days after the realisation of epoxy resin/inorganic agents solution in DMF and polymerized in external magnetic field

In the conditions already mentioned before, it could be concluded that, for the samples polymerized in the presence of the external magnetic field, the mechanical performance of the materials is improved for the material formed without other interventions and for the one in which a sinusoidal electric field is applied through the copper electrodes.
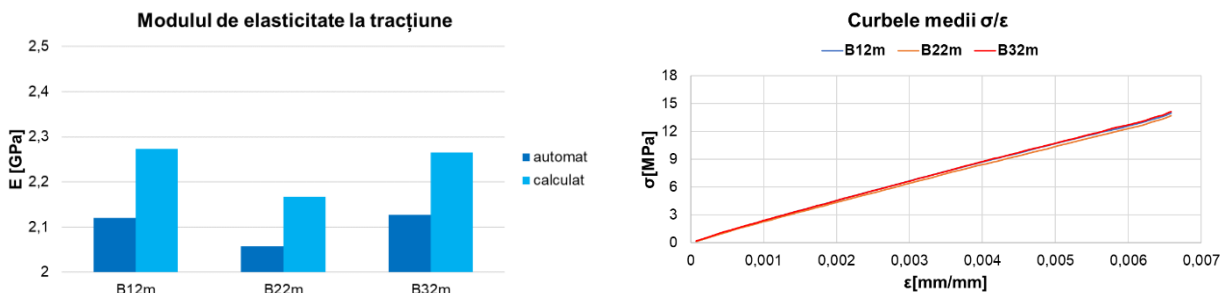
Fig.5.17. Elastic moduli and averaged evolutions of Bx2m materials

In Fig. 5.17. are displayed the elastic moduli (automatic and calculated) for the Bx2m materials and the average specific tension/deformation curves for these materials. It is obvious the curtail of the elasticity moduli values in relation to the homologous materials (Bx2) and obviously compared to the Bx1m materials.

As in the case of the materials analyzed in the previous subChapter, in Fig. 5.18. the percentage reductions of the modulus values (calculated) relative to the modulus value of the epoxy resin are shown (A1).
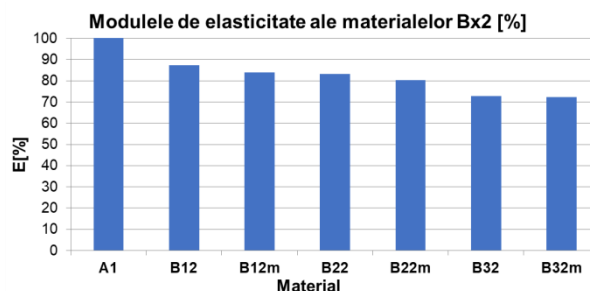
Fig.5.18. Percental reduction of elastic modulus values with respect to the epoxy resin –Bx2y materials

52

As in the case of materials formed immediately after making the epoxy resin/inorganic agent solution mixture in DMF, the magnetic field produces a deterioration of the elastic tensile response of the materials. In this case the exception is the pair B32, B32m.

In Fig. 5.19. are given the specific tension/deformation curves for each tested sample, along with the average of these curves. A noticeable change is related to the profile of the curves for B13 material, which becomes more curved than in the case of B11 and B12 materials.
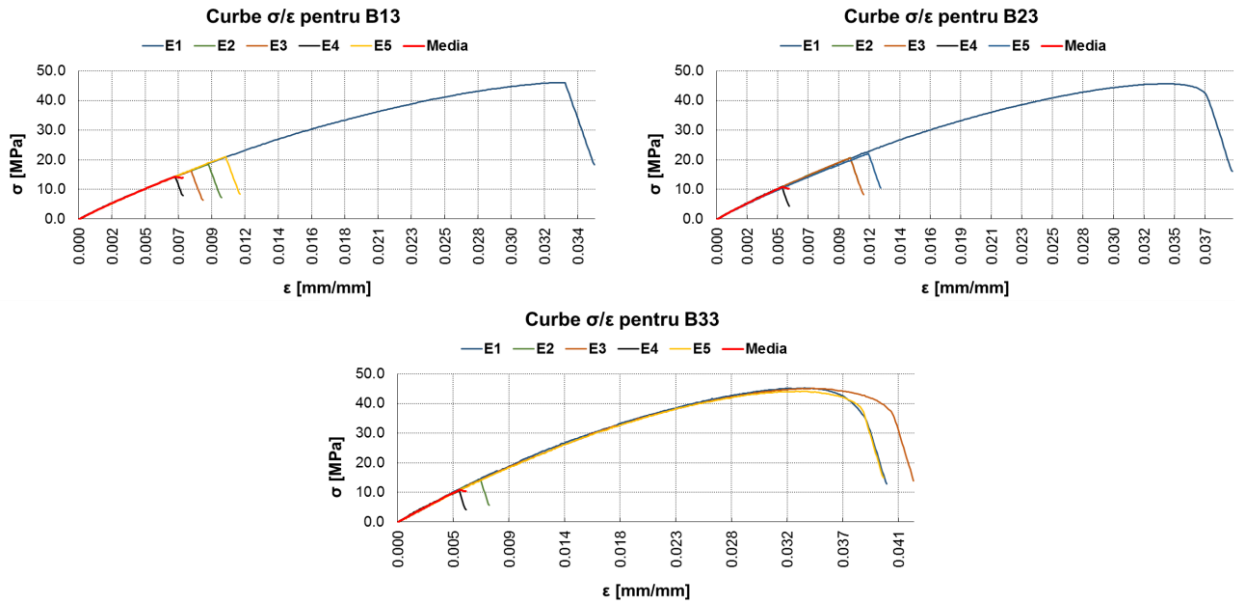
Fig.5.19. Tension/deformation curves of the materials formed at 61 days after the realisation of epoxy resin/inorganic agents solution in DMF

The calculated value of the tensile moduli of elasticity was determined from the fundamental law of elasticity in the range of specific deformations (0.000, 0.003) and the results are rendered in Fig.5.20., along with the average behavior of the samples of each material, also in the small deformations range (it can be noted that the breaking of the first sample for all materials occurs after the specific deformation exceeds the value of 0.005, that is, they are softer than those analyzed so far).
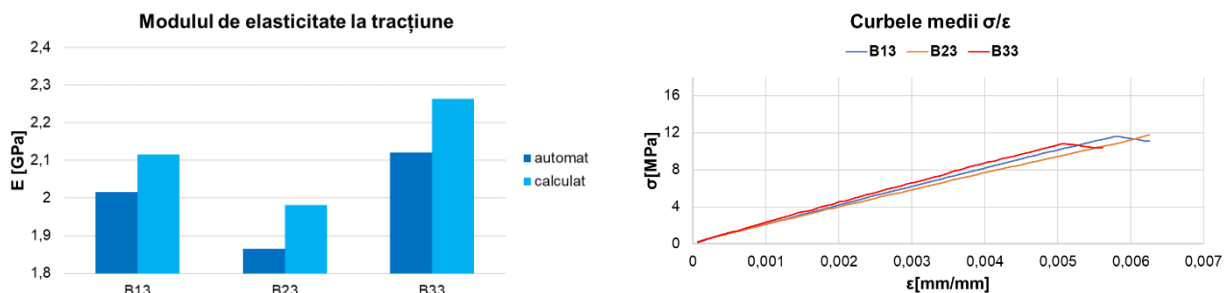
Fig.5.20. Elastic moduli and averaged evolutions of Bx3 materials

In Fig. 5.20. can be found the significant reduction of the modulus of elasticity of the B23 material, but also for the other two materials there are recorded decreases in the value of the parameter (this is the automatically determined value). For the calculated value of the parameter, in the range of small deformations, there are also observed reductions in the value

of the tensile modulus of elasticity - the smallest reduction corresponding to the material formed following the application of the sinusoidal electric field through the graphite electrodes.

As concerns the materials polymerized in the presence of an external magnetic field - Fig.5.21. – it can be noticed that the B13m material has linear responses (B13 shows a curved response profile).
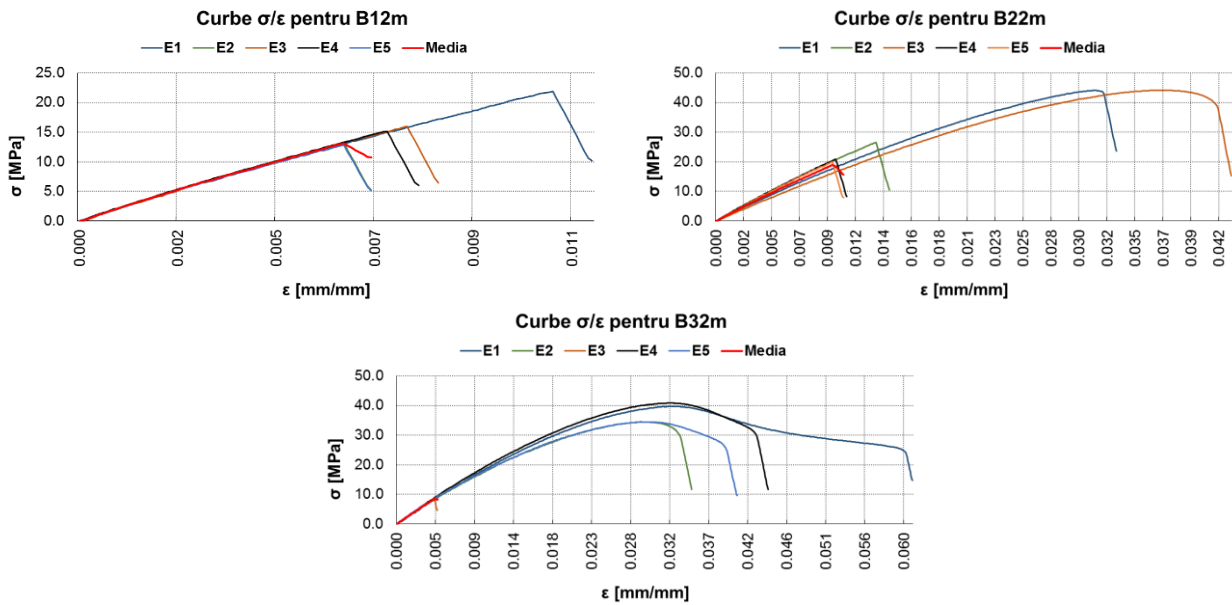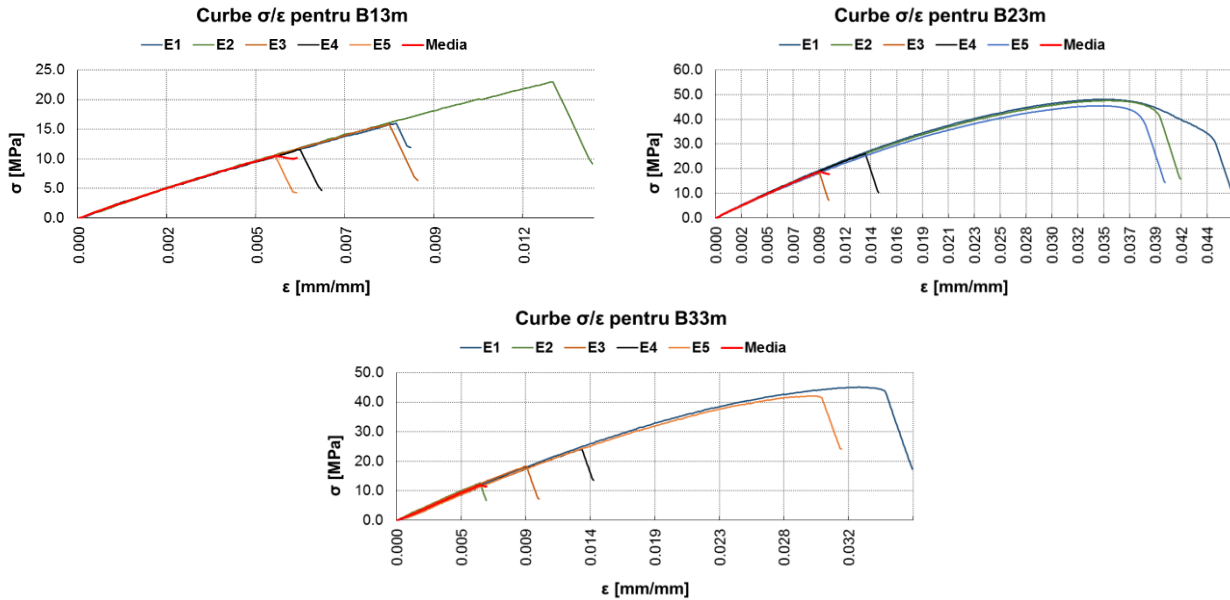

Fig.5.21. Tension/deformation curves of the materials formed at 61 days after the realisation of epoxy resin/inorganic agents solution in DMF and polymerized in external magnetic field

In this case, the coordinates of the breaking of the first samples are: (0.03, 34MPa), for B13m; (0.035, 7MPa) for B23m; (0.006, 12MPa) for B33m.

The values of the elasticity moduli, shown in Fig. 5.22., indicate that the values determined in the small deformations range are lower than those determined automatically, for B31m and B33m materials.

It can also be remarked that the values of the tensile moduli of elasticity are substantially diminished, for the B33m material, in relation to its counterpart, B33. In the case of B13 and B13m materials, it is also observed the reduction of the value of the elastic modulus following the application of the external magnetic field, while for the B23 pair, the application of the magnetic field seems to cause a slight increase in the value of the elastic modulus when stretched.

What is most important is that the Bx3m materials are the softest.
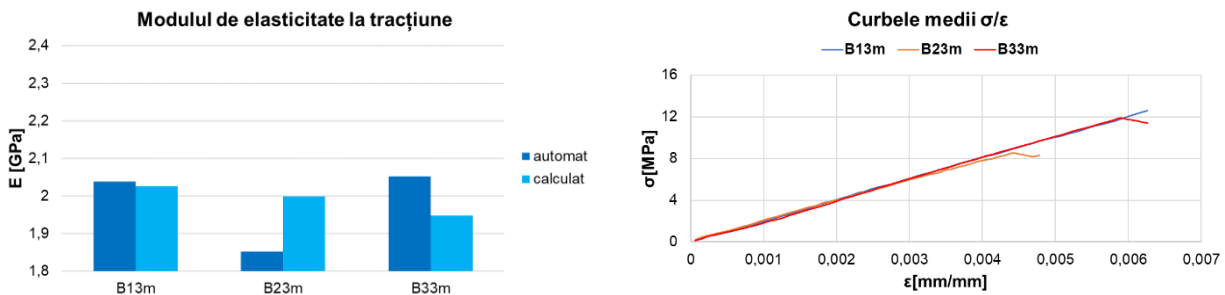
Fig.5.22. Elastic moduli and averaged evolutions of Bx3m materials

5.3.2. Tensile Tests of Type B Materials - Conclusions

- the amount of solution of inorganic precursors in DMF added to the epoxy resin is small enough not to cause radical changes in the properties of the matrix;
- the application of the sinusoidal electric field (either through the copper electrodes or through the graphite electrodes) contributes to the reduction of the elasticity modulus of the materials;
- keeping the mixture of epoxy resin/solution of inorganic agents in DMF under conditions of continuous stirring for longer periods of time, leads to acquiring materials with the modulus of elasticity when stretched with lower values (proportional to the duration of keeping);
- for a more thorough analysis, within these conclusions, in Fig. 5.24. are presented the comparative data concerning the modulus of elasticity to stretch (tension) of the materials got under different conditions;
- the time of preparing the blend leads to the obtaining of materials with a tensile modulus of elasticity higher than the value of the modulus of elasticity of the material formed immediately after the preparation of the blend of epoxy resin/solution of inorganic agents in DMF, with the maximum value, after 31 days of preparation;
- under the same conditions, polymerization in an external magnetic field leads to getting materials with a lowered modulus of elasticity;
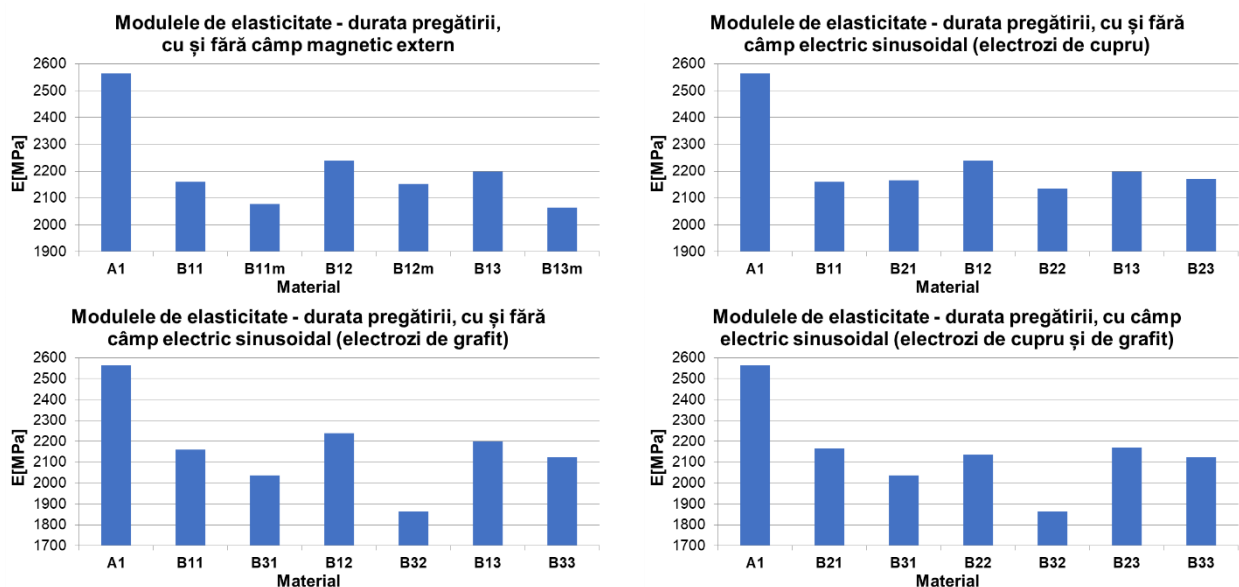
Fig.5.24. Comparative analysis of the results of the application of control techniques - stretching

- the application of the sinusoidal electric field, through the copper electrodes, produces a slight increase in the modulus of elasticity only in the case of the material formed immediately after making the polymerizable mixture;
- the application of the sinusoidal electric field, through the graphite electrodes, determines the reduction of the elasticity modules values for all the analyzed materials;
- the decrease in the values of the tensile elasticity modules of the formed materials is larger for the mixtures subjected to the sinusoidal electric field applied by means of graphite electrodes, than in the case of applying the field by means of copper electrodes.

5.3.3. Three-point Bending Tests of Type B Materials

Three-point bending tests were performed on rectangular samples using the same *Instron* machine at CCDCOMT. The forward speed of the horizontal bracket (loading speed) was set at 5mm/min for all samples and five samples of each material were tested.

The process of material making was a laborious one that I tried to control step by step, and for this reason I could not form more materials (boards) from which to extract more samples. Thus, this study can be considered, at this stage, a first step that allows the development of future studies.

Fig.5.25. Loading/displacement curves of the materials formed after the realisation of epoxy resin/inorganic agents solution in DMF

In Fig. 5.25. the individual curves and the average curves (this time the loading/displacement curves) are shown for the materials formed soon after making the epoxy resin/inorganic agent solution mixture in DMF, namely – on the model used to present the tensile test results – the Bx1 materials. For x=1 the material is formed directly, without other interventions, for x=2 the material is formed after subjecting the blend to the influence of the sinusoidal electric field applied through copper electrodes, for x=3 the material is formed after subjecting the blend to the influence of the sinusoidal electric field applied through graphite (carbon) electrodes.

As can be easily noted, the responses of the samples are much more diverse than those recorded in the case of tensile tests. In the case of B11 material, two samples show rigid fracture (E1 and E4), while the other three show an elasto-plastic behavior. Samples of B21 and B31 materials show closer responses. For this reason, unlike the analysis of tensile test results, the average behavior (presented in Fig.5.26.) is determined as the average for the samples with similar behavior – in the case of B11 material, E2, E3 and E5 samples – and I will keep this rule also for the following materials.
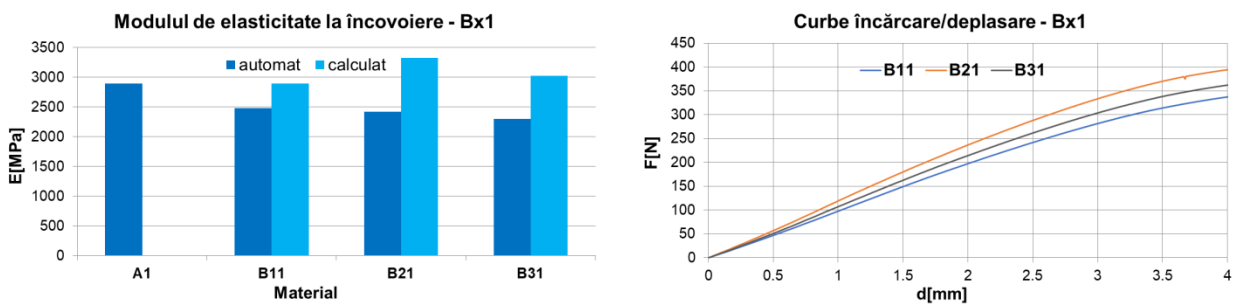
Fig.5.26. Elastic moduli and averaged evolutions of Bx1 materials – three point bending

In order to determine the modulus of elasticity of flexure of the epoxy resin (A1), the tests were performed, as shown in Chapter 4, on cylindrical samples. Under these conditions, I can only present the value of the automatically determined module.

For the materials polymerized in the presence of the external magnetic field, Bx1m type materials, the situation is shown in Fig.5.27, concerning the individual curves and the average curves of the tested samples.
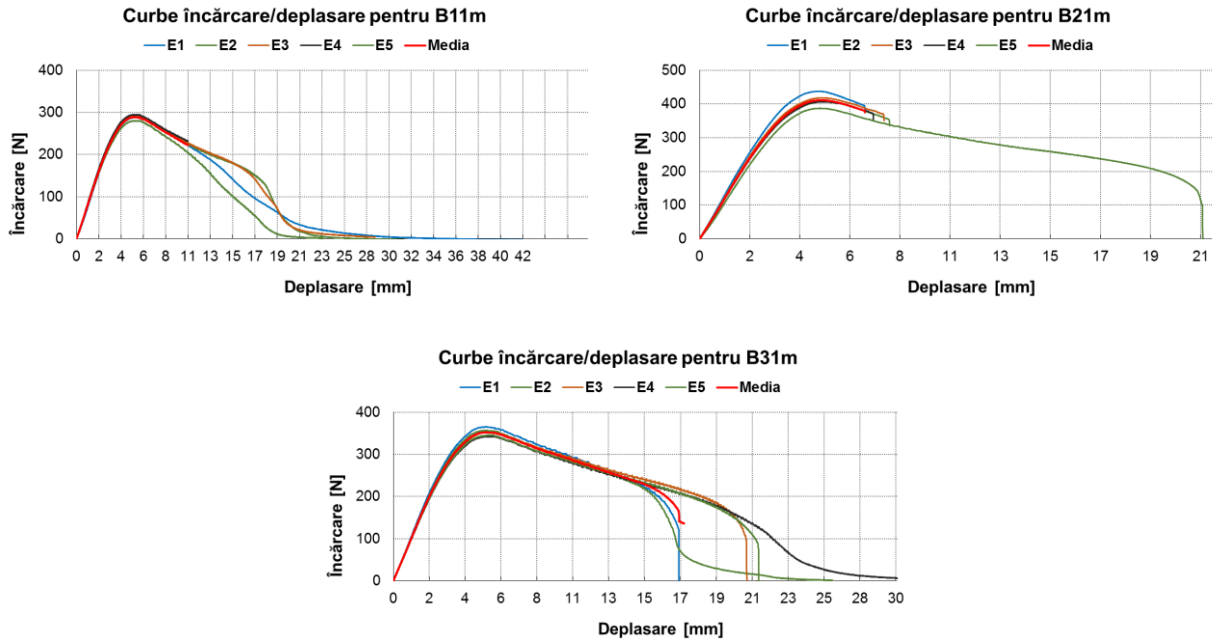
Fig.5.27. Loading/displacement curves of the materials formed after the realisation of epoxy resin/inorganic agents solution in DMF and polymerized in external magnetic field

In Fig. 5.31 are shown the results of the three-point bending tests for the Bx2m materials, namely materials formed after 31 days of making the epoxy resin/inorganic precursor solution mixture in DMF and which were polymerized in the presence of the magnetic field. There cannot be remarked very large changes in relation to the bending behavior of the previously presented materials (Bx2).
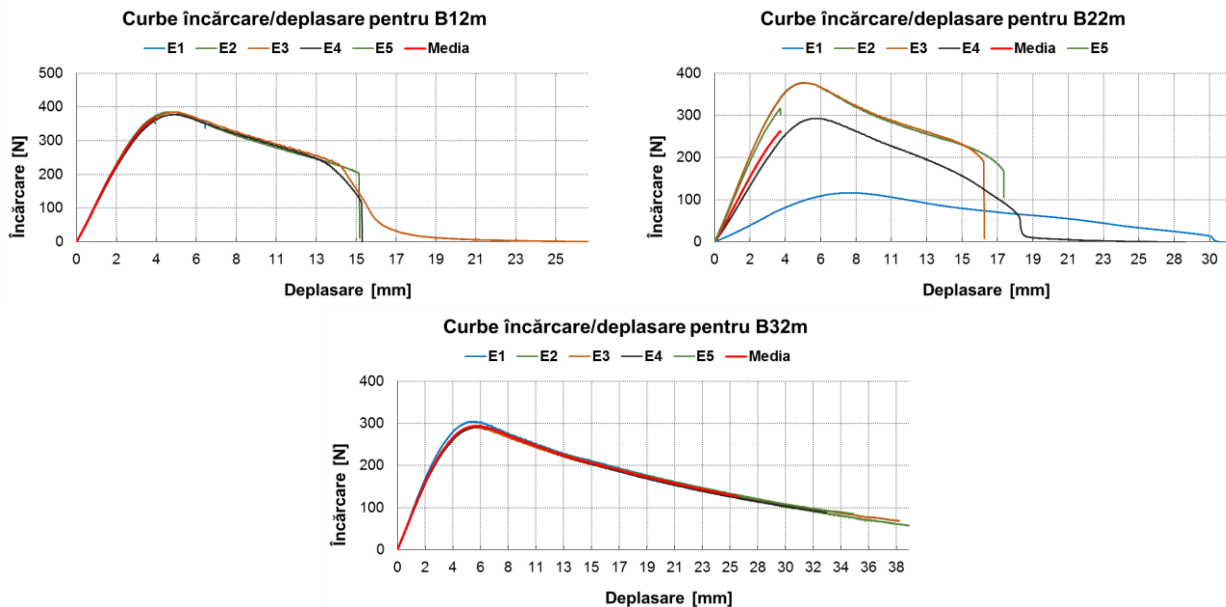
Fig.5.31. Loading/displacement curves of the materials formed at 31 days after the realisation of epoxy resin/inorganic agents solution in DMF and polymerized in external magnetic field

In the case of materials formed without the presence of an external magnetic field during polymerization, in fig. 5.33., it can be observed that there are no more rigid breaks in the samples (with one exception – sample E1 of material B23) and the maximum values of the sample loads are shifted towards higher deformations (compared to the previously analyzed materials). The maximum values of the loading of the samples correspond to the material formed after the application of the sinusoidal electric field through the copper electrodes.
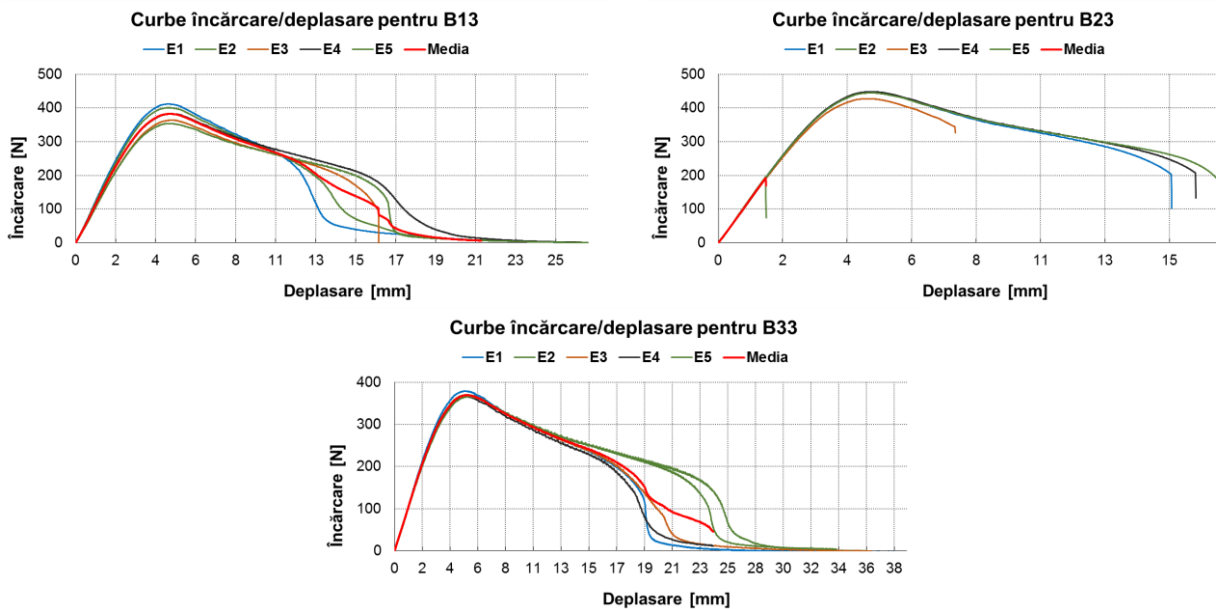
Fig.5.33. Loading/displacement curves of the materials formed at 61 days after the realisation of epoxy resin/inorganic agents solution in DMF
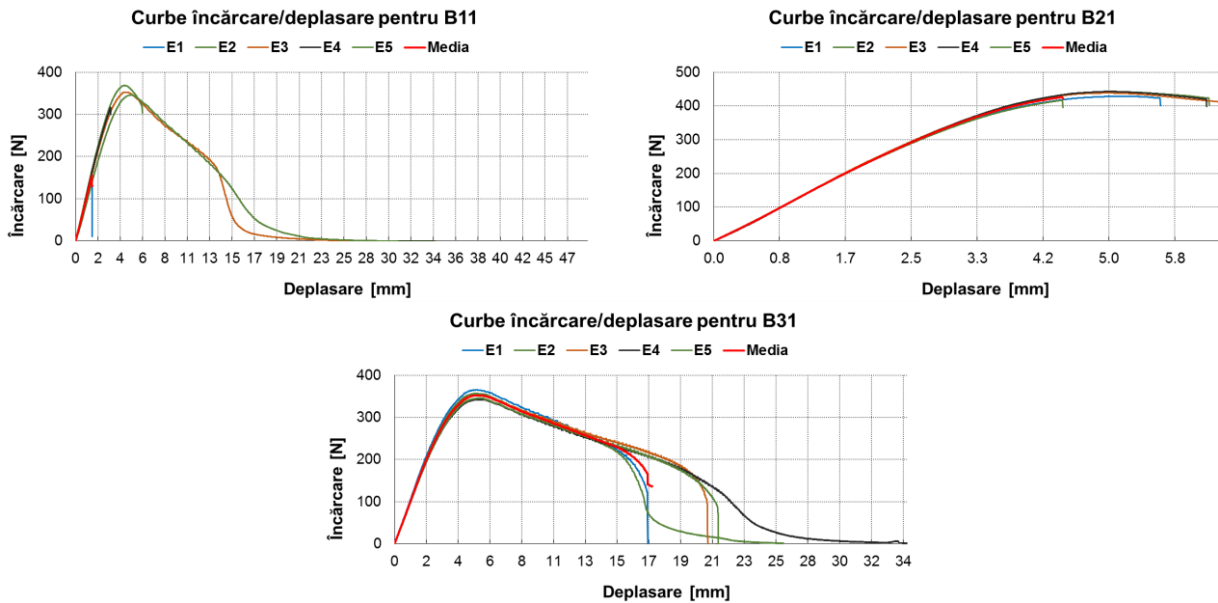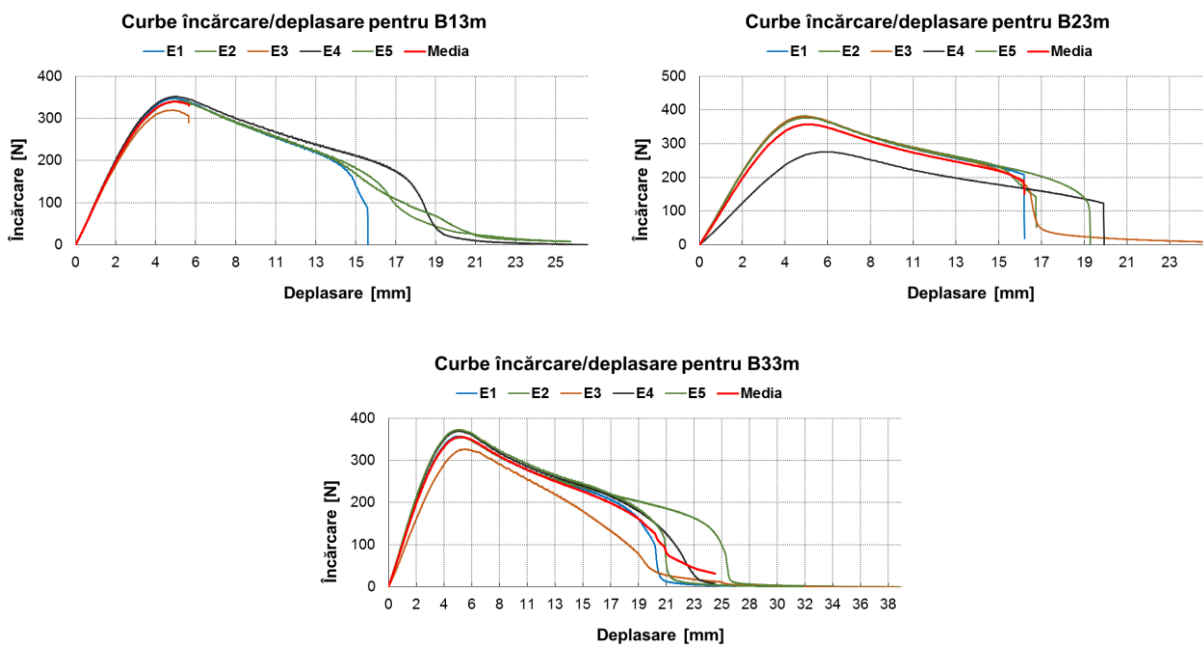

Fig.5.35. Loading/displacement curves of the materials formed at 61 days after the realisation of epoxy resin/inorganic agents solution in DMF and polymerized in external magnetic field

In fig. 5.35. the load/displacement curves for the tested samples of the polymerized materials in the presence of the magnetic field – Bx3m are presented, after 61 days of keeping the epoxy resin mixture/DMF solution of metal chlorides under controlled stirring conditions. In

this case, a reduction in the maximum load of the samples can be observed (compared to the homologous materials, presented previously).

These maxima are shifted to higher strains than in the case of the homologous materials. The smallest such displacement is observed in the case of material B33m.

Regarding the average load/displacement curves and the values of the modulus of elasticity in three-point bending, they are presented in fig.5.36. and slight reductions in modulus values can be observed compared to Bx3 materials.
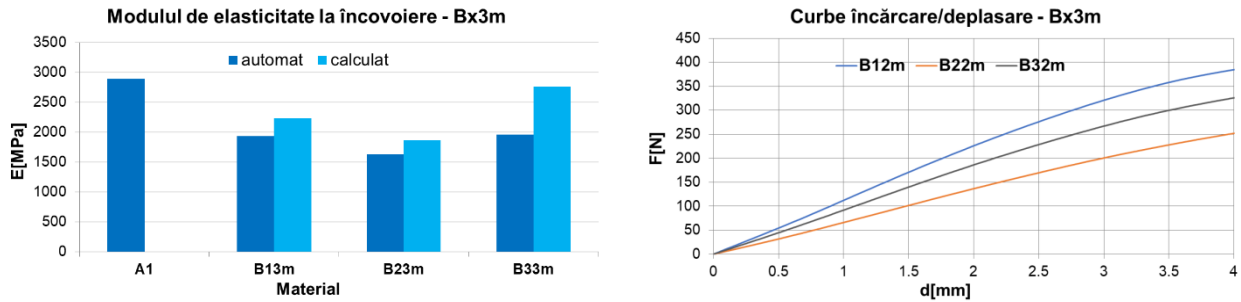
Fig.5.36. Elastic moduli and averaged evolutions of Bx3m materials – three point bending

5.3.4. Three point bending tests of type B materials – conclusions

- all the materials polymerized in the presence of the external magnetic field present flexural modulus of elasticity with lower values than those of the modulus of elasticity of the homologous materials, but formed in the absence of the external magnetic field;
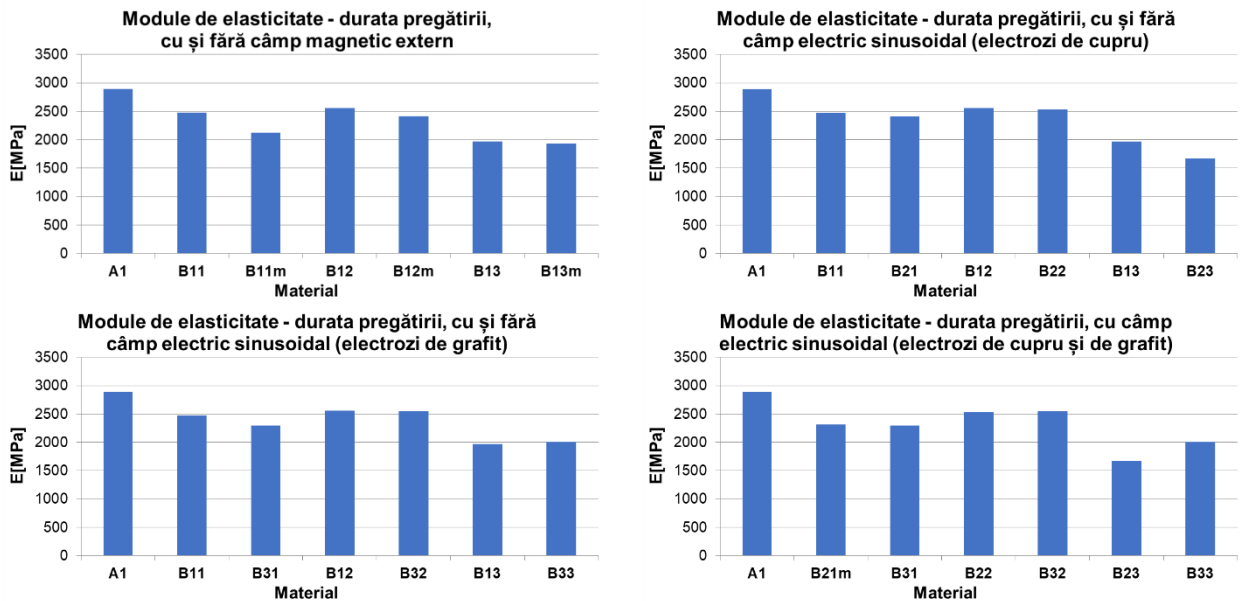
Fig.5.37. Comparative analysis of control techniques – three point bending

- the application of the sinusoidal electric field, by means of graphite electrodes, has the greatest effect in the case of materials formed immediately after the preparation of the epoxy resin mixture/solution of inorganic agents in DMF;

- the application of the sinusoidal electric field, by means of the copper electrodes, has no effect on the modulus of elasticity when bending for the material with intermediate preparation time (31 days);

- the application of the proposed control techniques produces - always - a reduction in the values of the bending elasticity modules of the materials to which they were applied.

5.4. Characterization of type B materials – conclusions

- the analysis of the variation of electrical conductivity of materials B indicates an increase of four to six orders of magnitude of this parameter, compared to epoxy resin;

- in the case of the analysis of the conductivity variation with temperature, two materials (B13 and B32) indicate an increase in conductivity with temperature, which means a semiconductor-type behavior;

- the application of the sinusoidal electric field, before pouring the polymerizable mixtures into the molds, produces effects on the photoconductivity of the analyzed materials, both when it is applied by means of copper electrodes and when it is applied by means of carbon electrodes (graphite);

- the smallest effect of the application of the sinusoidal field appears in the case of the materials formed after the application of the field through the copper electrodes and regardless of the duration of the preparation;

- for the materials with the longest preparation time, B31 (directly formed) and B33 (formed after the application of the electric field through the carbon electrodes) there is no dependence of the electrical conductivity on the temperature (on the analyzed temperature range);

- the photoconductivity of materials decreases when they are irradiated with radiation with wavelengths in the visible range and increases when they are irradiated with electromagnetic radiation in the IR range;

- materials B21m and B31m have a special thermal behavior, characterized by very high specific heat values (on the heating segments), but this behavior is no longer observable on the cooling segments;

- another remarkable behavior is that of the B32 material which presents higher specific heat values on the cooling segments compared to the values on the heating segments;

- the substance losses recorded during the thermal tests reveal that they are lower than in the case of class A materials, although NMP has a boiling point value higher than the boiling point value of DMF;

- in the case of the materials formed after the longest preparation time (Bx3), the mass losses of the materials formed in the presence of the magnetic field are lower than the substance losses of the homologous materials formed without the presence of the magnetic field;

- relatively high specific heat values (on the heating segments and on the two domains of positive temperature values) can also be observed in the case of Bx2 materials (B22 and B32), but they are not as high as those recorded in the case of materials B21 and B31;

- analyzing the data from this perspective, apparently, the extension of the pre-forming preparation duration leads to the reduction of the specific heat value (on the heating segments) of the materials subjected to sinusoidal electric fields (either with copper electrodes or with carbon electrodes);

- the amount of solution of inorganic precursors in DMF added to the epoxy resin is small enough not to produce radical changes in the properties of the matrix;

- the application of the sinusoidal electric field (either through the copper electrodes or through the graphite electrodes) contributes to the reduction of the elasticity modulus of the materials;

- keeping the mixture of epoxy resin/solution of inorganic agents in DMF under conditions of continuous agitation for longer periods of time, leads to obtaining materials with the modulus of elasticity when stretched with lower values (proportional to the duration of maintenance);

- the duration of the preparation of the mixture leads to the obtaining of materials with a tensile modulus of elasticity higher than the value of the modulus of elasticity of the material formed immediately after the preparation of the mixture epoxy resin/solution of inorganic agents in DMF, with the maximum value, after 31 days of preparation.

Chapter 6.

Characterization of Type C Materials

Following the analyzes carried out on the B-type materials, especially the photoconductivity analyses, I designed the C-type materials, for which I doubled the amounts of inorganic agents (metal chlorides) to check if the photoconductivity value is related to the concentration of the inorganic agents or only to their presence.

In addition, we designed materials modified with increasing amounts of inorganic agents solution in DMF and, although we no longer waited very long periods of time, we also provided for the analysis of the dependence of properties on the preparation time of the materials before formation. As in the case of type B materials, we also provided for the analysis of the effect of the presence of the magnetic field during polymerization.

6.1. Electric properties analysis of type B materials

In fig. 6.1. the temperature dependences of C-type materials depending on the casting time are shown and it can be seen that the Cx3 materials (those with the highest content of modifying agents) show the highest values of electrical conductivity and have a semiconductor-type behavior (increase in electrical conductivity value with increasing temperature). Moreover, these materials show a linear variation of electrical conductivity with temperature (the exception is material C33).
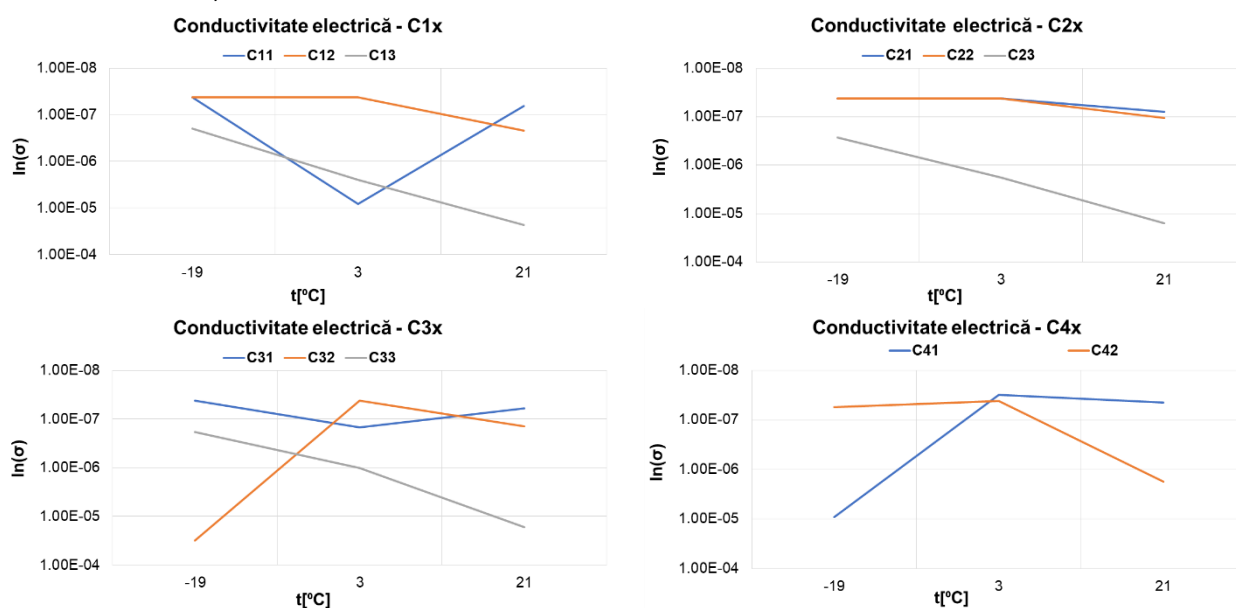
Fig.6.1. Electric conductivity dependence on temperature of C-type materials function of the forming moment

In fig. 6.2. what I described above can be seen even better. The behavior of all C1x type materials is almost identical (the exception being C41) – it is epoxy resin with the same amount of inorganic agent solution in DMF – there is a point of maximum conductivity (not necessarily at 3°C).

It is also surprising that the electrical conductivity values of the materials formed with 50ml of solution in DMF of metal chlorides, respect almost the same temperature dependence regardless of the time of casting (the exception, this time is the material C32).

With such a variety of results it is very difficult to say exactly what is going on. We built the research on the hypothesis that the duration of the preparation of the material (associated with the effect of applying the sinusoidal electric field – this time only through the graphite electrodes) could determine the formation of ceramic nanostructures with high electrical conductivity – this hypothesis is clearly invalidated by the Cx3 materials that have the same behavior at the same amount of solution of metal salts in DMF.
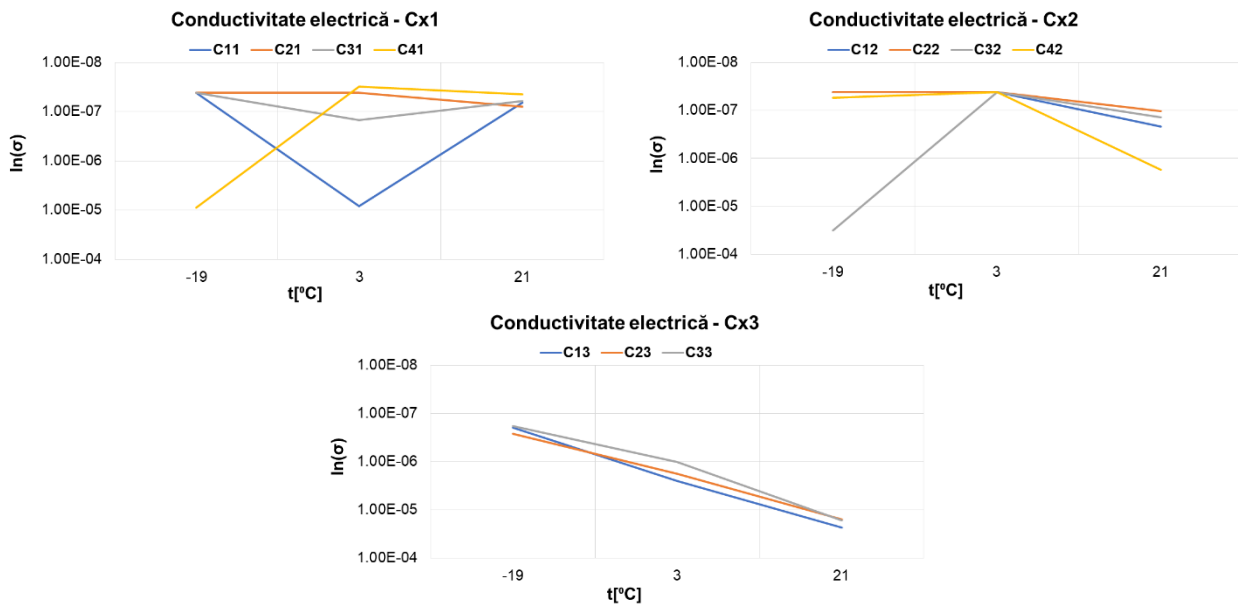
Fig.6.2. Electric conductivity dependence on temperature of C-type materials function of the inorganic agents solution in DMF volume

Regarding the photoconductivity of the materials, it was determined under the same conditions used in the case of materials of types A and B. Expectations were related to increases in the values of this parameter due to the higher concentration of inorganic agents. The results of the determinations are shown in fig.6.3.
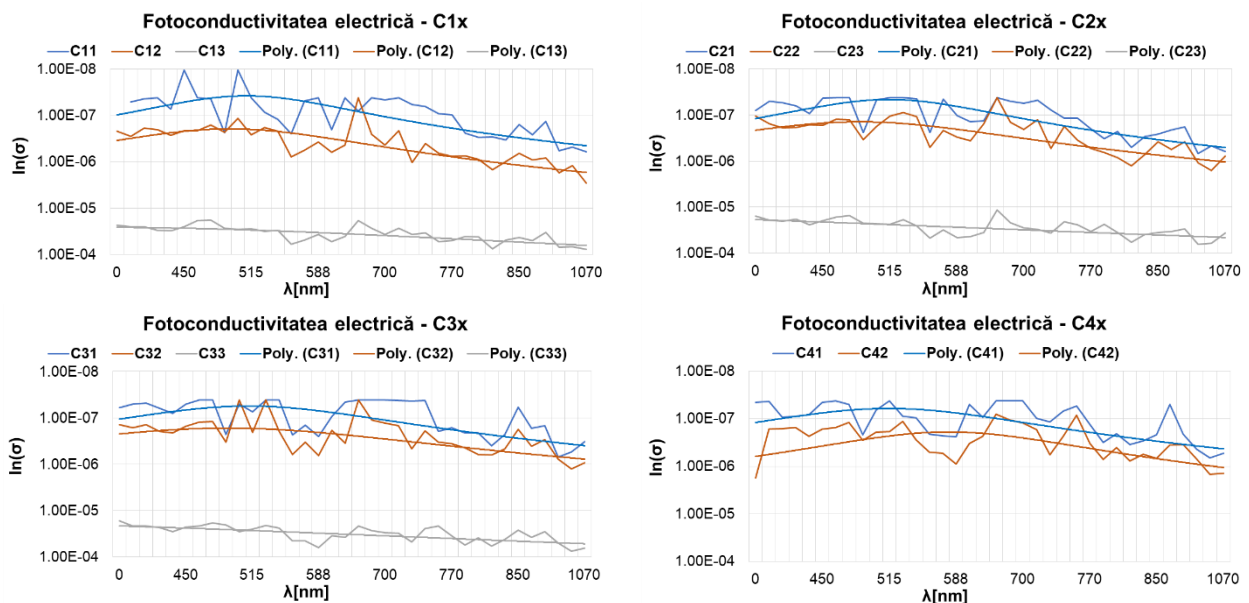
Fig.6.3. Electric photoconductivity of C-typr materials function of forming moment

Apart from the semi-conductor behavior found in the analysis of the previously presented data (the dependence of the electrical conductivity on the temperature value), the analysis of

the data presented in fig.6.3. indicates that x3 type materials (made with 75ml solution of inorganic agents in DMF) present the highest values of electrical photoconductivity and, if we also analyze the polynomial fits, these values increase linearly with the increase of the wavelength of the incident electromagnetic radiation. And this time I have to say that I am very sorry that I could not form the materials C43 and C43m as well.

If we associate this fact with the observation related to the lack of effects due to the application of the sinusoidal electric field, through the graphite electrodes, during the preparation it could be concluded that, in the case of Cx3 materials, stable structures were obtained (they are not affected by the application of the field sinusoidal electricity) with remarkable properties.
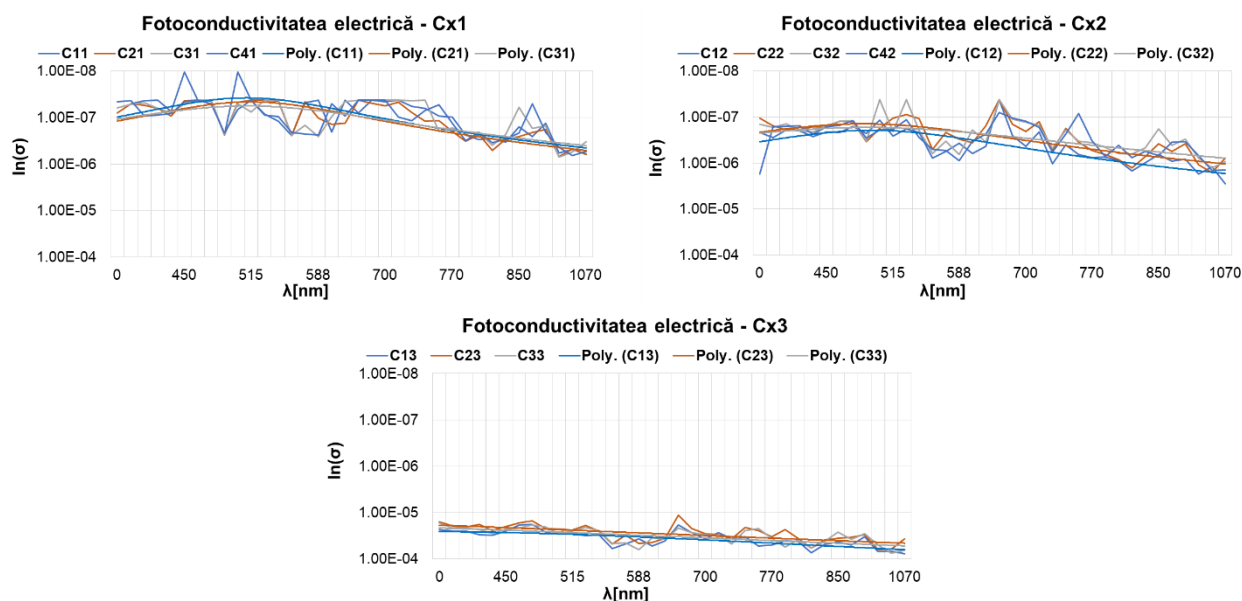
Fig.6.4. Electric photoconductivity of C-typr materials function of inorganic agents concetration

Analyzing the data presented in fig.6.4. it can be observed that the material C13 has the highest photoconductivity, followed by C33 and, finally, C23. Given that the polynomial fits are practically straight parallel and almost equidistant, the conclusion would be that the most photoconductive material is the one formed after a week of preparation of the modified polymerizable mixture.

6.1.1. Electric properties analysis of type C materials – conclusions

- Cx1 materials present a double concentration of inorganic agents, compared to type B materials (presented in chapter 5) and their behavior, from the point of view of the dependence of electrical conductivity on temperature and that of photoconductivity, is similar to that of type B materials ;

- the electrical photoconductivity of Cx2-type materials is slightly higher than that of Cx1-type materials, but not so high that it can be concluded that there is a direct proportional relationship of electrical photoconductivity with the concentration of inorganic agents (four to two times more high, in the case of Cx2 materials, compared to Cx1);

- for type C materials it can be said that there is no dependence of electrical conductivity or electrical photoconductivity on the duration of the preparation process of the polymerizable mixture.

6.2. Thermal properties analysis of type C materials

In fig. 6.6. are shown the curves describing the specific heat values of the Cx1 materials (which have twice the concentration of inorganic agents compared to the B materials) and which were formed at various times as shown above. Thus, instead of three analyzed materials, this time four materials are presented (eight if we take into account the fact that each of the analyzed materials were made in the natural polymerization variant, respectively, polymerization in an external magnetic field).

Fig.6.6. Specific heat of C-type polymer materials modified with the lowest value of concentration of inorganic agents in DMF, formed on the four different moments

In the case of type B materials, we have shown that there is a material with an extremely high value of specific heat (relative to the specific values of epoxy resin). In the case of materials of type Cx1 (fig. 6.6.), the only material with interesting behavior is C12 (cast after preparing the mixture for a week), which presents a high value of specific heat on the heating curves (at positive temperatures) compared to the other three materials, but a lower specific heat value, over the same temperature ranges) compared to the same other three materials.

Table 6 shows, as in the case of the analysis of type B materials, the mass losses recorded during the DSC tests (average values of the mass losses of the three samples analyzed from each material). A decrease in the amount lost can be observed in the materials formed in an external magnetic field, compared to the naturally polymerized counterparts. The exception is the pair C31, C31m.

Table 6. Loss of substance of Cx1 and Cx1m materials, during DSC tests

materials	C11	C11m	C21	C21m	C31	C31m	C41	C41m
Δm[mg]	1.27	1.17	1.47	1.07	1.27	1.30	1.03	0.83
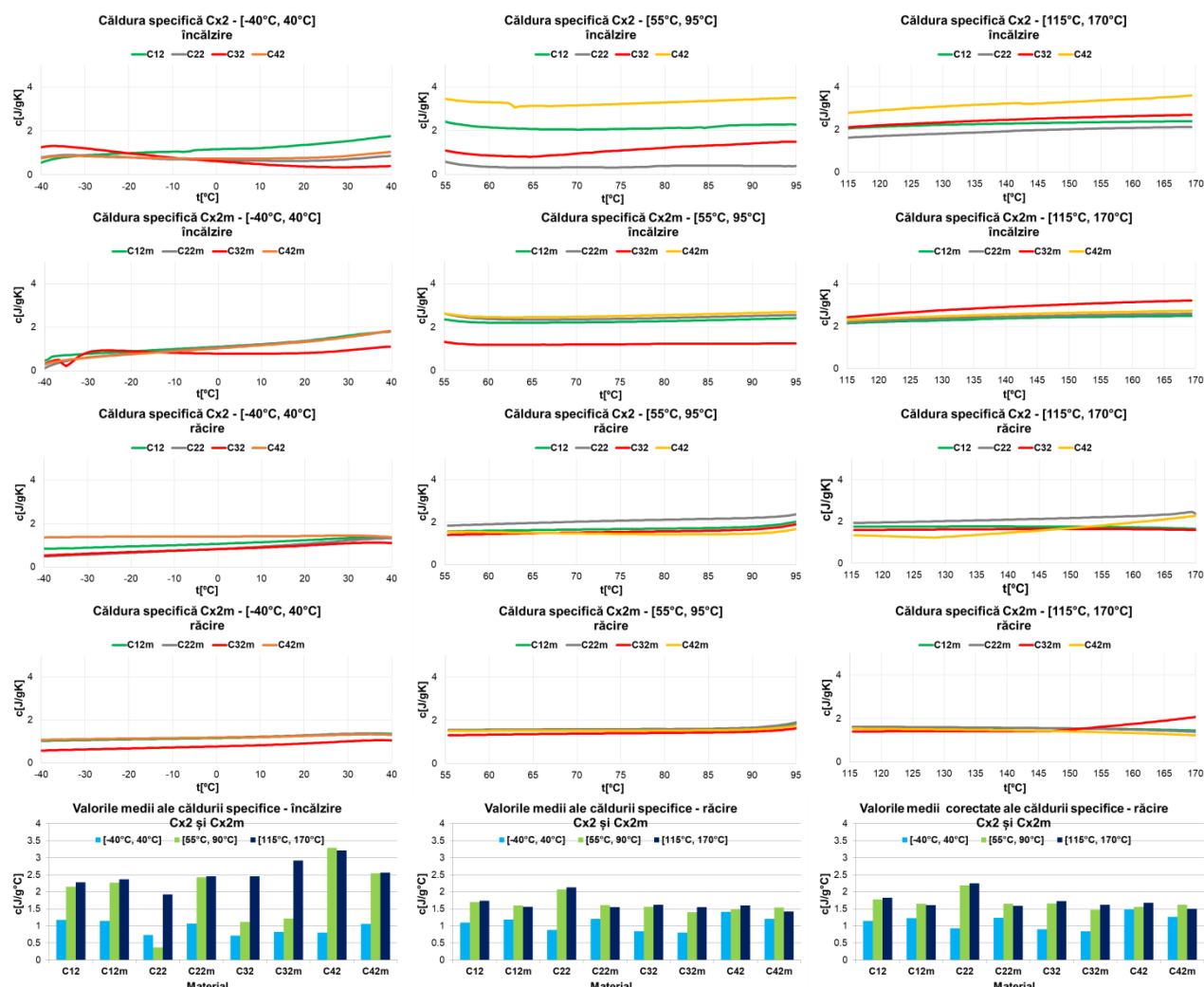
Fig.6.7. Specific heat of C-type polymer materials modified with the intermediate value of concentration of inorganic agents in DMF, formed on the four different moments

Regarding the materials with volume fraction 0.10 of the solution of inorganic agents in DMF – Cx2 type materials – the specific heat evolution situation (on the chosen temperature ranges) is presented in fig. 6.7. There may be differences in the concentration of inorganic agents between materials, given the fact that during the preparation period between castings, certain amounts of solvent have probably evaporated. As I took 50ml of solution (each time), if a certain amount of solvent evaporated, the concentration of inorganic agents increased.

Regarding the substance losses recorded during the DSC tests - table 7. - it can be observed, again, that the application of the external magnetic field causes the reduction of substance losses. Paired materials are formed at the same time and therefore have the same content of DMF and inorganic agents, respectively. The amount of DMF is double compared to Cx1 type materials (at the same x).

Table 7. Loss of substance of Cx2 and Cx2m materials, during DSC tests

materials	C12	C12m	C22	C22m	C32	C32m	C42	C42m
Δm[mg]	1.97	1.17	2.10	1.07	2.13	1.67	1.97	1.97

Under these conditions, it was expected that the recorded losses would be higher than in the case of materials of type Cx1 and Cx1m - which is obvious if we compare the data in tables 6 and 7. Thus it can be concluded that the loss of substance is mainly related to evaporation of the solvent (DMF). As the application of the external magnetic field during polymerization produces a significant reduction in mass loss (except for the C42, C42m pair) it can be concluded that the presence of the magnetic field causes a better binding of the solvent in the epoxy resin.

In fig. 6.8. the experimental data obtained for the three pairs of modified materials with the largest amount of solution – volume fraction 0.15 are shown.
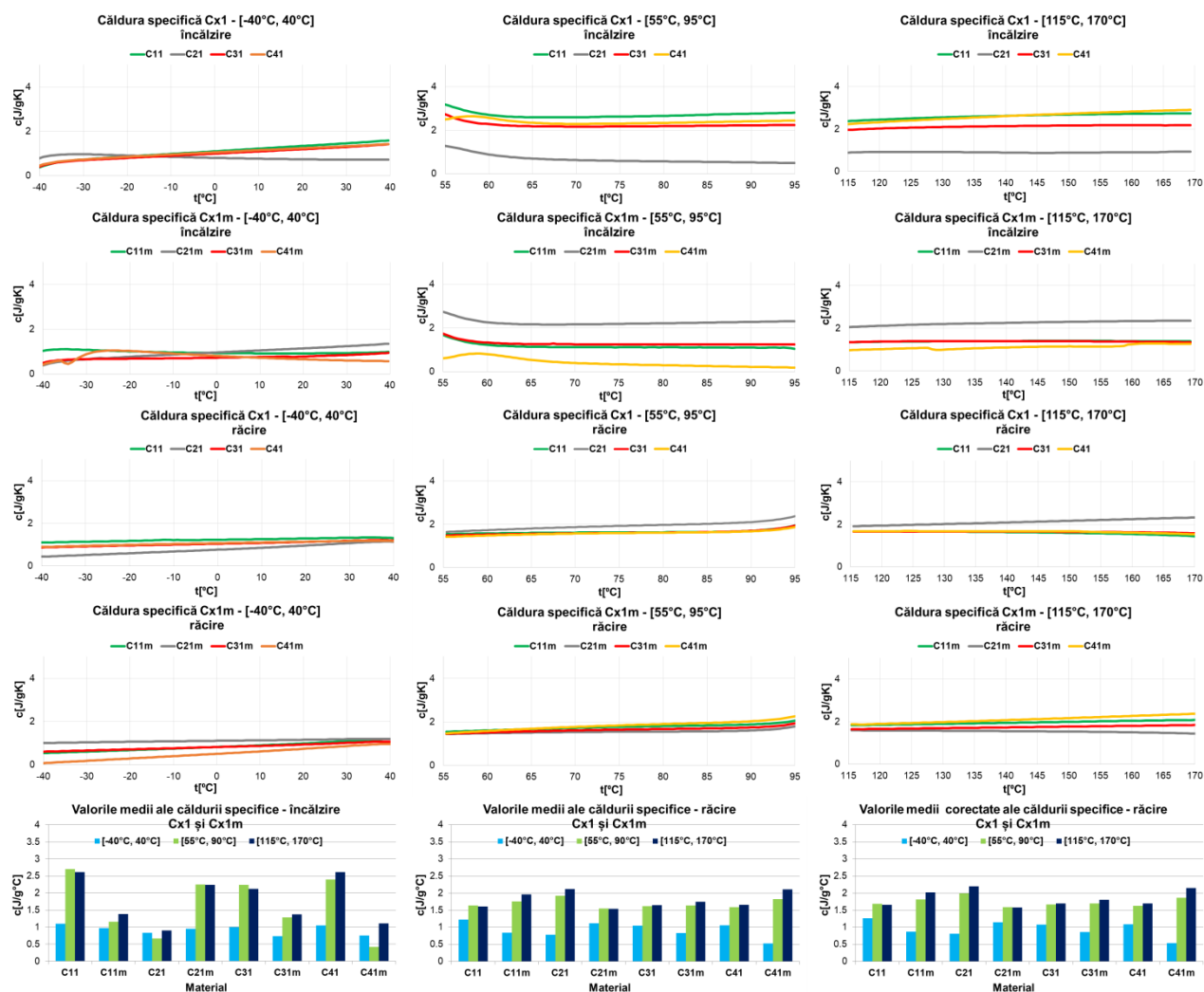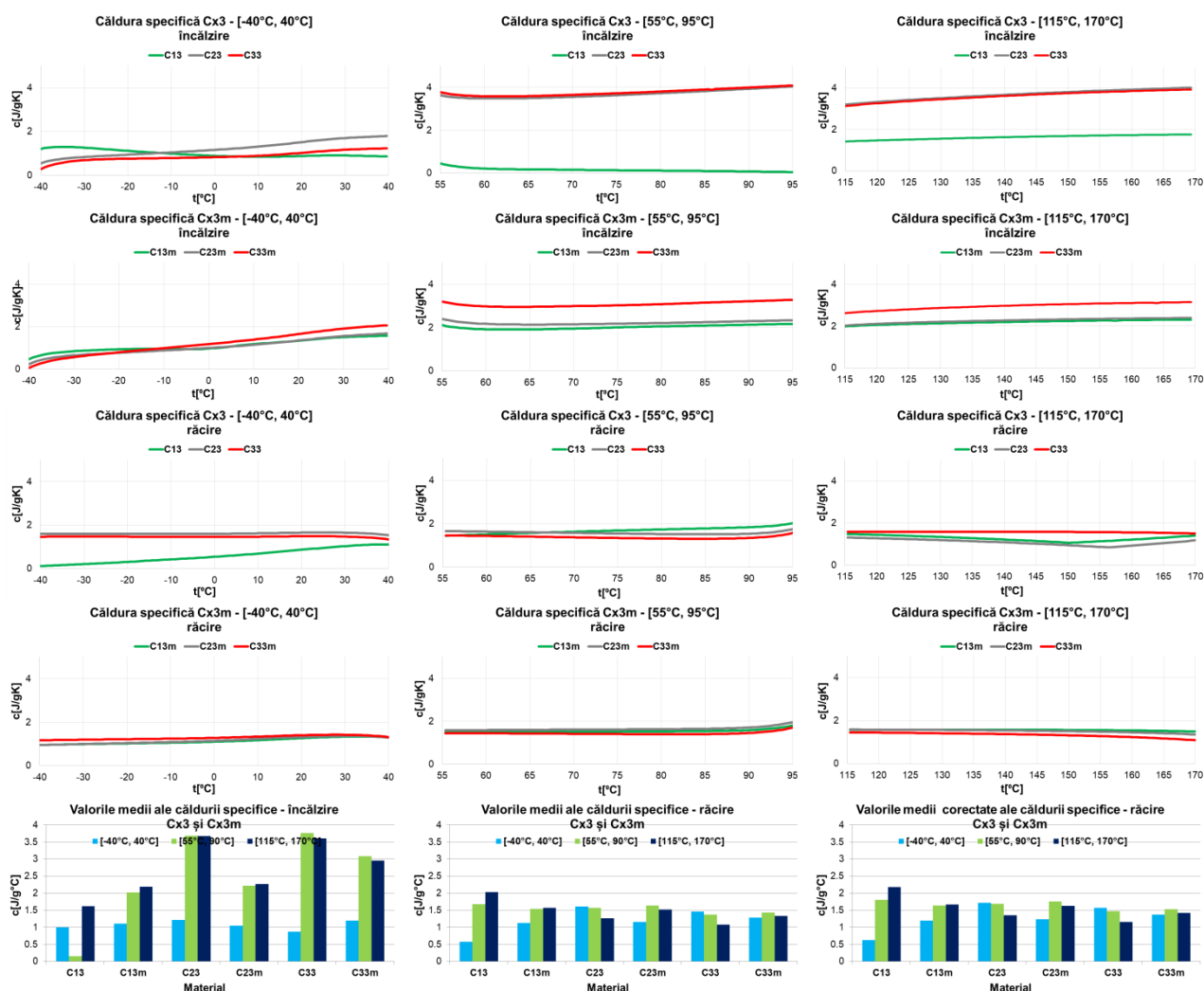

Fig.6.8. Specific heat of C-type polymer materials modified with the highest value of concentration of inorganic agents in DMF, formed on the four different moments

On the heating segments, especially at positive values of temperature, quite high values of specific heat can be observed - not so high, however, as those observed in the case of B-type materials.

As expected, in all cases the average corrected specific heat values are higher than the measured ones – this is only the cooling segments. No conclusions can be drawn regarding the effect of applying an external magnetic field during polymerization.

Table 8. Loss of substance of Cx3 and Cx3m materials, during DSC tests

material	C13	C13m	C23	C23m	C33	C33m
Δm[mg]	3.27	2.77	2.90	3.07	2.57	3.07

Table 8 shows the average mass losses recorded for Cx3 and Cx3m materials, and it can be seen that the substance losses of the materials polymerized in a magnetic field are higher than those of their naturally polymerized counterparts (except for the pair C13, C13m). This situation is opposite to that found in materials Cx1 and Cx2 and could be explained by the presence of a greater amount of inorganic agents in the epoxy matrix. The effect of the magnetic field would be due to this larger amount, which would counterbalance the larger amount of DMF.

6.2.1. Thermal properties analysis of type C materials – conclusions

- substance losses, following thermal tests, are higher than those recorded in the case of type B materials;
- very high specific heat values are not recorded (as in the case of type B materials), but there are materials that present (on the heating segments) relatively high values of this parameter;
- for low concentrations of the solution of inorganic agents in DMF, the external magnetic field (applied during polymerization) reduces substance losses, suggesting a coupling effect of DMF to the epoxy resin;
• a future study should be carried out with a uniform magnetic field, to be able to identify the real effect of its presence during polymerization.

6.3. Mechanical properties analysis of type C materials

For what follows, I must state that, based on the research carried out by Georgel Mihu and Mihaela-Claudia Gorovei, it is expected that the materials will be softer (moduli of elasticity with lower values) as the amount of solvent used increases to modify the properties of the epoxy resin, even if, at the same time, it increases the amount of inorganic agents.

6.3.1. Tensile tests of type C specimens

In fig. 6.9. the individual σ/ε curves (for each specimen) and the average (red) σ/ε curves describing the tensile behavior of the specimens of the materials formed with 25ml solution of inorganic agents in DMF, after applying the solution preparation treatments before pouring the mixtures are shown polymerizable.
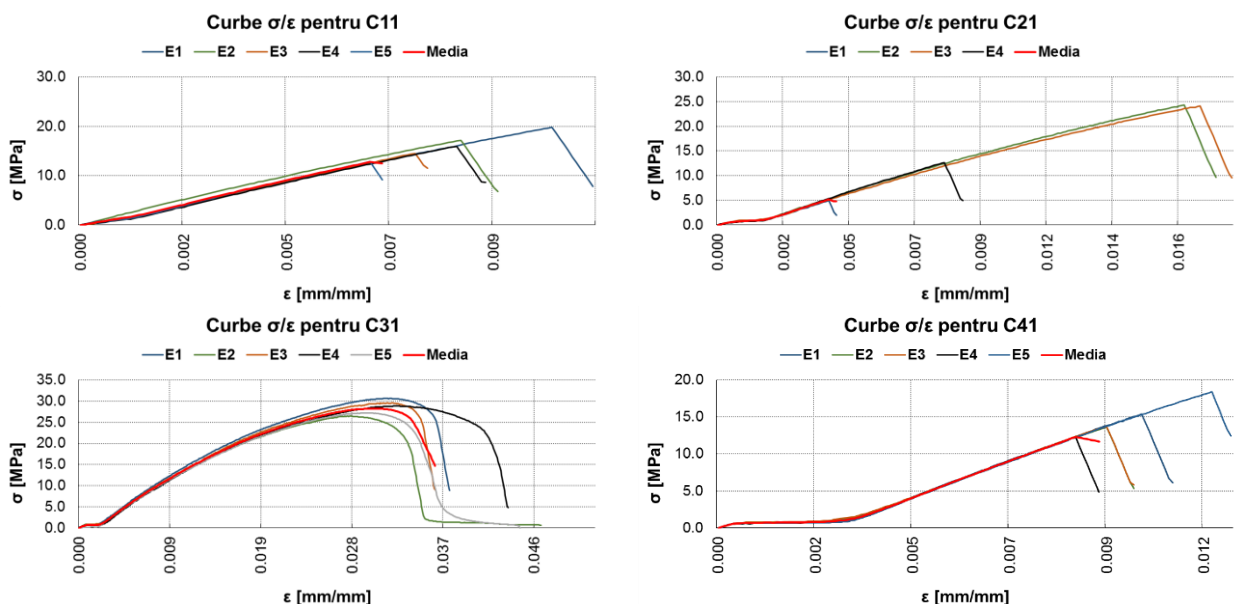
Fig.6.9. σ/ε curves of the 25ml solution of inorganic agents in DMF modified materials

The most obvious observation is related to the different appearance of the individual curves (and the average curve) corresponding to the samples of material C31. The passages, practically horizontal, appearing in the profiles of the σ/ε curves of materials C21, C31 and C41 are evident. These passages are easier to see in the details shown in fig. 6.10.
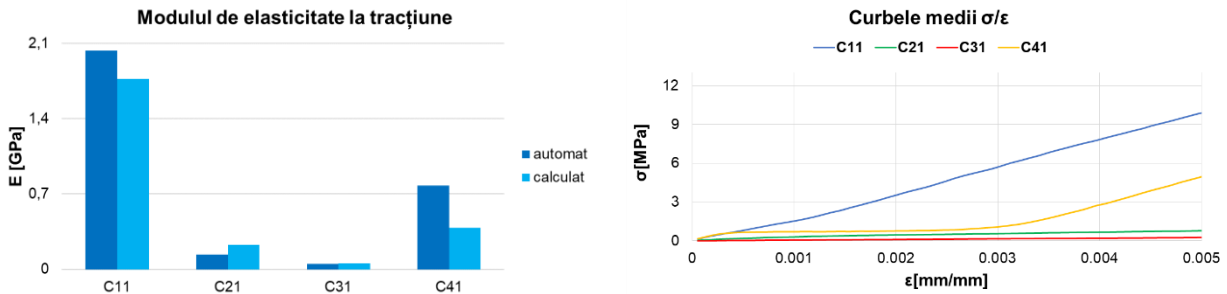
Fig.6.10. Elastic moduli and details of averaged σ/ε curves – Cx1

It is interesting that materials C21 and C31 show (in the domain of small specific strains) the same type of behavior (with a plus for C21), while material C11 keeps the characteristics of epoxy resin (rigid behavior). In the case of material C41, which exhibits rigid fracture, but after passing the horizontal bearing, the behavior is similar to that of materials C11 and C21. Regarding the tensile modulus values, it is obvious that C31 presents the lowest value of the parameter.

In fig. 6.11. the individual curves and the average curves obtained when testing samples of Cx1m materials (homologous to Cx1 materials, but polymerized in the presence of an external magnetic field) are shown.

From the analysis of the profile of the curves it can be concluded that the presence of the magnetic field does not change the type of response of the material. C31m, like C31, behaves differently compared to the other three analyzed materials which, in turn, do not show changes compared to their counterparts.

Fig.6.11. σ/ε curves of the 25ml solution of inorganic agents in DMF modified materials polymerized in external magnetic field

As for the values of the elasticity modules of the Cx1m materials, they are presented in fig. 6.12. and a reduction of these values can be observed compared to those recorded for the

homologous materials. Equally, the details of the average curves of the analyzed materials confirm the above statement related to the similarity of the curve profiles with the profiles of the homologous curves (Cx1).

Reductions in the values of the tensile modulus of elasticity, for materials polymerized in the presence of an external magnetic field, I recall, were also observed in the case of the analysis of type B materials.
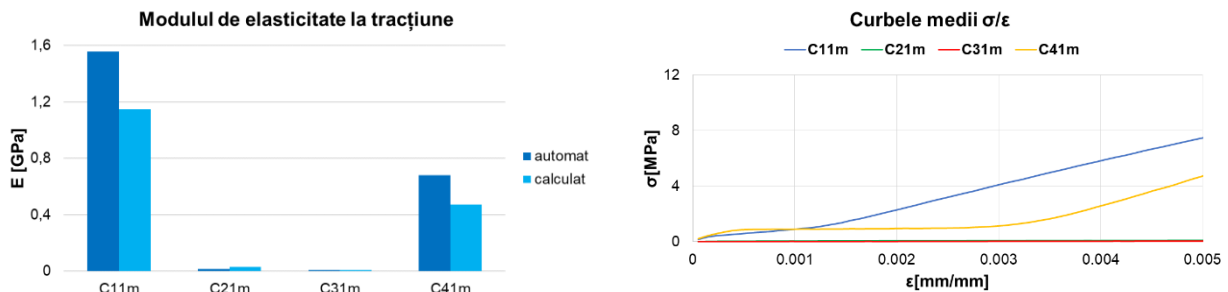
Fig.6.12. Elastic moduli and details of averaged σ/ε curves – Cx1m

The following materials are those modified with a volume fraction of 0.10 of the solution in DMF of the inorganic agents in the epoxy resin – Cx2 and Cx2m, with x taking the same values (from 1 to 4) and representing the time of material formation.

Relative to the presence of inorganic agents in the epoxy resin, it is four times higher than that corresponding to any type B material. At the same time, the presence of DMF is double and as it is a plasticizer the result should be softer materials.

In fig. 6.13. individual stress/strain curves and average stress/strain curves for the tested specimens of Cx2 materials are shown. The change in the profile of the curves (compared to the Cx1 materials) confirms what was written before – the materials have a different behavior, an aspect also confirmed by the significant reduction in the tensile strength values.
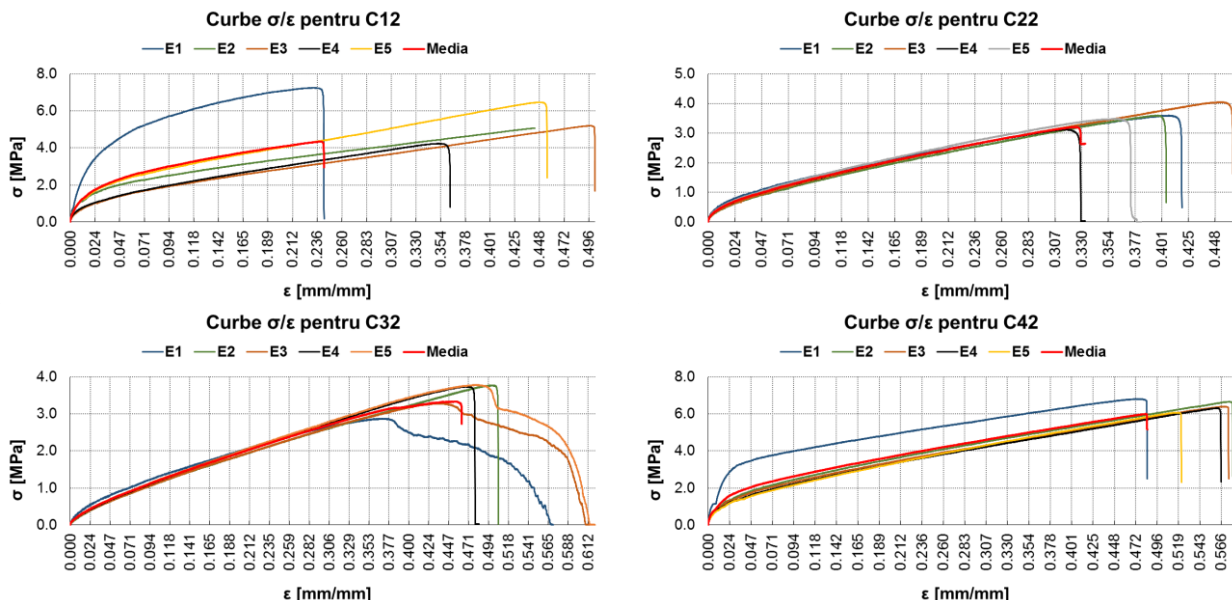
Fig.6.13. σ/ε curves of the 50ml solution of inorganic agents in DMF modified materials

It can also be noted that, for material C32 (cast after two weeks of preparation), three of the specimens do not break. It is also interesting that, among the analyzed materials, the samples corresponding to C22 and C32 show close responses (material C42 can also be

included here, with the exception of sample E1), while material C12 (poured immediately after obtaining the solution of the inorganic agents in DMF) shows a significant scatter of results. This could be a proof of the homogeneity of the materials formed after the long-term preparation of the solution of the inorganic agents in DMF.
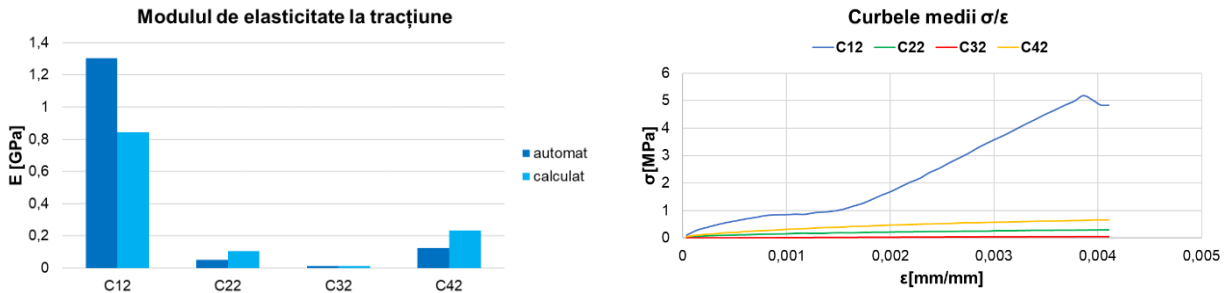
Fig.6.14. Elastic moduli and details of averaged σ/ε curves – Cx2

In fig. 6.14. the values of the elastic moduli and the details (in the area of small deformations) of the average stress/strain curves of the materials analyzed above are presented.

In fig. 6.15. the individual curves and the average curves (stress/strain) of the materials modified with 50ml solution of metal chlorides in DMF and polymerized in the presence of the external magnetic field are shown.

This time it can be seen that all the tested specimens break. In the case of C42m (as in the case of C42) only one specimen (also E1) has a different behavior. Specimen responses are less scattered for materials C12m and C32m (homogeneous materials?).

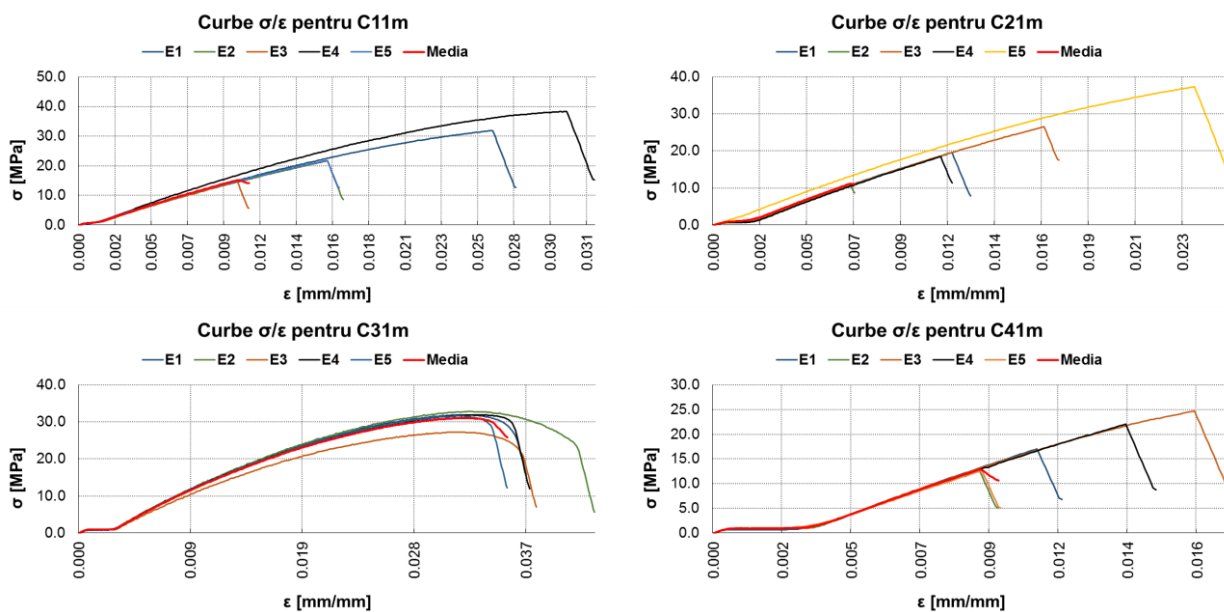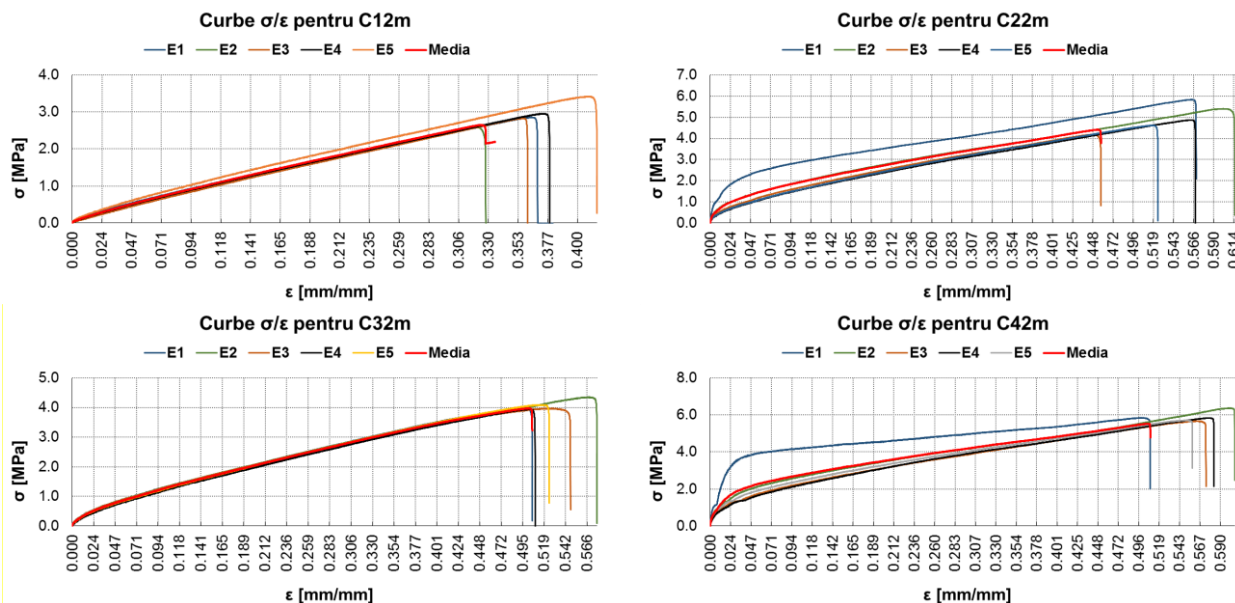**Fig.6.15.** σ/ε curves of the 50ml solution of inorganic agents in DMF modified materials polymerized in external magnetic field

An analysis of the tensile strength reveals that the presence of the external magnetic field during polymerization affects material C12, but has positive effects for the other three materials.
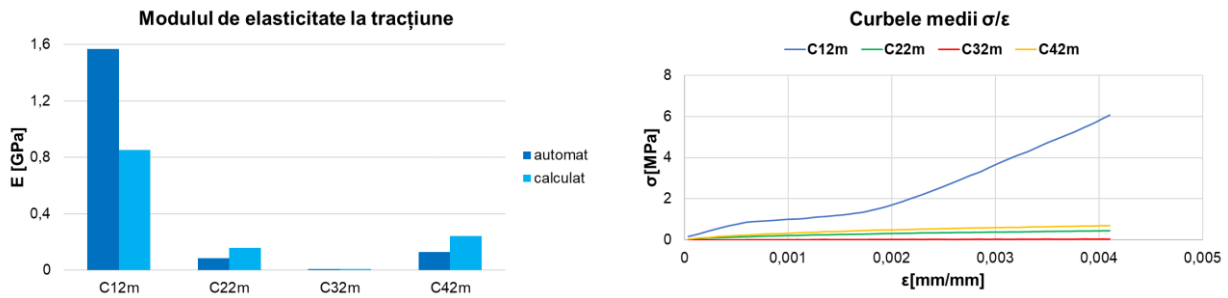
Fig.6.16. Elastic moduli and details of averaged σ/ε curves – Cx2m

Regarding the values of the tensile modulus of elasticity (fig. 6.16.) a slight increase can be observed regarding the C22m material, with higher values than the C22 counterpart, but also for C42m compared to C42.
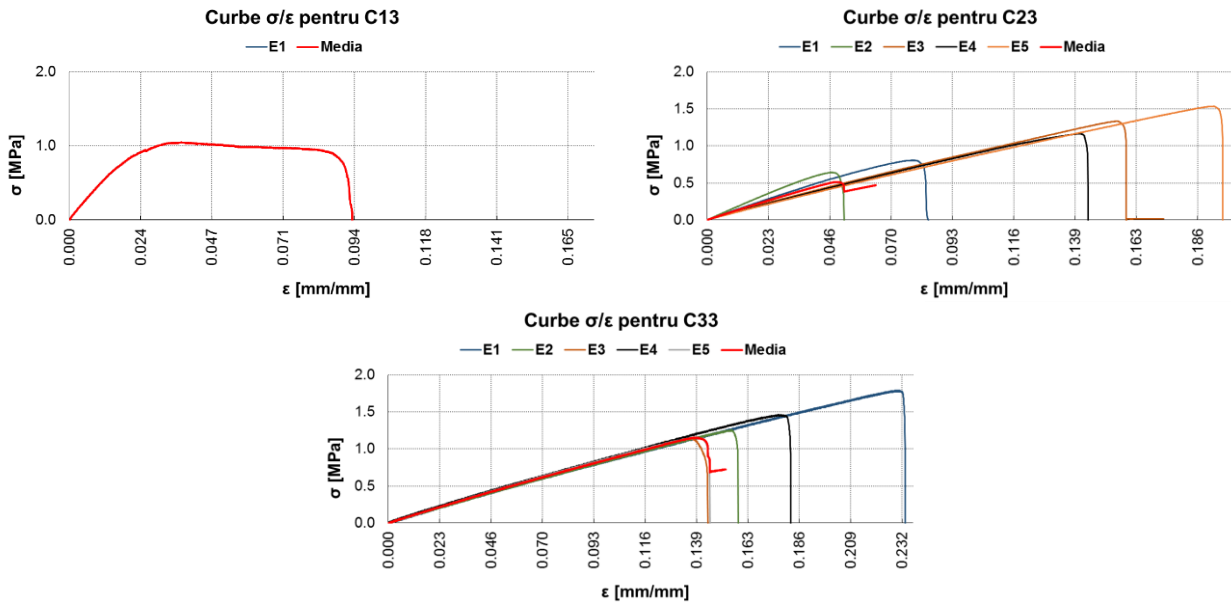
Fig.6.17. σ/ε curves of the 75ml solution of inorganic agents in DMF modified materials

The individual curves and the average curves corresponding to the tensile tests performed on the samples of Cx3 materials are shown in fig. 6.17. As can be seen, in the case of the C13 material, unfortunately, we only had one sample available. For this reason, obviously, only one curve appears in the representation. This (undesirable) situation was generated by the fact that, in the case of this material, we recorded losses of polymerizable mixture due to an imperfection in closing the mold.
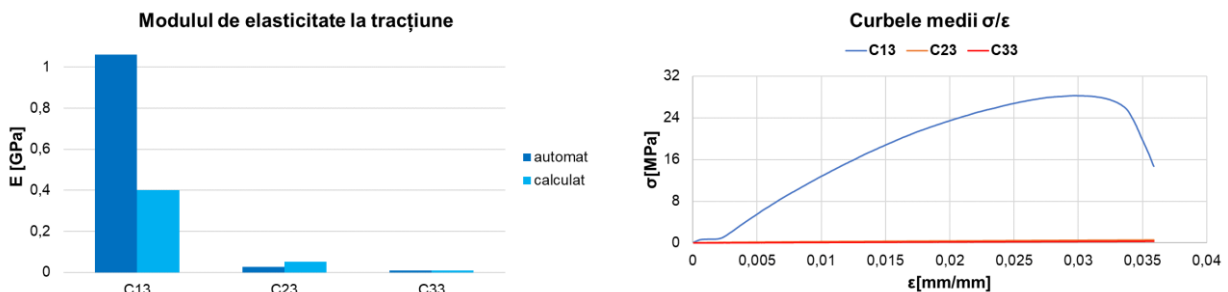
Fig.6.18. Elastic moduli and details of averaged σ/ε curves – Cx3

The values of the elastic moduli are much lower than those recorded in the case of materials Cx1 and Cx2 (due to the large amount of DMF), as can be seen in fig. 6.18. by comparison with fig. 6.10. and fig. 16.14.
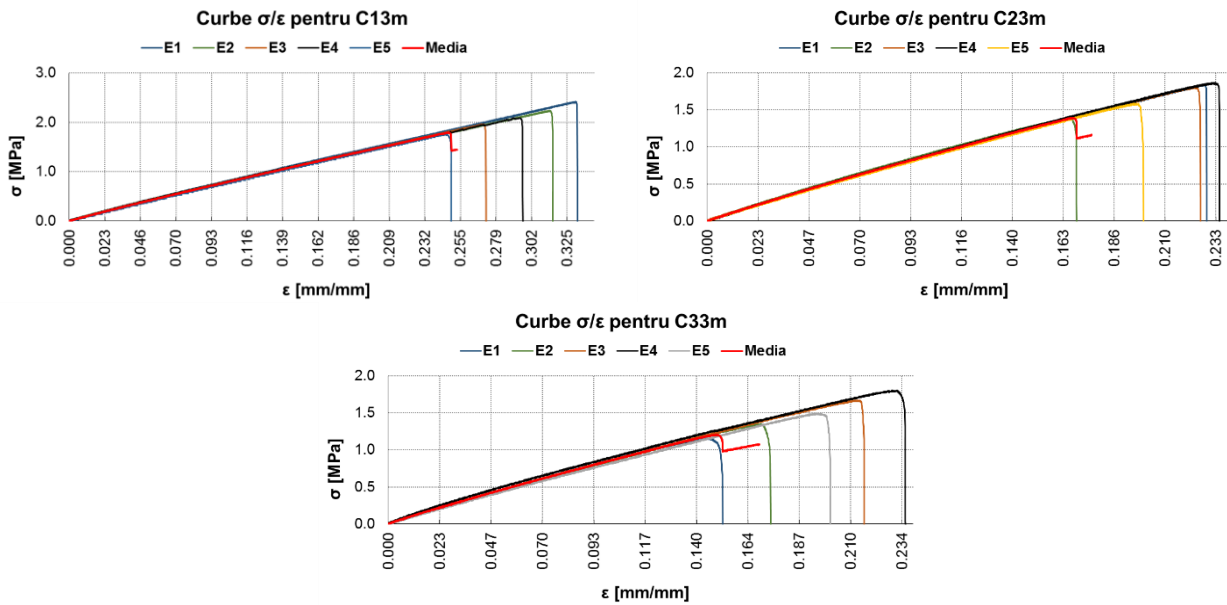
Fig.6.19. σ/ε curves of the 75ml solution of inorganic agents in DMF modified materials polymerized in external magnetic field

Surprisingly, the polymerization of Cx3 materials in external magnetic field, i.e. Cx3m materials have similar elastic responses (fig. 6.19.). A reduction in tensile strength can be observed with the duration of the precast preparation process. Probably if I had enough material and managed to cast the last two materials C43 and C43m, the same trend could have been found (I made a similar observation in the case of the electrical photoconductivity analysis of these materials).
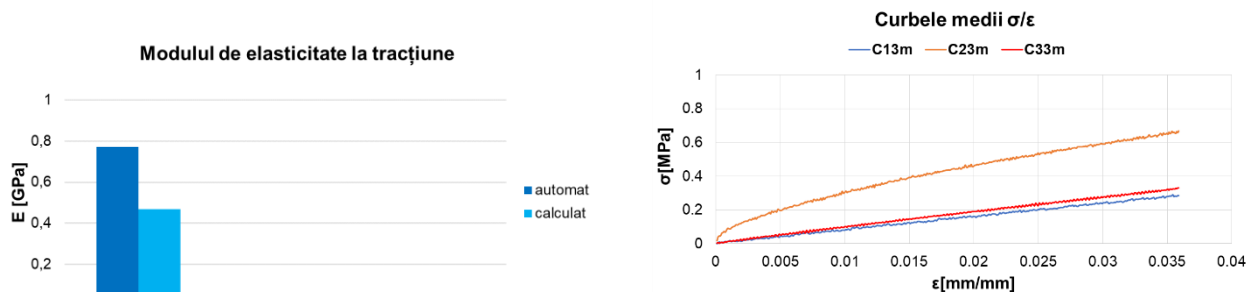
Fig.6.20. Elastic moduli and details of averaged σ/ε curves – Cx3m

In fig. 6.20. the values of the elastic moduli of the Cx3m materials (polymerized in the presence of the magnetic field) and the details of the stress/strain curves for the domain of small strains are shown. Compared with the data presented in fig. 6.18. the reduction of the values of the elasticity modules can be observed.

6.3.2. Tensile tests of type C materials - conclusions
- the materials with the best electrical photoconductivity (Cx3) show the worst mechanical performance;
- a reduction in the tensile strength values and, correspondingly, a reduction in the tensile modulus values can be observed, with the increase in the amount of inorganic agent solution used to modify the epoxy resin;

72

- no rules can be discerned regarding the effect of the duration of the preparation of the solution (at the same amount used to modify the epoxy resin) on the mechanical performances of the materials obtained;

- with the increase in the amount of metal chloride solution in DMF, used to modify the properties of the epoxy resin, the tested samples have close mechanical responses and this can be considered an indication of their homogeneity.

6.3.3. Three point bending tests of type C materials

As in the case of type B materials, the three-point bending tests were carried out on rectangular specimens having material thickness (5mm), width 15mm supported on supports located at a distance of 60mm.
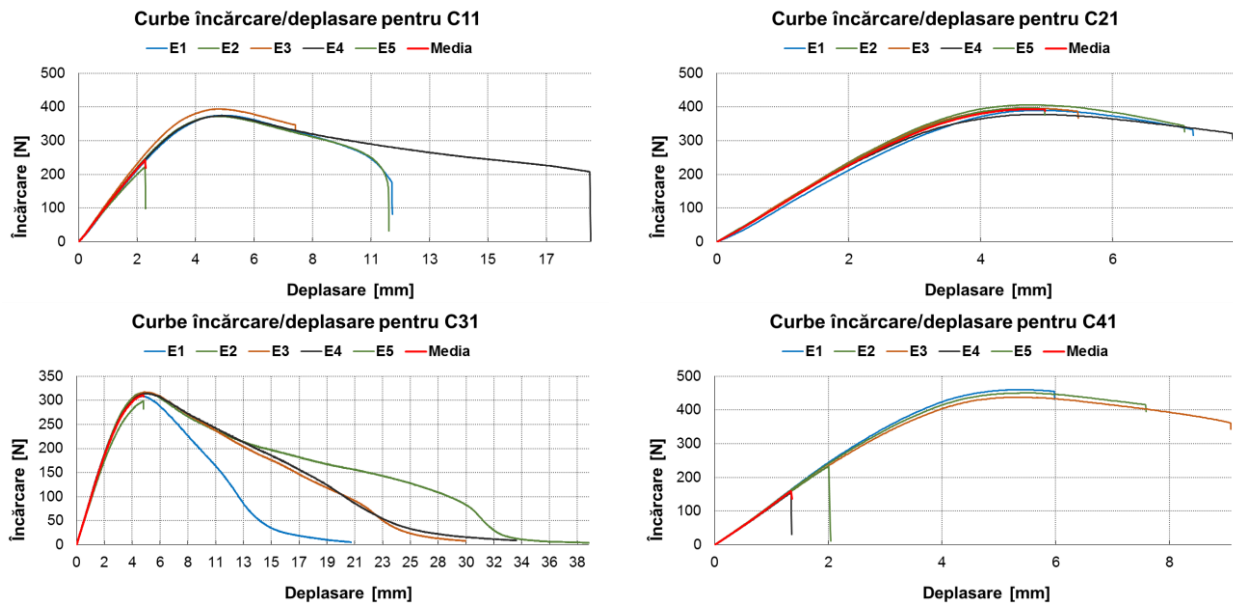
Fig.6.21. Loading/displacement curves of 25ml solution modified polymer materials – Cx1

In fig. 6.22. the elastic moduli of the analyzed materials and the details (in the area of small displacements) of the average load/displacement curves corresponding to the Cx1 materials are presented.
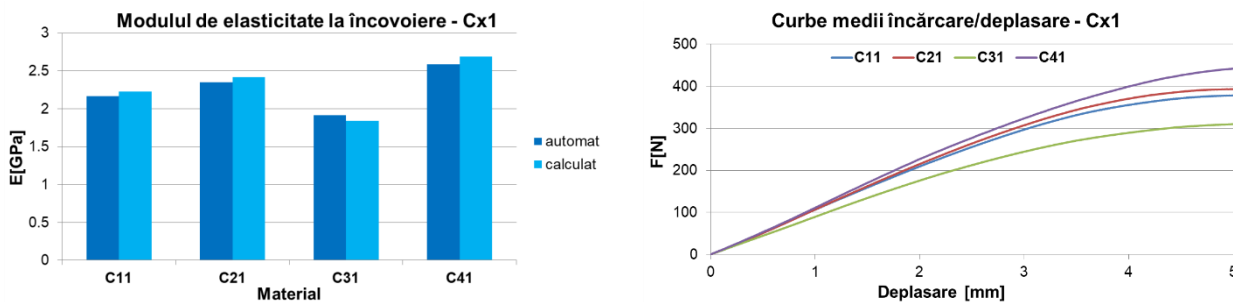
Fig.6.22. Elastic moduli and averaged curves (detail) – Cx1

The calculated values of the flexural modulus were determined as we showed in the analysis of type B materials, at a displacement of the punch of 2.5mm. The highest values of the modulus of elasticity correspond to material C41 – the one for which the solution preparation process took the longest (three weeks). This means that the 25ml of solution used contains a larger amount of inorganic agent.

Fig.6.23. Loading/displacement curves of 25ml solution modified polymer materials polymerized in external magnetic field – Cx1m

In fig. 6.23. the individual curves and the average curves corresponding to the three-point bending tests performed on the samples of materials modified with 25 ml of inorganic agents solution in DMF and polymerized in an external magnetic field – Cx1m are shown.

By comparison with the data presented in fig.6.21. it can be seen that the profiles of the load/strain curves do not change, nor do changes occur in the values of the maximum loads.

In fig. 6.24. the values of the elastic moduli and details of the average curves for the Cx1m materials are shown, and it can be seen that the effect of applying the external magnetic field is stronger on the C11m material – a 0.7GPa reduction in the elastic modulus compared to its C11 counterpart. For the materials cast after one week and two weeks of solution preparation, respectively, the application of the external magnetic field apparently produces no effects on the flexural modulus values. For the material cast after three weeks of solution preheating, the application of the external magnetic field leads to an increase in the value of the flexural modulus.
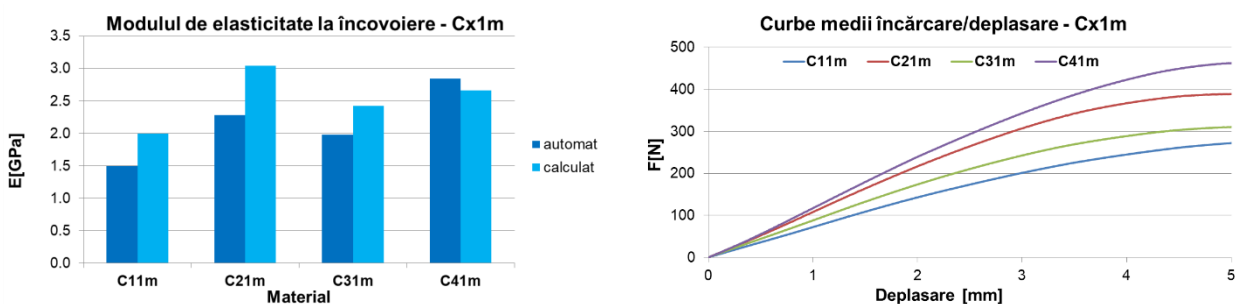
Fig.6.24. Elastic moduli and averaged curves (detail) – Cx1m

For the materials modified with 50ml solution of metal chlorides in DMF, as I stated in the stretch tests, I expected them to be softer. In fig. 6.25. the individual curves and the averages of the load-displacement curves obtained from the three-point bending tests are shown.

It can already be seen that – except for the C42 material – the curves are thicker. Being very soft, these materials rest on the supports producing oscillations of the load value and leading to this aspect of the curves.
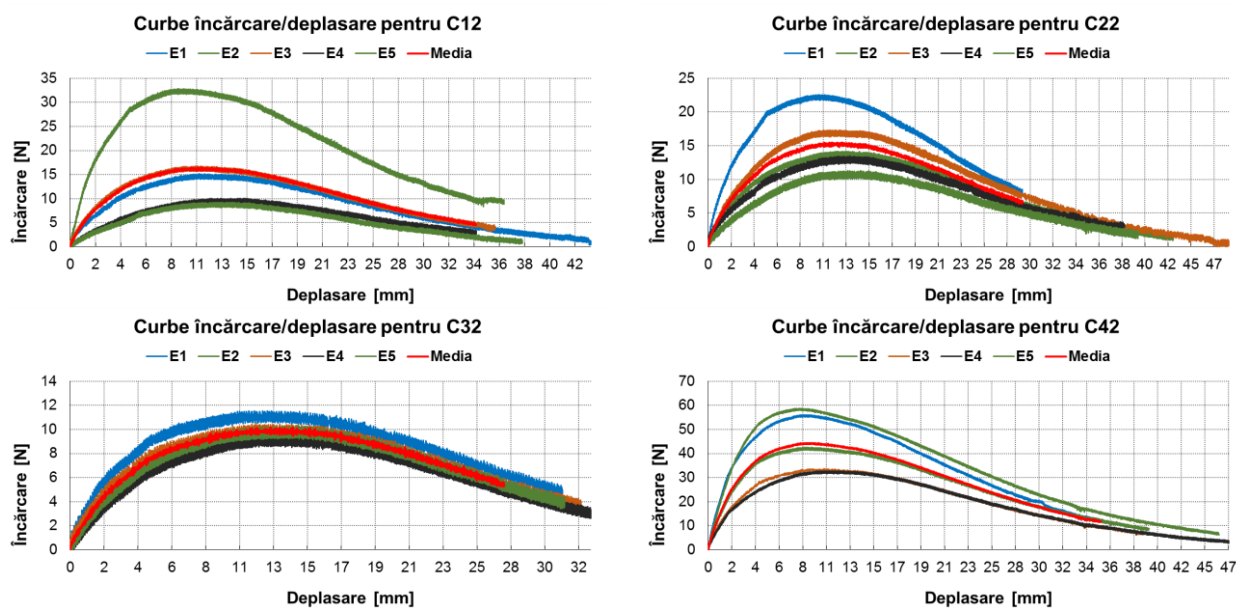
Fig.6.25. Loading/displacement curves of 50ml solution modified polymer materials – Cx2

It is easy to notice, by comparison with the information presented in fig.6.21., that the maximum load decreases by an order of magnitude. With the exception of material C32 whose samples behave practically identically, for the other three materials the experimental data are very scattered. This could be a consequence of the inhomogeneity of the materials or the consequence of an experimental error related to the non-uniformity of the thicknesses of the tested specimens. Equally, it is possible that - due to fatigue - some specimens were not placed with the long axis perpendicular to the axes of the two supports. Such a placement error leads to an error in the evaluation of the modulus of elasticity due to the larger apparent width of the specimen.
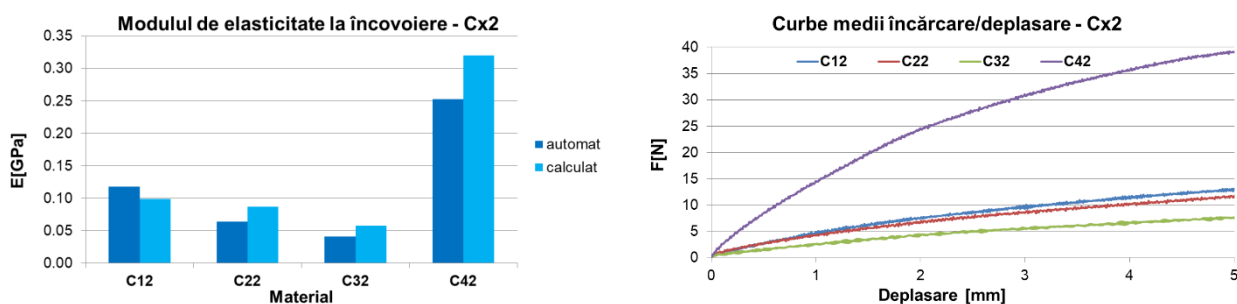
Fig.6.26. Elastic moduli and averaged curves (detail) – Cx2

In fig. 6.26. flexural modulus values and details of load/displacement curves for Cx2 materials are shown. Doubling the amount of solution of inorganic agents in DMF causes a reduction of the elastic modulus values by an order of magnitude (at least). Next, there remains the bending elasticity of the material C42 – with the highest value of the modulus of elasticity. The situation is the same as that observed for material C41 and, from this point of view, the three-week preparation period leads to the highest values of the elastic modulus.

In fig. 6.27. the experimental data obtained from the three-point bending tests of the materials modified with 50ml solution of metal chlorides in DMF and polymerized in an external magnetic field are presented. The curves preserve the profiles observed in the case of the naturally polymerized homologous materials (Cx2).
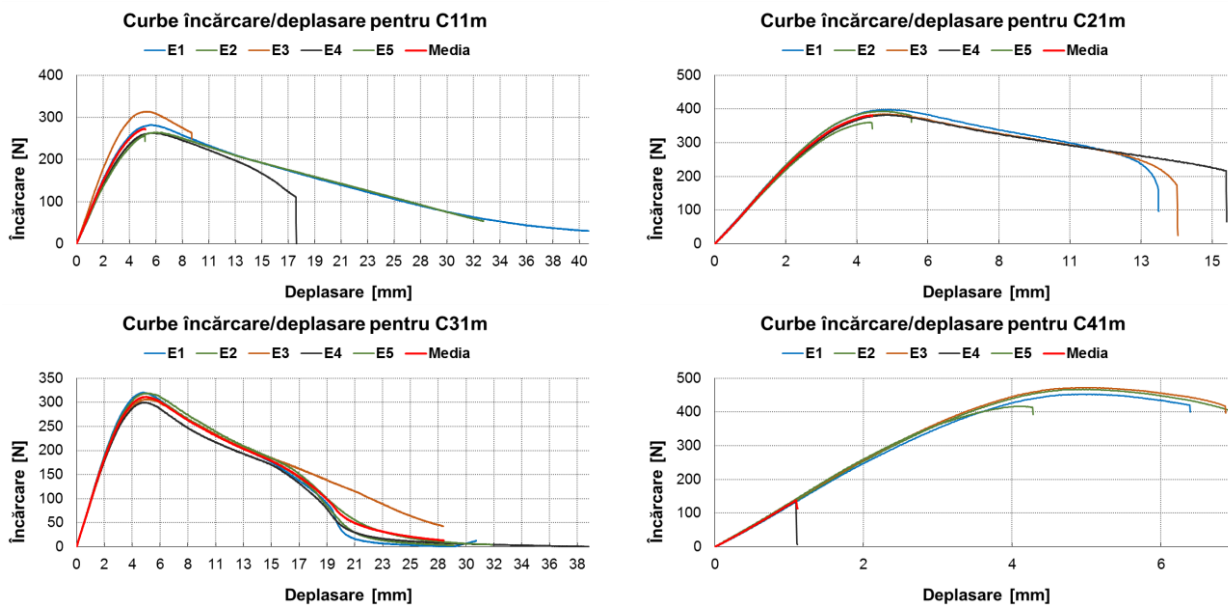
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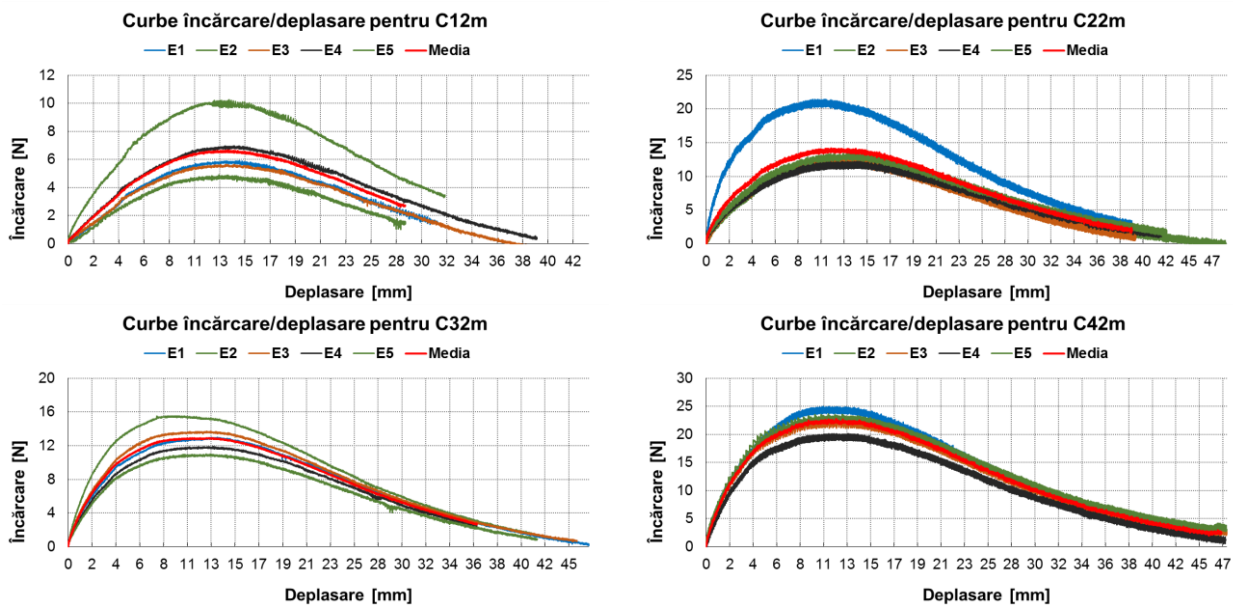
Fig.6.27. Loading/displacement curves of 50ml solution modified polymer materials polymerized in external magnetic field – Cx2m

Analyzing the curves, it can be seen that in the case of the C32m material, the lines are thinner than those observed in the natural polymerized counterpart (C32), which could mean that the stability of the polymerized material in an external magnetic field is greater. The situation is reversed for the C42, C42m pair.

In the case of these materials (Cx2m), the dispersion of the experimental data is lower than that observed in the case of naturally polymerized materials (Cx2).
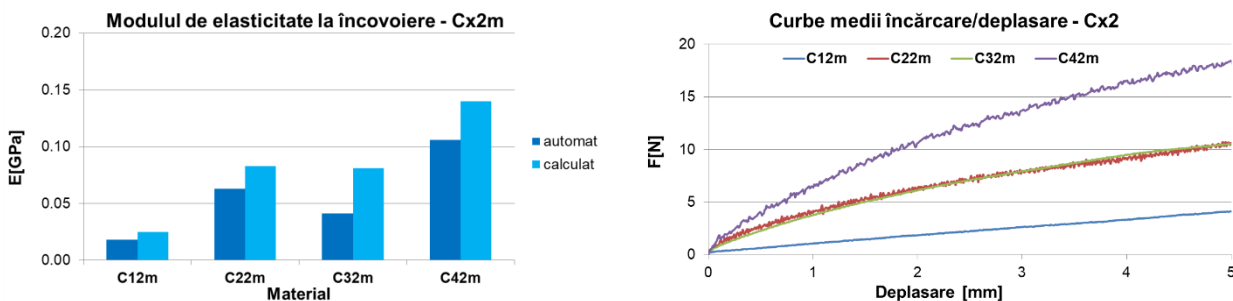
Fig.6.28. Elastic moduli and averaged curves (detail) – Cx2m

The values of the flexural modulus and the details of the average load/displacement curves of the materials are shown in fig.6.28. It can be observed the reduction of the values of the elasticity modules of the materials, compared to the homologous materials (fig. 6.26.). The strongest effect of the external magnetic field is visible on the C12m material. As in the case of materials Cx1 and Cx1m, apparently, polymerization in a magnetic field does not significantly change the values of the flexural modulus. The material with the longest duration of solution preparation presents, again, the highest value of the flexural modulus of elasticity.

For the last part of the analysis of the results of the three-point bending tests, the materials Cx3 and Cx3m remained. Cx3 materials are the ones that showed semiconductor-type behavior (directly proportional dependence of electrical conductivity on temperature) and the highest values of electrical photoconductivity.

As can be seen from the experimental data presented in fig.6.29. the materials are very soft. For material C13 we only had two samples available for testing. The values of the maximum loads are reduced compared to all the materials analyzed so far and the

displacements of the punch are enormous (practically the samples formed a U) but without cracking and returning, after a period of time, to the initial shape.
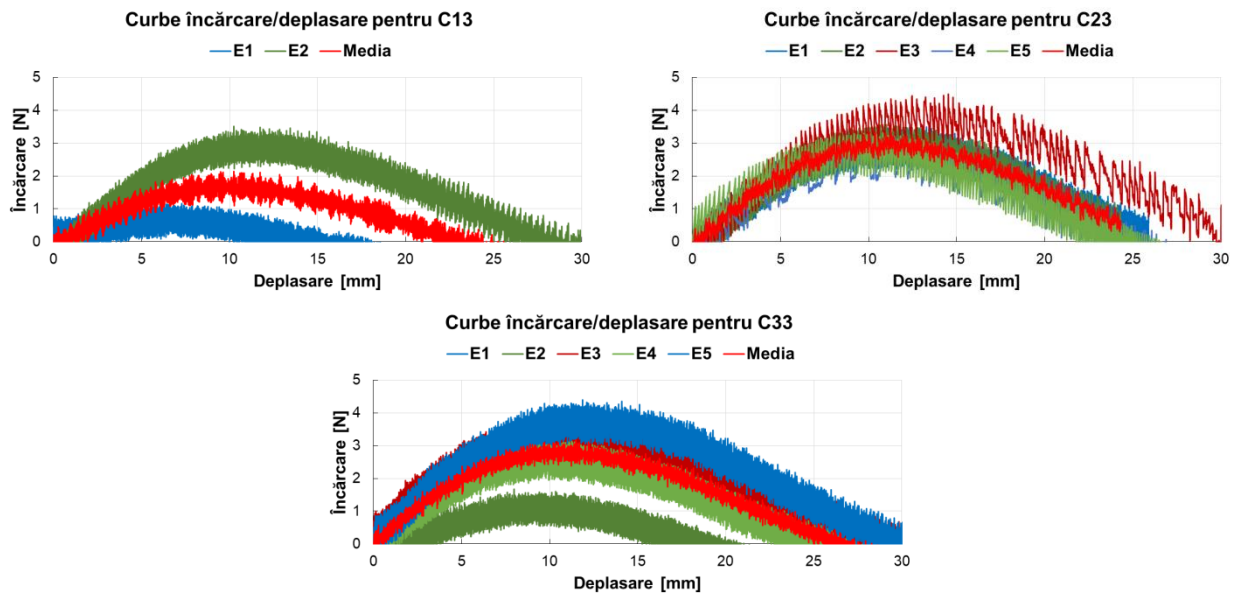
Fig.6.29. Loading/displacement curves of 75ml solution modified polymer materials – Cx3

If I had enough solution to form the C43 and C43m materials as well, it would have been interesting to see if the above observations would have held true in their case as well. That is, they are (in their class) the materials with the best three-point bending response, obviously superior to the natural polymer material.

For the materials modified with 75ml solution of inorganic agents in DMF and polymerized in the presence of the external magnetic field, the experimental results are presented in fig.6.31. Their appearance is not as shaky as that of their naturally polymerized counterparts and the peak load values are approximately equal.
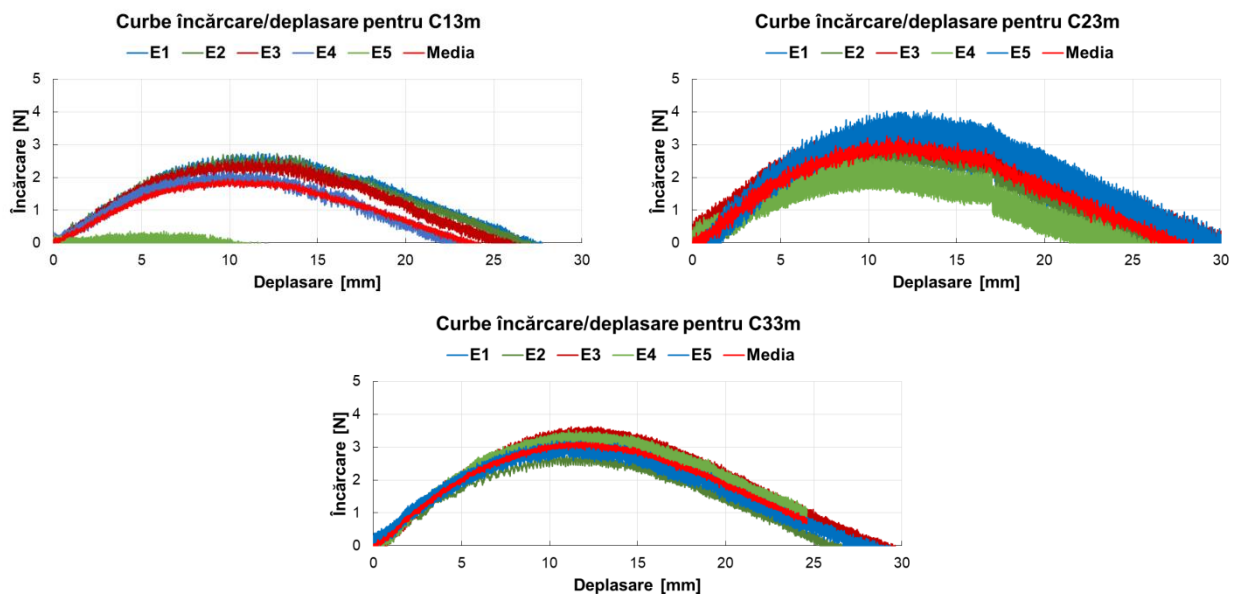
Fig.6.31. Loading/displacement curves of 75ml solution modified polymer materials polymerized in external magnetic field – Cx3m

Moduli of elasticity in bending are shown in fig.6.32. along with the details of the load/displacement curves (for displacements up to 5mm) of the punch. The values of the

flexural modulus are lower than those of the respective counterparts, but naturally polymerized.

The effect of the presence of an external magnetic field during polymerization is the same for all materials. It is possible that taking this aspect into account we can record higher values of photoconductivity. The photoconductivity was analyzed, however, on cylindrical samples because they best ensure the repeatability of the measurement conditions.

Modulus of elasticity in bending are shown in fig.6.32. along with the details of the load/displacement curves (for displacements up to 5mm) of the punch. The values of the flexural modulus are lower than those of the respective counterparts, but naturally polymerized.

The effect of the presence of an external magnetic field during polymerization is the same for all materials. It is possible that taking this aspect into account we can record higher values of photoconductivity. The photoconductivity was analyzed, however, on cylindrical samples because they best ensure the repeatability of the measurement conditions.
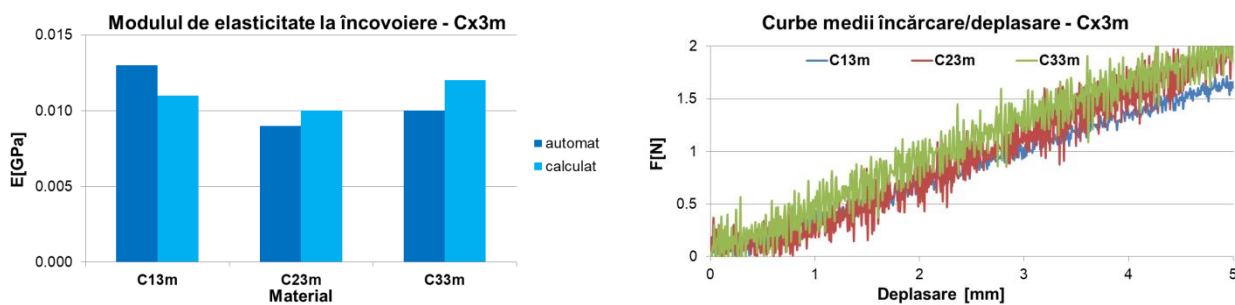
Fig.6.32. Elastic moduli and averaged curves (detail) – Cx3m

6.3.4. Three point bending tests of type C materials – conclusions
- as the amount of solution used to modify the properties of the epoxy resin increases, the value of the flexural modulus decreases;
- for very soft materials – Cx3 and Cx3m – the curves are strongly affected by the level of accuracy of load measurement;
• a future study should also be completed with the materials that I have not been able to form due to the lack of solution, I mean C43 and C43m, although I believe that the use of the magnetic field will not produce other effects than those found here.

6.4. Anaysis of type c materials properties – conclusions
- the materials modified with 75ml solution of metal chlorides in DMF have semiconductor behavior, regardless of the duration of the preparation of the solution;
- the same materials – Cx3 – present a photoconductivity three orders of magnitude higher than the other C-type materials, from this point of view these materials represent a research success;
- a reduction in the tensile strength values and, correspondingly, a reduction in the tensile modulus values can be observed, with the increase in the amount of inorganic agent solution used to modify the epoxy resin;
- no rules can be discerned regarding the effect of the duration of the preparation of the solution (at the same amount used to modify the epoxy resin) on the mechanical performances of the materials obtained;
- with the increase in the amount of metal chloride solution in DMF, used to modify the properties of the epoxy resin, the tested samples have close mechanical responses and this can be considered an indication of their homogeneity;
- as the amount of solution used to modify the properties of the epoxy resin increases, the value of the flexural modulus decreases;

- for very soft materials – Cx3 and Cx3m – the curves are strongly affected by the level of accuracy of load measurement;

- the application of the external magnetic field during polymerization produces a reduction in the value of the bending elasticity modulus, but not as important as that produced by increasing the amount of solution;

- the values of the flexural modulus of the materials formed after one week and two weeks of solution preparation, respectively, suggest that these materials have basically the same properties.

Chapter 7.

Personal contributions, conclusions and further studies purposes

The results presented in this paper represent, and I believe that the observation is valid for any doctoral thesis, only the measurable part of the activity carried out by a doctoral student. Of course, the actual execution of the tests consumes an enormous amount of time (and nerves), but presenting them in a concise, concise and concise thesis cannot include the hours spent gathering experimental data.

I was lucky, as an electrical engineer, the topic suited me even though I made great efforts to understand the electrical properties of polymers. The bibliographic study carried out helped me a lot to understand mechanisms of electrical conductivity (other than those I knew). Speaking of epoxy resins, I had access to the research of other colleagues, at the Research and Development Center for Composites with Thermoset Matrices - CCDCOMT, and I managed to put together a research plan.

Epoxy resins are not very comfortable to work with, and from that point of view, making the A-type materials was useful training, especially since I only formed cylindrical specimens. The working hypothesis was to increase the electrical conductivity of the polymer by introducing into its network d-type metals, metals that have a large number of free energy levels on which electrons could move.

A great challenge was related to the analysis of the electrical properties of these materials, but I was understood and performed all the analyzes at home with the measuring devices provided by the team at CCDCOMT. The thermal tests were carried out in the laboratory, as well as the mechanical ones. We knew, at the time of the formation of the materials, that the addition of NMP produces plasticization of the epoxy resin and NMP was the solvent used to obtain solutions of complex ammonium salts and manganese chloride assuming that in the volume of the solution it would be possible to make ammonium chloride. The main results of the study of materials A are:

- regarding the specific heat of the analyzed materials, in general it can be said that there are not very big differences compared to the specific heat of epoxy resin, nor are the variation curves of this parameter with temperature very different;

- the mass losses recorded during the DSC analysis, calculated as the average of the mass loss values of the three samples analyzed from each material, are proportional to the NMP content, with the exception of the A4 material and, obviously, with the exception of the epoxy resin;

- the mass losses consist, in addition to the vaporization of volatile substances (including atmospheric water) from the surfaces of the samples and the vaporization of NMP, in the case of epoxy resin samples modified with the solution of inorganic agents in NMP;

- the material with the most different thermal behavior, compared to the epoxy resin, is the A3 material;

- the coefficient of linear thermal expansion of the modified materials has higher values than the value of the same parameter for the epoxy resin, the differences are not, however, of orders of magnitude (as in the case of electrical photoconductivity) and are between 33 and 45ppm/°C;

• even if NMP is a widely used solvent in the polymer industry, it is very difficult to obtain solutions with high concentrations of inorganic agents, in this sense, a future study should consider chemical methods to increase the solubility of inorganic agents in NMP.

The second stage of the study – the formation and characterization of type B materials, represented, somewhat, a change of approach, inspired by the researches of Dr. Mihaela-Claudia Gorovei, which I proposed to the PhD supervisor, and which found in the use of another solvent – DMF – and the chlorides of the precursors of the YBCO ceramic compound (yttrium, barium and copper). The solubility of the salts is much better and offers – at least theoretically – the possibility of using sinusoidal electric fields to destabilize the metal ions and allow the elimination of chlorine.

Because copper chloride was also found among the salts, we proposed the application of the sinusoidal electric field by means of copper electrodes. After discussions with the PhD supervisor and members of the advisory committee, I decided to also use graphite electrodes, considering that the carbon atoms could be detached from the electrode surfaces and would ultimately remain in the polymer network and contribute to the growth electrical conductivity. In addition, I proposed to analyze the effect of polymerization in external magnetic field. To achieve this last step, we proposed the use of magnetic foils (stickers) fixed on one of the two glass sheets that constituted the mold in which the polymerization was to take place.

The realization of these materials was a challenge, from the preparation of the molds (cylindrical for the electrical tests, parallelepiped for the other tests), to the observance of a very rigorous program for the formation of the materials, so that the differences in preparation could not influence the properties of the formed materials. The main results of the analyzes performed on type B materials are:

- the analysis of the variation of electrical conductivity of materials B indicates an increase of four to six orders of magnitude of this parameter, compared to epoxy resin;

- in the case of the analysis of the conductivity variation with temperature, two materials (B13 and B32) indicate an increase in conductivity with temperature, which means a semiconductor-type behavior;

- the application of the sinusoidal electric field, before pouring the polymerizable mixtures into the molds, produces effects on the photoconductivity of the analyzed materials, both when it is applied by means of copper electrodes and when it is applied by means of carbon electrodes (graphite);

- materials B21m and B31m have a special thermal behavior, characterized by very high specific heat values (on the heating segments), but this behavior is no longer observable on the cooling segments;

- another remarkable behavior is that of the B32 material which presents higher specific heat values on the cooling segments compared to the values on the heating segments;

- the substance losses recorded during the thermal tests reveal that they are lower than in the case of class A materials, although NMP has a boiling point value higher than the boiling point value of DMF;

- in the case of the materials formed after the longest preparation time (Bx3), the mass losses of the materials formed in the presence of the magnetic field are lower than the substance losses of the homologous materials formed without the presence of the magnetic field;

- relatively high specific heat values (on the heating segments and on the two domains of positive temperature values) can also be observed in the case of Bx2 materials (B22 and B32), but they are not as high as those recorded in the case of materials B21 and B31;

- under the same conditions, polymerization in an external magnetic field leads to materials with a reduced modulus of elasticity;

- all the materials polymerized in the presence of the external magnetic field present flexural modulus of elasticity with lower values than those of the modulus of elasticity of the homologous materials, but formed in the absence of the external magnetic field;

- the application of the sinusoidal electric field, by means of graphite electrodes, has the greatest effect in the case of materials formed immediately after the preparation of the epoxy resin mixture/solution of inorganic agents in DMF;

- the application of the proposed control techniques produces - always - a reduction in the values of the bending elasticity modules of the materials to which they were applied.

With the analysis of type B materials completed, we proposed doubling the amounts of inorganic agents and using different amounts of their solution in DMF to modify the properties of the epoxy resin. For these materials, the sinusoidal electric field was no longer applied to the mixture between the base component of the epoxy resin and the solution of the inorganic agents, but directly to the solution of the metal chlorides in DMF. We kept, like B-type materials, the formation of the materials - obviously - with the same strict regime. This time the results – in terms of the electrical properties of the materials – were very promising. The effect of the magnetic field is, rather, a negative one on the mechanical properties of materials. Effect observed, however, also in the case of type B materials. The main conclusions, after analyzing the properties of type C materials, are:

- the materials modified with 75ml solution of metal chlorides in DMF have semiconductor behavior, regardless of the duration of the preparation of the solution;

- the same materials – Cx3 – present a photoconductivity three orders of magnitude higher than the other C-type materials, from this point of view these materials represent a research success;

- from the point of view of specific heat, class C materials have a behavior similar to those of class B, but without presenting very high values of the mentioned parameter as in the case of B materials;

- on the cooling segments, all materials have similar thermal behavior;

- substance losses, recorded during thermal tests, are directly proportional to the amount of solution used and seem to depend on the application or non-application of the magnetic field during polymerization;

- the application of the external magnetic field during polymerization produces a reduction in the value of the bending elasticity modulus, but not as important as that produced by increasing the amount of solution;

- the values of the flexural modulus of the materials formed after one week and two weeks of solution preparation, respectively, suggest that these materials have basically the same properties.

In the future, to improve the materials, other studies would be necessary, from which the application of the external magnetic field in the manner we proposed and used should be excluded. Among these studies I would list:

• the influence of the external magnetic field on the electrical conductivity and on the electrical photoconductivity of the formed materials, this time, the magnetic field should be uniform and aligned in the direction of the axes of the cylindrical molds;

• an SEM analysis, accompanied by an EDAX analysis, to identify the eventual formation of some nanostructures in the solution of inorganic agents or following the interaction with the components of the epoxy system;

• a study, based on the results obtained for type C materials, in which the concentration of inorganic agents will be further increased (up to the limit of supersaturation), possibly by gradually reducing, through vaporization, the solvent.

Materials with significant electrical properties are unfortunately mechanically inadequate. However, under the conditions of forming some reinforced materials, these modified polymers could be used inside the material, if their adhesion to the fibers is comparable to that of epoxy resin. To improve the mechanical properties, starch could be used.

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