

IOSUD – UNIVERSITATEA „DUNĂREA DE JOS” DIN GALAȚI

Școala doctorală de Inginerie Mecanică și Industrială



ABSTRACT

A study regarding the mechanical properties of nanostructured thermoset matrix

**Doctoral student,
Irina DANAILA (ȚÎCĂU)**

Scientific coordinator,

Prof. univ. dr. ing. Iulian-Gabriel BÎRSAN

Prof. univ. dr. fiz. Adrian CÎRCIUMARU

Seria I6 Inginerie Mecanică Nr 66

GALAȚI

2023

IOSUD – UNIVERSITATEA „DUNĂREA DE JOS” DIN GALAȚI

Școala doctorală de Inginerie Mecanică și Industrială



ABSTRACT

A study regarding the mechanical properties of nanostructured thermoset matrix

Doctoral student

Irina DANAILA (ȚÎCĂU)

President,

Prof univ. dr. ing. Mihaela BUCIUMEANU

Scientific coordinator,

Prof univ. dr. ing. Iulian-Gabriel BÎRSAN

Prof univ. dr.fiz. Adrian CÎRCIUMARU

Scientific refernces

Prof univ. dr. ing. Anton HADĂR

Prof univ. dr. ing. Dan-Mihai CONSTANTINESCU

Prof univ. dr. ing. Costel-Iulian MOCANU

Seria I6 Inginerie Mecanică Nr 66

GALAȚI

2023

Seriile tezelor de doctorat susținute public în UDJG începând cu 1 octombrie 2013 sunt:

Domeniul fundamental ȘTIINȚE INGINEREȘTI

- Seria I 1: **Biotehnologii**
- Seria I 2: **Calculatoare și tehnologia informației**
- Seria I 3: **Inginerie electrică**
- Seria I 4: **Inginerie industrială**
- Seria I 5: **Ingineria materialelor**
- Seria I 6: **Inginerie mecanică**
- Seria I 7: **Ingineria produselor alimentare**
- Seria I 8: **Ingineria sistemelor**
- Seria I 9: **Inginerie și management în agricultură și dezvoltare rurală**

Domeniul fundamental ȘTIINȚE SOCIALE

- Seria E 1: **Economie**
- Seria E 2: **Management**
- Seria E 3: **Marketing**
- Seria SSEF: **Știința sportului și educației fizice**

Domeniul fundamental ȘTIINȚE UMANISTE

- Seria U 1: **Filologie- Engleză**
- Seria U 2: **Filologie- Română**
- Seria U 3: **Istorie**
- Seria U 4: **Filologie - Franceză**

Domeniul fundamental MATEMATICĂ ȘI ȘTIINȚE ALE NATURII

- Seria C: **Chimie**

Domeniul fundamental ȘTIINȚE BIOMEDICALE

- Seria M: **Medicină**
- Seria F: **Farmacie**

ROMÂNIA
MINISTERUL EDUCAȚIEI
UNIVERSITATEA „DUNĂREA DE JOS” DIN GALAȚI



DECIZIA

nr. 19 / 6 01 2023

Conform Hotărârii de Guvern nr. 681/29.06.2011 privind aprobarea Codului studiilor universitare de doctorat, cu toate modificările și completările ulterioare;

conform Regulamentului instituțional privind organizarea și funcționarea studiilor universitare de doctorat în școlile doctorale din Universitatea „Dunărea de Jos” din Galați, aprobat prin Hotărârea Senatului Universitar nr. 118/24.03.2022 (Anexa 2);

conform Metodologiei privind susținerea publică a tezei de doctorat la IOSUD – Universitatea „Dunărea de Jos” din Galați, aprobată prin Hotărârea Senatului nr. 140/29.09.2020 (Anexa 3);

având în vedere referatul conducătorului științific Prof. univ. dr. fiz. Adrian CÎRCIUMARU cu numărul C94/05.01.2023, privind propunerea comisiei de susținere publică a tezei de doctorat;

conform aprobării Consiliului pentru studiile universitare de doctorat în data de 06.01.2023;

în baza Ordinului Ministrului Educației și Cercetării nr. 3041/15.01.2020 privind numirea rectorului;

Rectorul universității decide:

Art. 1. Se numește comisia pentru evaluarea și susținerea publică a tezei de doctorat de către doctorand/a/ul **DĂNĂILĂ V. IRINA (ȚÎCĂU)**, domeniul **Inginerie mecanică**, în următoarea componență:

- | | |
|----------------------------------|---|
| 1. Președinte | Prof. univ. dr. ing. Mihaela BUCIUMEANU
Universitatea „Dunărea de Jos” din Galați |
| 2. Conducător de doctorat | Prof. univ. dr. fiz. Adrian CÎRCIUMARU
Universitatea „Dunărea de Jos” din Galați |
| 3. Referent oficial | Prof. univ. dr. ing. Anton HADĂR
Universitatea POLITEHNICA din București |
| 4. Referent oficial | Prof. univ. dr. ing. Dan-Mihai CONSTANTINESCU
Universitatea POLITEHNICA din București |
| 5. Referent oficial | Prof. univ. dr. ing. Costel-Iulian MOCANU
Universitatea „Dunărea de Jos” din Galați |

Art. 2. Școala doctorală de Inginerie mecanică și industrială, Secretariatul doctorat, Biroul salarizare și Serviciul financiar vor duce la îndeplinire prevederile prezentei decizii.

Prof. dr. ing. **Puiu-Ducian GEORGESCU**



Content

Content	5
Introduction	7
Chapter 1	11
1.7. Applications of composite materials	11
Chapter 2	15
Research objectives	15
Chapter 3	17
Formation of materials and methods of analysis	17
3.1. The materials used in the research	17
3.2. Epoxy resin - epoxy novolac modified vinylester resin mixtures	17
3.3. Polymer mixtures modified with inorganic and organic agents	20
3.4. Ternary polymer mixtures modified with inorganic agents	20
3.5. Mechanical tests	20
3.6. Tribological tests	21
3.7. Thermal tests	21
3.8. Thermomechanical tests	20
3.9. SEM analysis	20
Chapter 4	21
Analysis of properties of binary mixtures	21
4.1. Tensile test results	21
4.2. Tensile tests – partial conclusions.....	24
4.3. Compression test results.....	24
4.4. Compression tests – partial conclusions	27
4.5. Three-point bending tests results	27
4.6. Three-point bending tests – partial conclusions	30
4.7. Tribological test results	31
4.8. Tribological tests – partial conclusions	33
4.9. Thermal test results	33
4.10. Thermal tests – partial conclusions	35
4.11. Conclusions – Binary mixtures	36
Chapter 5	37
Binary mixtures modified with organic and inorganic agents	37
5.1. Tensile test results	37
5.2. Tensile tests – partial conclusions.....	37
5.3. Three-point bending test results.....	37
5.4. Three-point bending tests – partial conclusions	40
5.5. Conclusions	41
Chapter 6	43
Ternary mixtures modified with inorganic and organic agents	43
6.1. Tensile test results	43
6.2. Tensile tests – partial conclusions.....	43
6.3. Compression test results.....	43
6.4. Compression tests – partial conclusions	44
6.5. Three-point bending test results.....	45
6.6. Three-point bending – partial conclusions	46
6.7. Tribological test results	46
6.8. Tribological tests – partial conclusions	51

6.9. Thermal test results	51
6.10. Thermal tests – partial conclusions.....	51
6.11. SEM analysis of modified ternary mixtures	51
6.12. SEM analysis – partial conclusions.....	61
6.13. Conclusions.....	61
Chapter 7	61
Personal contributions, conclusions and future research directions.....	61
Bibliography.....	63

Introduction

Organized knowledge is science.

Organized living is wisdom.

Immanuel Kant

On a closer analysis, the current stage of technological development depends on the progress made in the field of materials and especially composite materials. Generally speaking, composite materials are nothing more than a giant step in the pursuit of high-performance materials. The idea of composite materials is not new or recent, but at the same time it persists to be current and necessary, being widely used in different fields.

Polymer composites are the most widely used materials in today's world and in all industrial fields. It is known that polymers represent a special class of materials with special properties and by reinforcing them it is possible to obtain materials with, at least, valuable mechanical properties.

At the Research and Development Center for Composites with Thermoset Matrices within the Lower Danube University in Galati, research was initiated on changing the basic properties of polymers by means of inorganic compounds, other polymers, other organic compounds or solvents. Inorganic substances such as barium chloride (BaCl_2), copper chloride (CuCl_2), silver nitrate (AgNO_3), scandium chloride (ScCl_3), yttrium chloride (YCl_3), lanthanum oxide (La_2O_3), with encouraging results, and the formed materials presented special properties. Working with thermoset polymers and especially epoxy resins, such inorganic compounds are hardly soluble and the attempt is followed by technical difficulties. In an attempt to solve this problem, other polymers were tested as well as vinyl ester resins which showed better responses to the solvation of inorganic substances.

So it is possible to disperse the modifying agents in the vinyl ester resin and then mix this mixture with the epoxy resin. Moreover, it is possible to initiate some chemical reactions between two or more substances dispersed inside the polymer volume (analogous to the method of citrate gels for nano-sized particles) resulting in nano-structuring of the polymer. Thus, an important problem arises, namely that of the characterization of the materials obtained by mixing two polymers, whether they are thermosetting, thermoplastic or one thermosetting and one thermoplastic.

Polymeric materials are increasingly used as an alternative to eliminate the shortcomings of classic materials. The characteristics of polymeric materials: corrosion resistance, tear resistance, wear resistance, high temperature resistance, generally low thermal conductivity, practically zero electrical conductivity, low density, stability in various environments, etc., make them increasingly desirable for applications in various fields: the creation of a multitude of components for the aerospace, automotive, dental applications, surgery, energy (wind power) industries - it is almost impossible to enumerate all the applications in which polymer materials are found. In addition to these, we must also mention the disadvantages of these materials: huge impact on the environment starting from the production of the basic substances to the actual formation of the polymers (gas emissions, use of harmful solvents), low recycling rate (for thermoplastic polymers) and zero (for thermosetting polymers). On the other hand, from an economic point of view, polymers and polymer composites are characterized by a very high rate of formation and by a relatively low price of raw materials.

Probably the most important property of polymer composites (regardless of their type) is related to the designability of the properties, in the sense of maximizing the response of the

Introducere

material to a certain external stress. In this sense, we can talk about the nanostructuring of polymers - obtained, as a rule, by dispersing nanometer-sized powders in the liquid volume of a polymer or polymerizable mixture.

Among the methods for obtaining nanometric powders are the methods that take into account the creation of structures of these dimensions by developing local chemical reactions - the citrate gel method or the oxalate gel method, the emulsion method, the foam method. All these methods prevent the development of chemical reactions between reactants in the entire volume of the reactive mixture forcing the localization of chemical reactions either by isolating very small amounts of reactants in small gaseous spheres (foams) or by increasing the viscosity of the mixture (which reduces the mobility of the reactants). The essential condition for obtaining nanostructures is that the gel or emulsion medium is combustible, to provide the necessary energy.

At CCDCOMT, several studies were developed on the possibility of direct nanostructuring of epoxy resins by developing local chemical reactions directly in the resin (this having a controllable viscosity and limiting the mobility of the reactants). Mihaela Gorovei, for example, researched the possibility of nanostructuring using nitrate solutions in 1-methyl 2-pyrrolidinone, Gabriel Săracu studies the possibility of nanostructuring using nitrate solutions in NN-dimethylformamide.

As for the present study - which I don't know if it led to the nanostructuring of the polymer or just to obtaining a modified polymer - it is based on the observed fact that most inorganic substances are very difficult to dissolve or insoluble in epoxy resins but are soluble in a epoxy novolac modified vinylester resin. Thus, this latter resin could be used as a vector (after solubilization of inorganic substances) for the placement of reactants in epoxy resins.

Such an approach requires knowing the properties of some materials obtained from the mixture of epoxy resin and epoxy novolac modified vinylester resin. At CCDCOMT there is an unspoken rule related to the testing and characterization of each material produced in research (whether it is the research of students, or whether it is the research of those who represent, through their work, this Center).

The specialized literature abounds in studies related to obtaining nanostructures (of powders, especially ceramic, nanometers level), but the process of nanostructuring polymers by dispersing these nanopowders is a particularly complicated one because all these nanodimensional aggregates tend to agglomerate (clusterize) leading to obtaining a polymer where, like a wrong pole, there are areas where the material properties differ greatly (from polymer to aggregate). Such a material certainly does not meet the criteria for classification in nanostructured and from a macroscopic point of view it would be nothing more than a non-uniform dispersion of stress centers in a homogeneous and isotropic matrix.

On the other hand, the method proposed in this study is also not infallible (it is rather fallible) because the realization of chemical reactions between reactants guarantees obtaining a small number of molecules of reaction product which, at a given moment, should be forced somehow to form assemblies of several hundreds or thousands, thus constituting a nanostructure.

In the world of ceramic composites (a little different from that of polymer composites), in the case of nanostructures, we talk about the dependence of the results on the dimensions of the precursors, which can lead to the conclusion that, in the case of nanomaterials with a ceramic matrix, in fact, the components that are to be part of the nano structures bind to the components of the future matrix and only sintering followed by an aggressive heat treatment leads to obtaining the final material. In such a technique it is almost certain that a wrongly designed or made material is brittle and therefore mechanically worthless.

As far as polymer composites are concerned - because the basic materials are affordable - no approach is wrong because the knowledge of these materials and their properties is somehow at the beginning given that the properties of a polymer composite do not only depend on the nature of its components but also of the forming conditions. Many studies carried out at CCDCOMT on epoxy resins showed that good results can be obtained in a certain direction with disastrous consequences on the properties of the formed material (of course, from a mechanical point of view) but this did not mean stopping the investigations but looking for solutions that keeping the positive results to lead to materials with properties closer to those of the polymer

It was not easy for me to get involved in such a study. At first I thought it was impossible to control and manage the starting assumptions, then the absolutely necessary stoichiometric calculations and a real nightmare if the ingredients are hydrated, then making an overwhelming number of samples and spending a large number of hours on the test machines and finally, the processing and interpretation of the obtained data.

I know that, like the time I spent during my master's university studies, my doctoral studies meant constantly taking a step beyond the last step I thought I was capable of taking. It meant a sinusoidal function of self-confidence which, obviously, in the descending parts meant loss of confidence to the point of despair. Each time I found resources that I didn't know existed and that I was pushed towards by those around me.

Chapter 1

1.7. Applications of composite materials

Chuan Li et al. his [19], fabricated shape-stabilized inorganic salt-based phase change composite materials for medium and high temperature thermal energy storage. It was concluded that the performance of the selected salts in various aspects directly influences the thermal loading/discharging behavior and also the thermal energy storage capacity of the composite. In cases where heat transfer is viewed as a restriction, thermal conductivity additives are required to improve heat transfer in salt-based composites.

In [176], a new type of functionalized silicone polymer was designed and synthesized. The DMA test showed that the functionalized silicon polymer preserved the temperature resistance of the epoxy composite material to a certain extent while strengthening the epoxy. SEM images of the fracture surface of the composites confirm that the novel silicone polymer PSOL-(N-TMSPrVaC) is uniformly dispersed in the epoxy resin. The impact resistance reaches the highest value with 3.0phr PSOL-(N-TMSPrVaC), the percentage was increased by 18.2% compared to pure epoxy resin.

Polymer matrix composites were produced from type I collagen fibers as reinforcement and epoxy matrices with varying fiber volume fractions, namely 10%, 20%, 30% and 40% [177]. The obtained results were tabulated and the following conclusions were drawn: the specific wear rate of the composites decreased as the percentage content of fibers increased, from the investigation the minimum wear rate for collagen reinforced composites of 30% volume loading was observed of 15%, collagen fibers embedded in epoxies can greatly reduce abrasive wear losses. At a fiber composition of 30% volume fraction, the best wear resistance property was obtained.

In [178], materials based on Multicast polyurethane resin and ISO 2 hardener and copper wires were designed. Based on the results of the experimental tests, in the case of the characteristic curves for the specimens reinforced with three copper wires, an increase in the maximum force can be observed, compared to the unreinforced specimens, by 17.51% and a significant increase in the maximum elongation, by 42.25% compared to of the not reinforced specimens. This research [179], investigated the feasibility of polyurethane as a rapid thin layer maintenance material for airport concrete pavement. The following conclusions were summarized: the microphase separation characteristics and degree of separation of polyurethane were determined by the compositional ratio of isocyanate to polyols. The microphase region of the hard segment provided the mechanical strength and hardness of the polyurethane, while the elasticity and flexibility of the polyurethane were affected by the soft segment.

The effect of environmental conditioning on the properties of resin-infused thermosetting and thermoplastic matrix composite materials for marine applications was studied in [180]. Glass fiber reinforced polymer (GFRP) laminates, a range of thermosetting resins and an infusible thermoplastic were used. SEM showed a transition from matrix-dominated failure in the dry state to failure at the fiber-matrix interface in wet and organic-wet specimens. The overall performance of the infusible thermoplastic was good compared to marine resin systems, however, environmental performance could be improved if the thermoplastic resin is used in conjunction with a fiber size that is tailored for use with acrylic resin systems.

Researchers [181], used vinyl ester (VE) resin for additive manufacturing of high performance vinyl ester resin by direct writing with dual UV-thermal curing ink. The printed and dual-cured VE nanocomposites achieved a Young's modulus of 3.7GPa and a tensile strength of about 80MPa, which exceeds by about 10% conventionally cast pure VE cured with methyl ethyl

ketone peroxide (MEKP) and, by also indistinguishable from the tensile properties of VE nanocomposites cast with the same composition. The fracture strength of dual-imprinted and reinforced VE nanocomposites was 16% higher than MEKP-reinforced neat cast VE.

The influence of resin-based bonding agents loaded with different inorganic filler content, with or without adhesive, on the microtensile strength, biaxial bending strength and adhesive interface morphology of bonded ceramic specimens was investigated [182]. It was shown that increased inorganic filler content of experimental resin-based bonding agents strengthened bonded feldspathic ceramics. The bonding agent with high filler content produced significantly higher viscosity and film thickness. In contrast, bond strength was lower and structural reliability decreased if no adhesive was used.

An electrically conductive carbon fiber reinforced plastic (CFRP) was developed for lightning protection by infusing the carbon fiber (CF) fabric with a thermoset resin [198]. The new CFRP fabrication method used a liquid dispersion of thermosetting resin based on styrene derivatives, including micron-sized polyaniline (PANI)/dodecyl benzene sulfonic acid (DBSA) composite particles. The results indicated a non-uniform distribution of PANI-CP particles between the CF fabric layers and the presence of very small particles on the surface of the CFs inside the bundles, which contributed to high electrical conductivity. Non-uniform particle size distribution was found to increase the density of CFs in bundles.

Sputtered polyurea (SPUA) was used to develop a nonlinear visco-hyperelastic tensile constitutive model over the wide strain rate range [199]. The mechanical properties of SPUA were shown to be strain rate sensitive, i.e. the elastic modulus and tensile stress increase with increasing strain rate, while the strain at fracture is linearly negatively correlated with the logarithm of the strain rate. SPUA is a strain rate sensitive material.

Three types of epoxy systems and glass-coated cobalt-based microwires (GCM) were used to predict the interfacial shear strength before use for fiber-reinforced thermosetting composites based on the impedance-stress effect of ferromagnetic microwires [201]. The local interfacial stress induced by the resin microdroplets significantly improved the microwire impedance, but the stress concentration reduces this improvement effect. The increase in impedance has a non-monotonic linear relationship with the total embedded length, and the absolute value of the slope for the descending side shows the same trend as the IFSS of the GCM-3/resin composites. The proposed IFSS prediction method using Co-based microwires can dramatically simplify the testing process and reduce industrial costs, facilitating the performance optimization and application of advanced fiber-reinforced polymer composites.

This paper [203] is an overview of manufacturing defects in fiber-reinforced resin matrix composites, including: resin defects, fiber defects, interface defects, and processing defects. To characterize the defects of composites, the authors synthesize the non-contact detection of composite defects and prospect the development of composite defects in the future. This article analyzes and discusses the generation mechanism, distribution, and optimization methods of manufacturing defects in hot press molding, resin transfer molding, and additive manufacturing molding. The main manifestations of defects produced by the carbon fiber reinforced composites processing process are delamination and breakage. Delamination is the most serious machining defect, which results in many problems occurring in engineering applications, such as decreased strength and short lifetime in composite structures.

The static and dynamic compressive and tensile response of highly elastic polyurea was investigated in [204]. Curing of thermoset resin and thermoplastic resin, resin infiltration process during hot pressing, resin transfer molding and 3D printing were described in this article. The

formation mechanism of fiber reinforcement defects such as fiber puckering and curling in composites was introduced and the influence of these defects on the flexural and compression properties of composites was analyzed, which showed that fiber misalignment defects will seriously reduce the modulus, strength and stability of the supporting structures. The main manifestations were delamination and breakage, which will seriously affect the strength and reliability of the connections between the components.

Chapter 2

Research objectives

The present study is based on a hypothesis launched by Adrian Cîrciumaru and studied by Mihaela Gorovei in the sense of modifying the gel method to obtain inorganic nanostructures directly in one of the two components of a thermosetting polymer (resin or hardener). The hypothesis works if all the inorganic precursors used are soluble in either the resin or the thermosetting polymer hardener.

Tests carried out at CCDCOMT in other studies have shown that organic salts are insoluble or very poorly soluble (under conditions that risk denaturing the chemical structure of the polymer) in one of the two liquid components of epoxy resins. Mihaela Gorovei chose the path of solubilizing metal nitrates in 1-methyl 2-pyrrolidinone, after which these solutions were dispersed in the epoxy resin - with the aim of obtaining nanostructures. Iulia Păduraru-Graur, also at CCDCOMT, used a commercial solvent to place complex salts – sodium dichromate and potassium dichromate – in the epoxy resin, with the aim of obtaining an increase in the electrical conductivity of the material formed.

The present study is based on the observation that inorganic salts (chlorides, nitrates) are soluble in the modified epoxy novolac vinylester resin diluted with styrene (probably styrene has the determining role in solubilization). In this regard, a method was proposed by which inorganic substances are placed in the epoxy resin by means of their solutions in the modified epoxy novolac vinylester epoxy novolac resin. If the hypothesis regarding the formation of nanostructures is valid (that is, the nanostructures are formed) then it is no longer a matter of nanostructuring of the epoxy resin but of nanostructuring of the mixture of thermosetting polymers.

In order to lay the foundations of a correct scientific approach the first step is related to the analysis of the properties of polymer mixtures and, mixtures of three epoxy resins with modified epoxy novolac modified vinylester resin were tested (all polymers are of commercial use and for none of them we know the exact chemical formulation). Based on the results obtained for these polymer mixtures, it is possible to proceed to the next stage, the one of the formation of polymer mixtures modified with inorganic agents (but, as we will see, also organic). Unfortunately, the six mixtures proposed and made were a painful failure (two of them did not even polymerize, in the case of the other four the polymerization was incomplete or partial).

For this reason we decided that the binary mixture (epoxy resin, epoxy novolac modified vinylester resin) modified with organic and inorganic substances should be supplemented with a third component to increase the viscosity in order to obtain more homogeneous mixtures. For the third polymer I used – epoxy resin, four polyurethane resins, three silicone resins and polyurea (all commercial polymers, for which the chemical formulations are unknown). In these tertiary mixtures of thermosetting polymers, the working hypothesis must be verified – obtaining nanostructures.

To achieve the proposed goal, a series of objectives have been established, which are:

- Completion of an extensive documentary report on the current state of international and national scientific research in the field of composites with thermoset and nanostructured polymer matrices.
- detailed study of formation and test types of composite materials modified with various modifying agents;
- the bibliographic study regarding organic solvents and mixtures of thermosetting polymers;

Capitolul 2

- Obtaining mixtures of tremor-rigid polymers:
 - establishing the mixture ratios of epoxy/resin epoxy novolac modified vinylester resin;
 - establishing the forming method so that the necessary samples for all tests can be ensured;
 - the formation of materials and their consolidation by applying thermal treatments;
 - establishing test methods;
 - preparation of samples;
 - testing thermosetting polymer mixtures;
 - tensile tests;
 - compressive tests;
 - three-point bending tests;
 - tribological tests;
 - thermal tests;
 - interpretation of the obtained results;
 - formulating conclusions;
- Making polymer mixtures modified with organic and inorganic agents to test the hypothesis of the formation of nanostructures directly in the resin;
 - stoichiometric determination of the necessary amounts of inorganic agents;
 - establishing the mixing method that ensures the uniform dispersion of the solutions of the inorganic agents in the epoxy resin;
 - establishing the formation technique and the formation of materials;
 - formation of materials and consolidation through thermal treatments;
 - preparation of samples;
 - testing of materials
 - tensile tests;
 - three-point bending tests;
 - interpretation of the results;
 - formulating conclusions;
- Making ternary polymer mixtures (three thermosetting polymers) modified with inorganic and organic agents;
 - establishing the forming method so that the necessary samples for all tests can be ensured;
 - formation of materials;
 - establishing analysis methods;
 - obtaining samples;
 - testing thermosetting polymer mixtures;
 - tensile tests;
 - compressive tests;
 - three-point bending tests;
 - tribological tests;
 - thermomechanical tests;
 - thermal tests;
 - SEM analysis;
 - interpretation of the obtained results;
 - formulating conclusions.

Chapter 3

Formation of materials and methods of analysis

3.1. The materials used in the research

The base materials used in this study are three commercial epoxy resins two produced by R&G Faserverbundwerkstoffe - Epoxy resin C and Epoxy resin HT and one produced by Bostik - Epiphen RE4020-DE4020. Because the three epoxy resins are obtained by mixing two liquid components (generally called resin and hardener), when we talk about an epoxy resin we will use the phrase epoxy system (ie the combination of the two liquid components). The three epoxy resins mentioned above have also been used in other studies at CCDCOMT, most notably the Epiphen RE402-DE4020 system. The main technical data for the three epoxy systems can be found in [205-206] for the C and HT epoxy systems and in [207] for the Epiphen RE4020-DE4020 epoxy system. Of course, these are properties measured by the manufacturer.

Apart from the epoxy systems, another fundamental material for the realization of the study was the epoxy novolac modified vinylester resin diluted with styrene, Sirester VE-64-M-140 produced by Sir industriale [208]. From this resin I only used the base (resin) and not the hardener. The same observation applies to the following resins (ie. we used only the resins, not the hardeners): Polyurethane resin Multicast 1 [210], Polyurethane resin Multicast 2 [209], Polyurethane resin Multicast 6 [211], Polyurethane resin Multicast 12 [212] all produced by Altropol, silicone addition resin ZA 13 [213], silicone addition resin ZA 22 [214] and silicone addition resin HT 33 [215], all produced by Zhermack and polyurea.

As inorganic agents for modifying the properties of polymers, we used barium chloride BaCl_2 , Yttrium chloride YCl_3 , copper chloride CuCl_2 , silver nitrate AgNO_3 , lanthanum oxide La_2O_3 and scandium chloride ScCl_3 , all substances with a purity of over 99%. The entire scientific approach was based - as in the study carried out by Mihaela Gorovei - on the knowledge that there is a quaternary compound with special properties $\text{YBa}_2\text{Cu}_3\text{O}_7$ that can be obtained under special conditions (at high energies, that is, at high temperatures) whose acronym YBCO is almost a common noun, like other acronyms (laser, led, etc.).

3.2. Epoxy resin - epoxy novolac modified vinylester resin mixtures

To make the mixtures, I used the three epoxy resins mentioned at the beginning of this article, which I modified by replacing a volume of resin (the basic component of the epoxy system) with an equal volume of epoxy novolac modified vinylester resin (still only the first component of system) so as to obtain mixtures with percentage volume rates of 5%, 10%, 15% and 20% presence of the modifier in the epoxy resin. These materials, from the preparatory stage of the study, will hereafter be denoted using the letters C, E and H (corresponding to the trade names of the three epoxy resins) followed by +PX which represents the volume ratio. Thus, for example, the E+P15 material is the polymer mixture of the Epiphen epoxy resin with the epoxy novolac modified vinylester resin, with a 15% volume presence of the latter.

3.3. Polymer mixtures modified with inorganic and organic agents

The first operation in the formation of the modified materials was the solubilization of the inorganic agents in the epoxy novolac modified vinyl ester resin. To ensure the complete solvation of the inorganic compounds, the stoichiometrically established amounts were solvated in 50 ml of novolac modified vinyl ester resin. Where necessary, the amount of resin was increased by 20ml (in situations where saturation of the solutions was observed, i.e. the existence of crystals of inorganic substances in the solutions). All mixtures were made on magnetic stirrers set at 50°C and a stirring speed of 600rot/min. The initial finding was that barium chloride was the most difficult to dissolve, and for this reason it was always the first salt to be solubilized. Furthermore, to stabilize the solution, we added collagen (5g) which, through solubilization, is expected to cover the barium and chlorine ions respectively, changing their mobility.

As I mentioned, the amounts of inorganic substances were stoichiometrically determined and were measured on the electronic balance with the precision in the table (to $\pm 0.1\text{mg}$) and then solvated in the epoxy novolac modified vinylester resin - fig. 2.



Fig. 1 Electronic balance (left), mixed solutions in novolac epoxy modified vinylester resin, heat setting oven (right)

3.4. Ternary polymer mixtures modified with inorganic agents

For the final materials of the study, I made, again, the solution for the M2 material, changing only the volume of the solution in the epoxy novolac modified vinylester resin - I used 150g of it to solvate (stabilized with collagen) the amounts of salts specified in the recipe from M2. To this solution I added 850g of epoxy resin (Epiphen RE4020) and homogenized the mixture on a magnetic stirrer (under the conditions described in 3.3.), only that the homogenization lasted longer (60min compared to 10min). From this mixture I took 90g and added another 10g of epoxy resin. After a homogenization of 10 min at 50°C and 600rpm, on the magnetic stirrer I added the epoxy resin hardener (Epiphen DE4020) calculated for 100g of resin. A new 10min homogenization followed under the same conditions, after which the pre-polymer mixture was poured into the polypropylene tubes described previously.

The same procedure was applied for the following eight materials with the only difference that the 10g of Epiphen RE4020 added were replaced, in turn, in the same recipe by 10g each of the polyurethane resins, the silicone resins and the polyurea, respectively, described at the beginning of this chapter. The homogenization conditions were the same, the casting conditions were also the same.

3.5. Mechanical tests

All mechanical tests performed were performed on an Instron 8802 universal testing

customized machine that is controlled by a specialized software application (BlueHill 3). The same application can be used to determine significant parameters regarding the mechanical responses of materials. For the tests carried out, a load cell with a maximum capacity of 25kN was used and appropriate equipment was installed - grips for tensile tests, plates - for compression tests and the specialized set - for three-point bending - fig. 3.



Fig. 2. Mechanical tests

3.6. Tribological tests

The tribological tests were carried out in the pin-on-disk geometry with the steel disk and the pin in the material to be analyzed, on a customized machine TRM1000 Tribometer, manufactured by Wazzau (Germany). In fig. 4. the equipment used is presented.



Fig. 3 TRM1000 tribometer

Three different tribological regimes were established for the performed tribological tests. Thus, the loading forces of 15N, 20N and 25N and corresponding sliding speeds of 2.0m/s, 1.5m/s and 1.2m/s so as to ensure the same value of the product of the force modulus and the velocity modulus (again from the need to ensure conditions for comparative analyses).

3.7. Thermal tests

The thermal tests aimed to determine the specific heat values of the formed materials and were performed on a DSC 1 equipment (Mettler Toledo) - fig. 5. According to the standards for the determination of the specific heat value, it must be evaluated on a cooling curve, and therefore we established a test program that included two complete heating-cooling cycles, all the more so from

Capitolul 3

discussions with colleagues at CCDCOMT I understood that between the first and second cycle (on the heating segments) there are noticeable differences between the parameter values.



Fig. 4 DSC 1 (Mettler Toledo)

3.8. Thermomechanical tests

The tests were carried out on a TMA-SDTA 810 machine (Mettler Toledo) controlled with the Stare software application, made available by the equipment manufacturers (and which also controls the DSC 1 equipment) – fig. 6.

For each of the analyzed materials (and it is only the ternary polymer mixtures modified with organic and inorganic agents) discs of material with a thickness between 1.5mm and 3mm were used (as can be seen in the image on the right side of fig. 6.). The measurements were performed over the temperature range (30°C - 200°C).

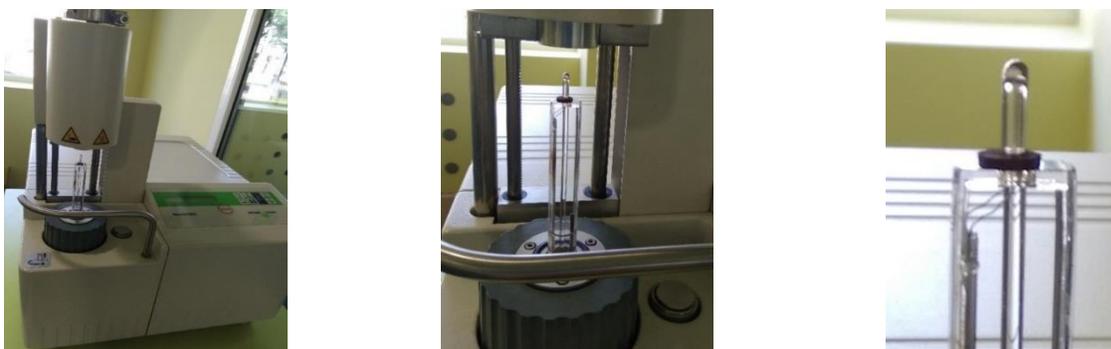


Fig. 5 TMA – SDTA 810 (Mettler Toledo)

3.9. SEM analysis

Microscopic analysis was carried out by analyzing fractured areas of samples of ternary materials modified with organic and inorganic agents. The analyzes were carried out on the Qanta electron microscope with the samples covered with a 6nm gold layer. For each material analyzed, a single sample was used and the analysis aimed to identify some nanometric structures in the polymer matrix, which would confirm the correctness of the initial hypothesis.

Chapter 4

Analysis of properties of binary mixtures

4.1. Tensile test results

The tensile tests performed on the samples of binary mixtures (an epoxy resin and epoxy novolac modified vinylester resin) – like all the tests performed on these materials, aimed to identify the effects of the presence of modified vinylester resin in the epoxy matrix. This purpose is imposed by the intention to use solutions of the inorganic substances in the epoxy novolac modified vinylester resin diluted with styrene to (possibly) obtain nanostructures in the matrix of the used epoxy resin. These tests also aim to establish which of the three analyzed epoxy resins is the most susceptible to achieve the objective without this approach fundamentally changing the properties of the epoxy resin.

In fig. 7. the stress-strain curves obtained for each of the five samples of the three epoxy resins tested are shown.

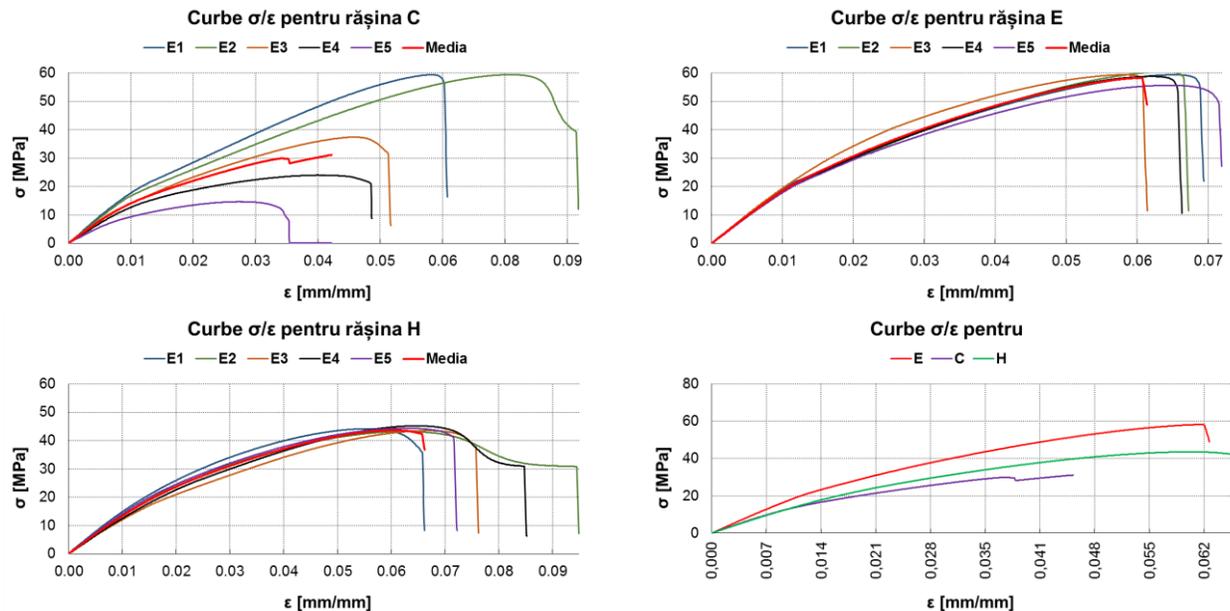


Fig. 6 σ/ϵ curves of epoxy resin specimens - tensile

It can be seen that the responses of the C resin are very different and the explanation could be related to the fact that it is a brittle resin and when it is squeezed into the grips cracks may appear and their development during the tests affect the mechanical response of the sample. For the other two resins the answers are more grouped but it can be seen that the E resin resists higher stresses than the H resin.

Polymerization of the materials was done, as I specified in chapter 3, only with the epoxy resin hardener, so that the results recorded for the tests performed on the materials with 5% epoxy novolac modified vinylester resin - fig. 8. – could be interpreted as consequences of the different chemical formulations of the three epoxy resins. A slight increase in peak stress can be observed for E+P5 and H+P5 materials.

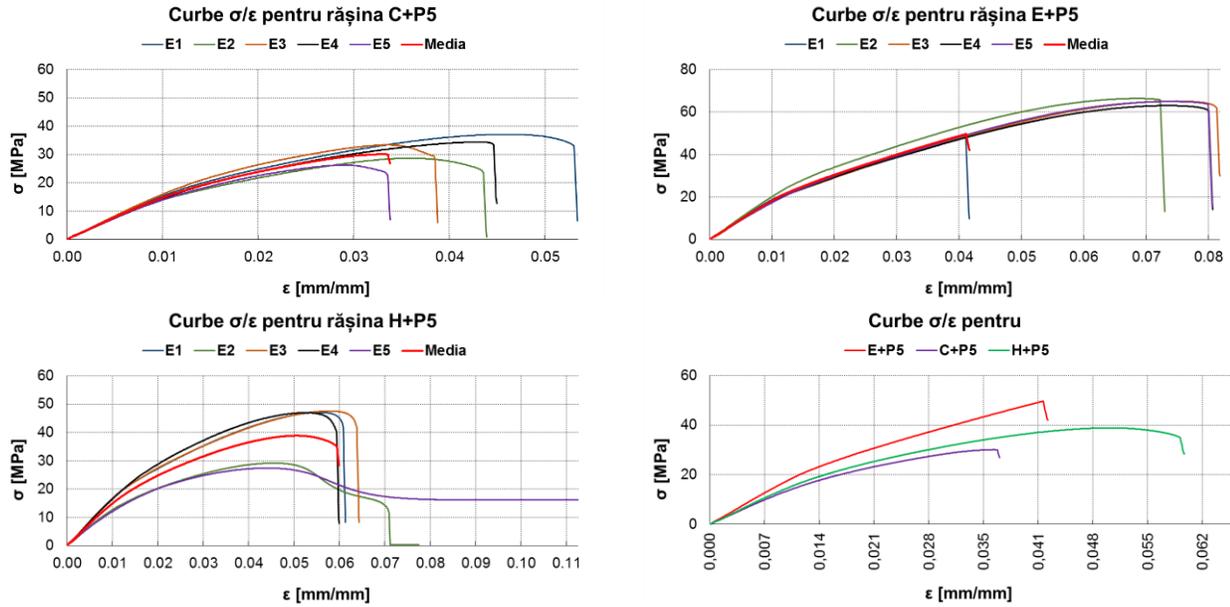


Fig. 7 σ/ϵ curves of binary mixtures (5%) – traction

The average curves of the materials with 5% epoxy novolac modified vinylester resin are shown in the last plot (lower right) and indicate that, on average, the maximum stress in the case of E+P5 is reduced by about 10MPa, in the case of H+P5 by 5Mpa and, for C+P5 remains unchanged.

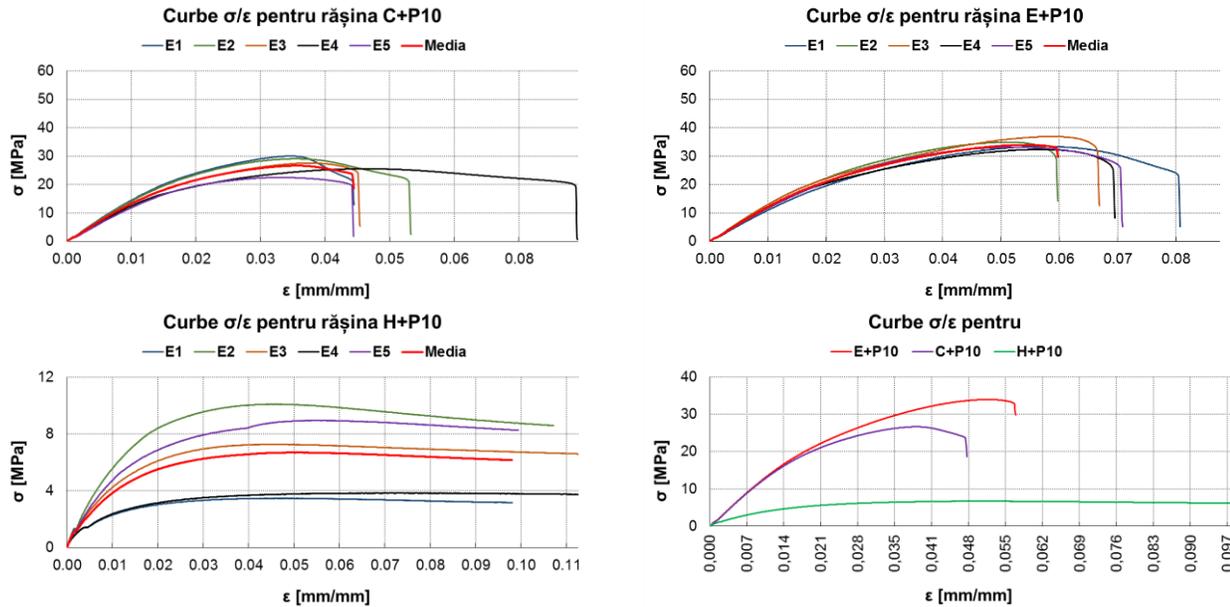


Fig. 8 σ/ϵ curves of binary mixtures (10%) – traction

Regarding the materials with 15% epoxy novolac modified vinylester resin - fig. 10. – it can be observed that the highest effort corresponds to the material C+P15 and the materials have a plastic behavior. The material that is easiest to deform (the most plastic) is the one with H epoxy resin.

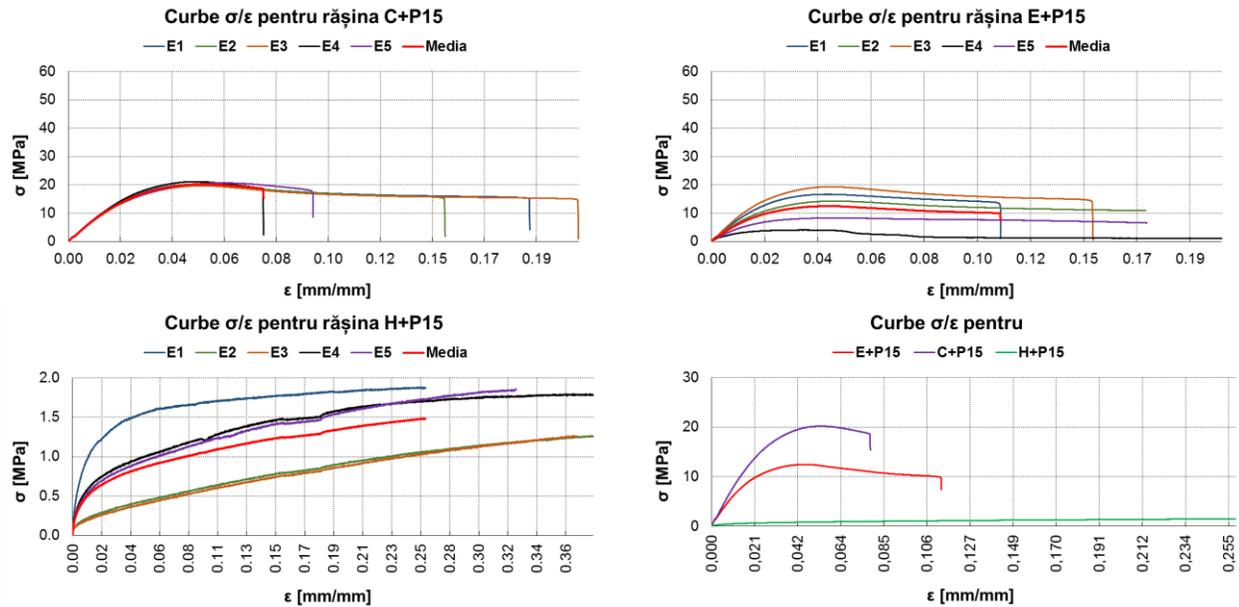


Fig. 9 σ/ϵ curves of binary mixtures (15%) – traction

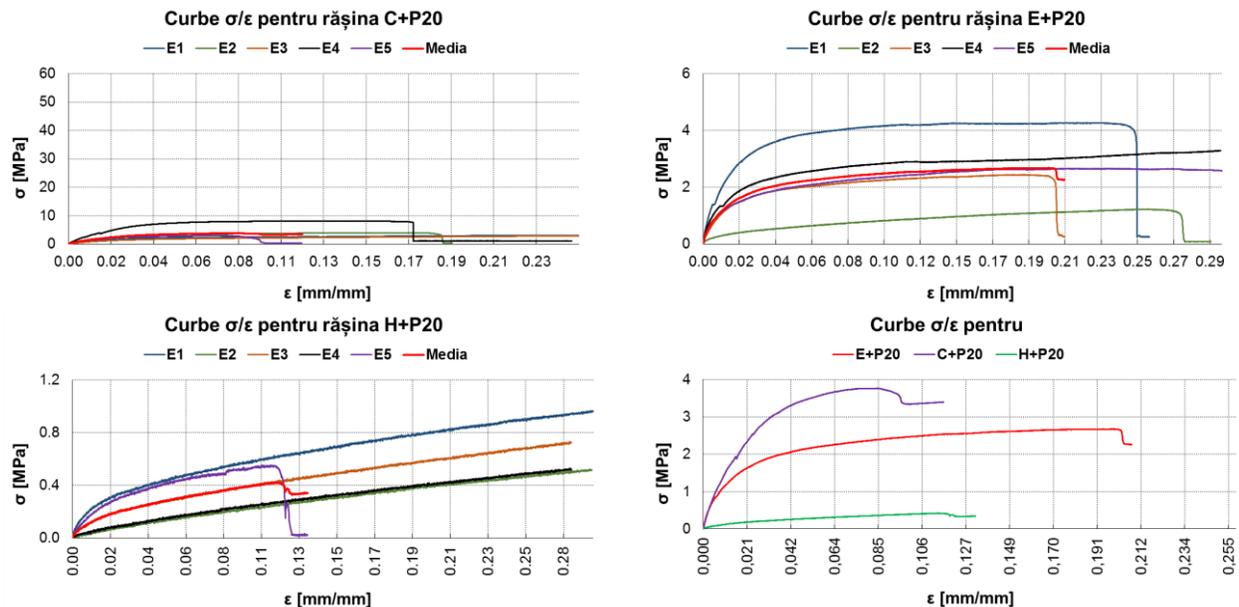


Fig. 10 σ/ϵ curves of binary mixtures (20%) – traction

Finally - fig. 11. – contains the stress/strain curves of materials with 20% epoxy novolac modified vinylester resin. All materials behave plastically, in the case of E-epoxy resin materials there is still a majority of specimens that break (three out of five), for C-epoxy resin materials only two are broken and for H-resin materials only one specimen is broken. The materials become increasingly plastic as the volume fraction of the vinylester resin increases.

It is important to quickly decrease of the elasticity of the materials formed with resin H which means either there is a chemical reaction (without directly visible effects) between the two resins or there is a chemical reaction between the vinylester resin and the hardener of resin H which limits the polymerization of the latter - similar effects were observed by George Mihiu [219] when he

Capitolul 4

diluted epoxy resins with various organic solvents or solutions in organic solvents of some thermoplastic polymers. These things can be easily observed in fig. 12.

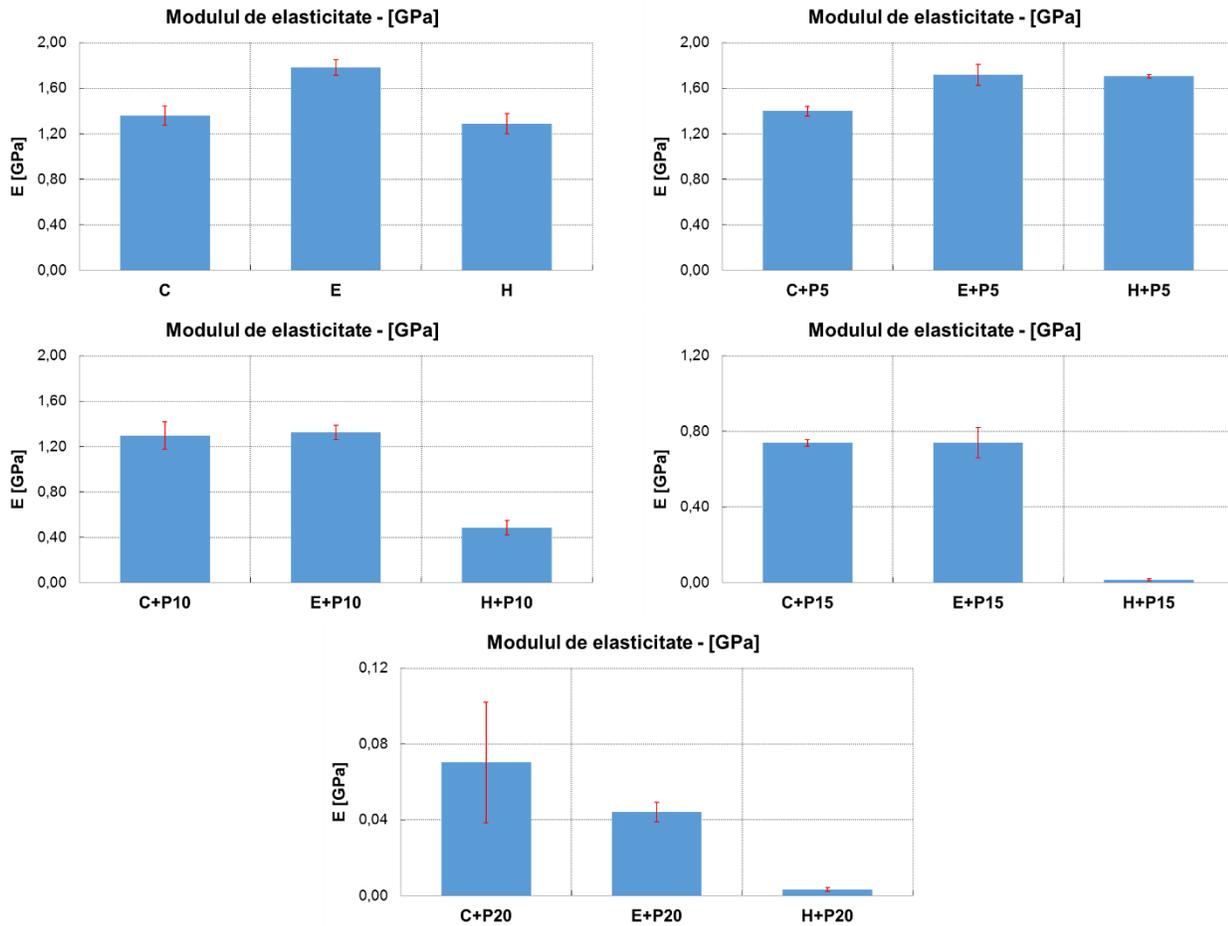


Fig. 11 Elastic modulus of binary materials – tensile tests

4.2. Tensile tests – partial conclusions

- the elastic response of the materials is reduced with the increase in the volume fraction of the epoxy novolac modified vinylester resin;
- in the case of epoxy resin H, the deterioration of the elastic response is much faster than in the case of the materials formed with the other two studied epoxy resins (C and E);
- for the samples of epoxy resins and for those of resins modified with 5% vinylester resin, there is a possibility that cracks may have appeared when the samples were tightened in the grips, but this hypothesis must be checked;
- for possible applications of binary mixtures - with the exception of verifying the hypothesis of nanostructuring – there are opportunities to use less elastic materials to design reinforced composites. In this case the adhesion of polymer mixture to the reinforcement has to be verified.

4.3. Compression test results

The compression tests were performed on cylindrical specimens with a height of 16mm and a base diameter of 8mm. The travel speed of the horizontal console of the testing machine was set to 5mm/min. The compression tests for the analyzed epoxy resins – fig. 14. – indicates an elastic

behavior for very small strains, followed by a flow-type behavior. Analyzing the average curves for each of the three resins (bottom right graph) it can be seen that the highest compressive strength is presented by resin C while the lowest compressive strength corresponds to resin E.

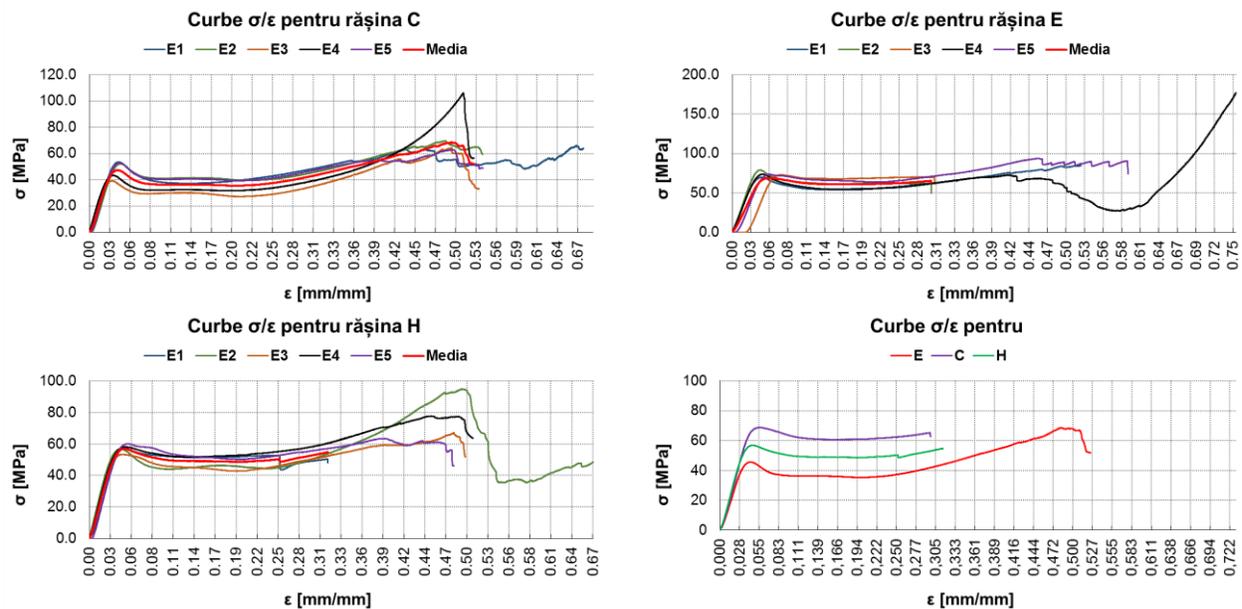


Fig. 12 σ/ϵ curves of epoxy resins – compression tests

As with the tensile test results, the best compression response (compressive strength) corresponds to the H+P5 material, even better than the H epoxy resin response. For the +P5 materials made with the other two resins, the compressive strengths are reduced compared to compressive strengths of epoxy resins - fig. 15.

The most dispersed individual responses are also observed in the case of the material formed with epoxy resin E. The average behaviors are similar to those of the base materials (epoxy resins).

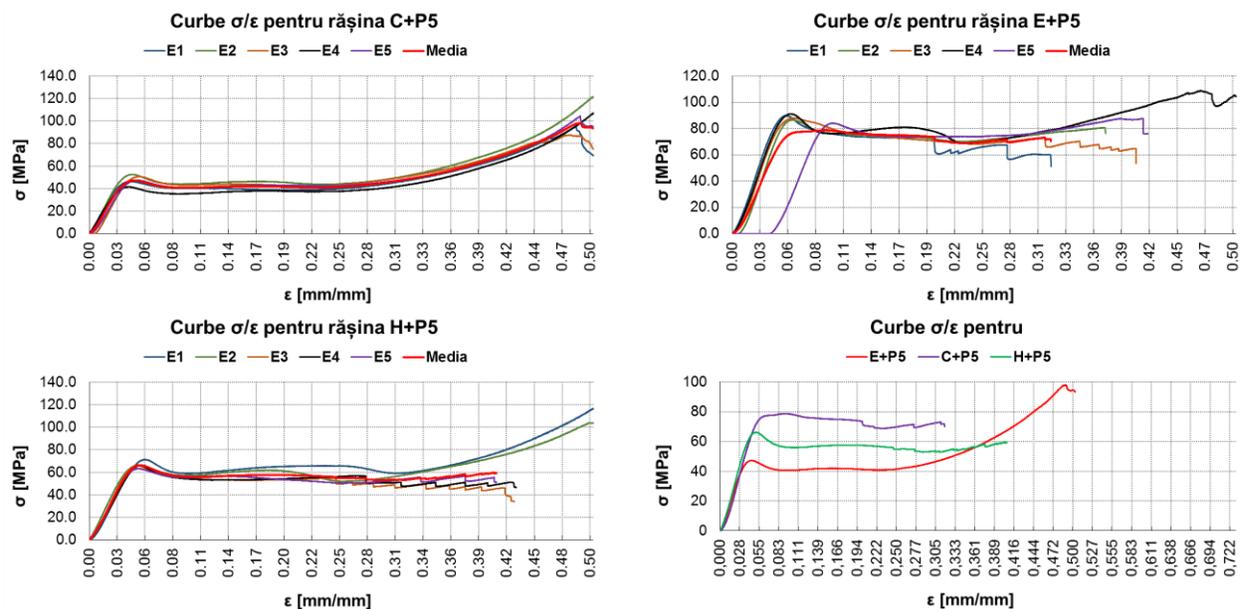


Fig. 13 σ/ϵ curves of binary mixtures (5%) – compression tests

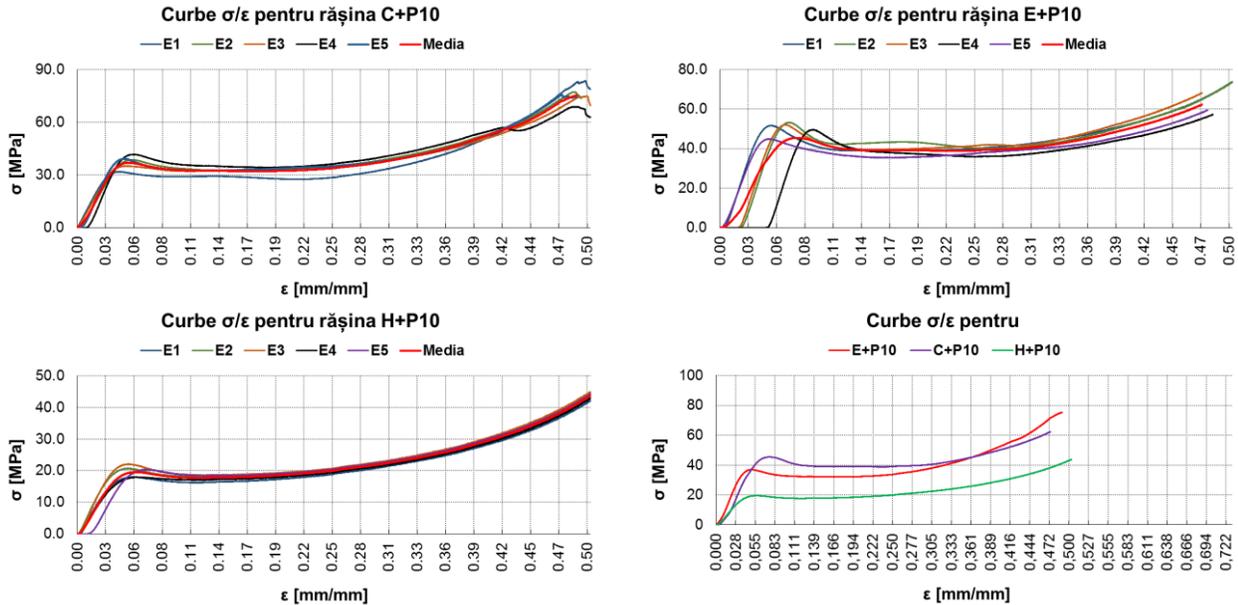


Fig. 14 σ/ϵ curves of binary mixtures (10%) – compression

For the binary mixtures with a volume rate of 10% of the epoxy novolac modified vinylester resin - fig. 16. – it can be seen that the mixture containing epoxy resin H changes its behavior by becoming plastic (easily deformable). The same is observed for the other two materials. The plot of average curves indicates that the C+P10 and E+P10 materials retain the response profile of the corresponding epoxy resins with significant reduction in compressive strength. In the case of these two materials there is still an elastic response.

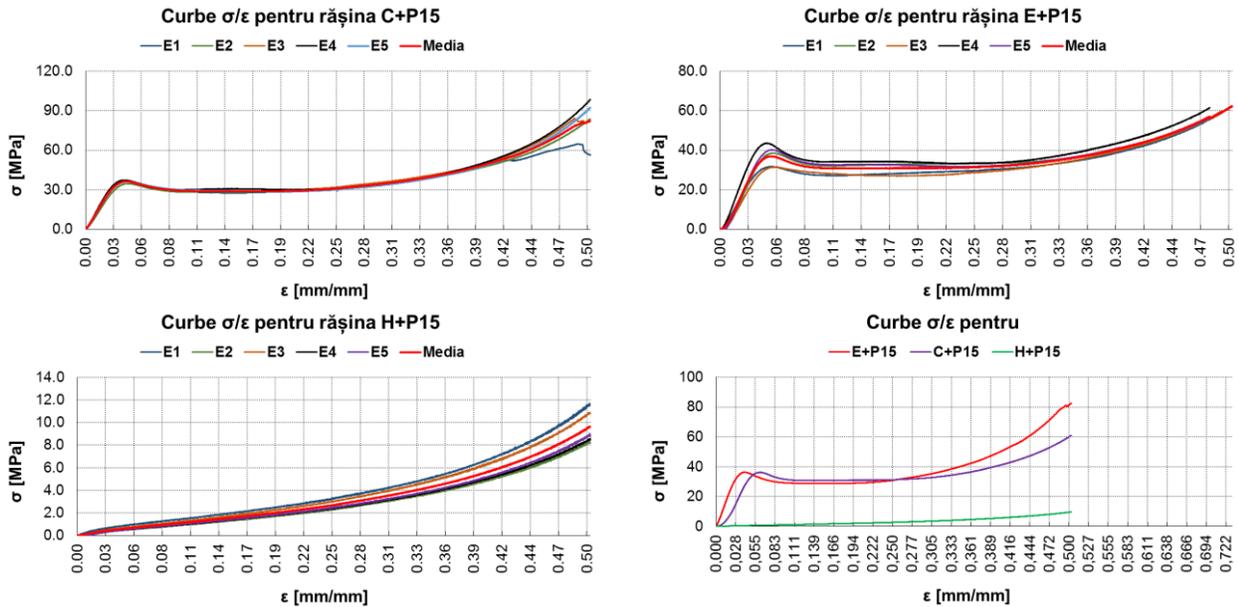


Fig. 15 σ/ϵ curves of binary mixtures (15%) – compression

The more plastic the materials are, the smaller the dispersion of the σ/ϵ curves is, as can be seen in fig. 17. The blend of H resin with 15% epoxy novolac modified vinylester resin no longer

has any elastic response (as in tensile tests). The compressive responses of the other two mixtures with 15% vinylester resin retain the trend observed for the results discussed previously.

In the case of the highest volume ratio of the vinyl ester modified epoxy novolac resin, only the mixtures with epoxy resin C and those with epoxy resin E retain a slight elastic response - fig. 18.

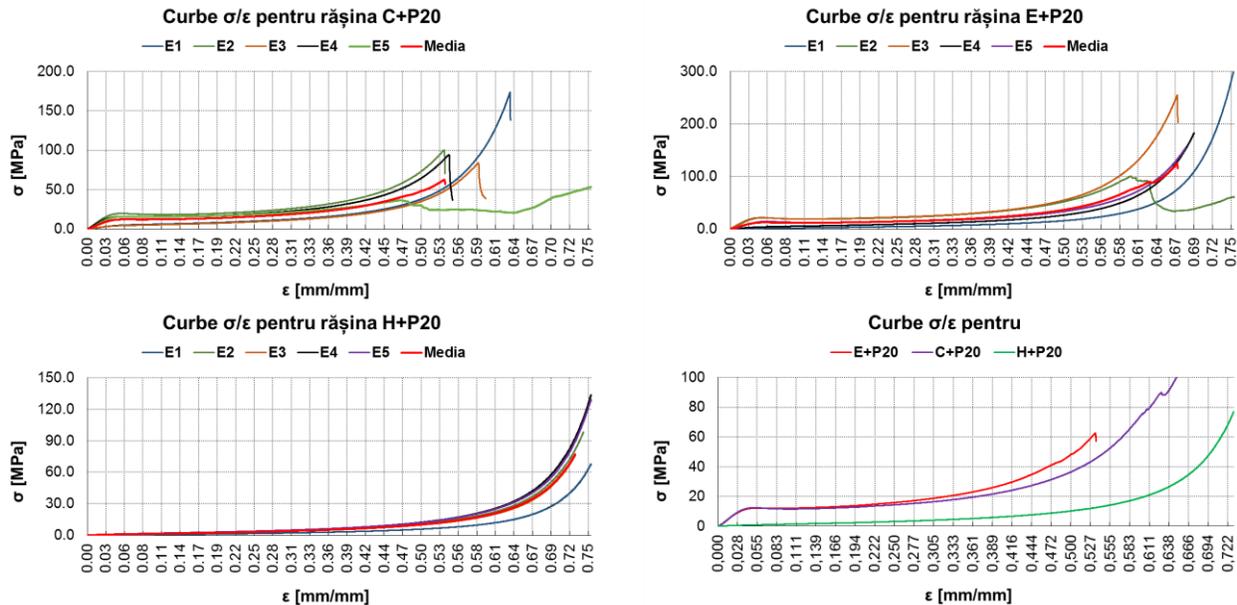


Fig. 16 σ/ϵ curves of binary mixtures (20%) – compression

After exceeding this threshold, the increase in effort is due to the compaction of the material between the plates. Probably, as we have shown in the analysis of tensile test results, mixtures with high volume ratios of vinylester resin could be used for impact resistant materials.

4.4. Compression tests – partial conclusions

- the elastic response to compression of the materials is all the more reduced the higher the volume ratio of the epoxy novolac modified vinylester resin in the epoxy resin - fig. 19.;
- for all the epoxy resins used, it can be observed that the modulus of elasticity under compression has higher values for the mixture with 5% epoxy novolac modified vinylester resin;
- the value of the elastic modulus in compression of the mixtures decreases with the increase in the volume ratio in the mixture of epoxy novolac modified vinylester resin;
- the mixtures made with epoxy resin H no longer show any kind of elastic response to volume rates of vinylester resin starting at 10%;
- for these mixtures, a study with a smaller step of variation of the volume rate of the vinylester resin would be interesting, in order to identify the exact volume rate at which the behavior changes;
- errors are lower than those recorded in the case of tensile tests because the samples are much smaller and the probability of the existence of defects is reduced;

4.5. Three-point bending tests results

Three-point bending tests were performed on cylindrical specimens (similar to bending tests for plastic tubes) with a length of 100mm and a base diameter of 8mm. The descending speed of

Capitolul 4

the mobile crossbar of the testing machine was set to 5mm/min (the same value as in the other two tests) to ensure quasistatic loading of the specimen.

The load/displacement curves for the three-point bending tests of the specimens made of the studied epoxy resins are shown in fig. 20. It can be seen that the best response (highest loading) corresponds to epoxy resin E. It can also be seen that the largest dispersion of individual responses corresponds to epoxy resin C, which also has the lowest maximum loading value .

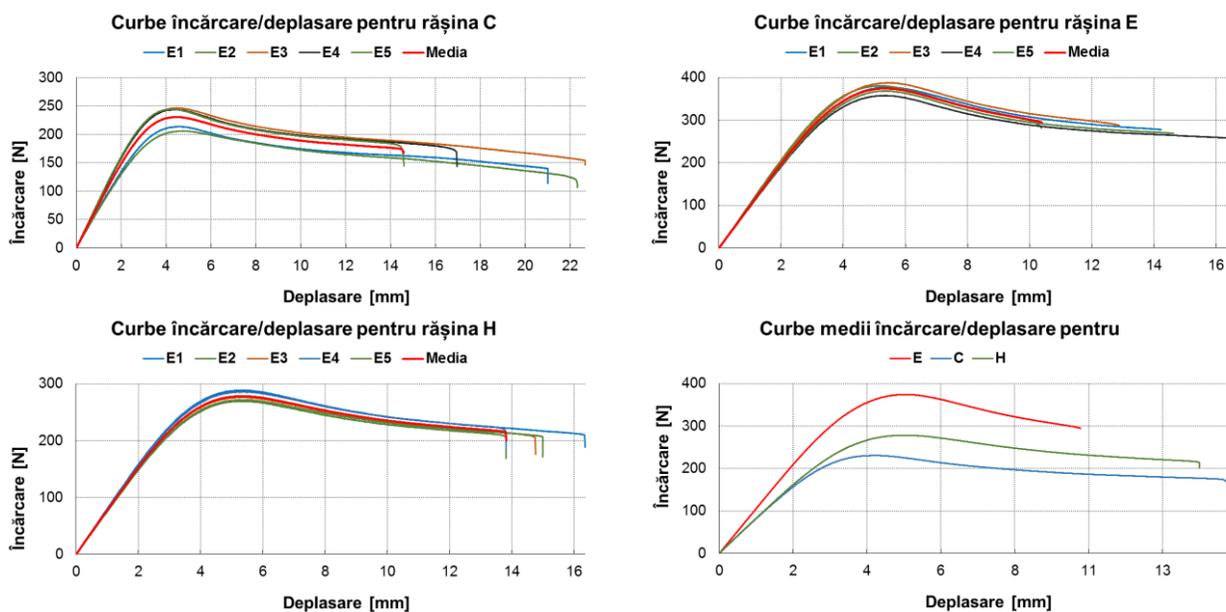
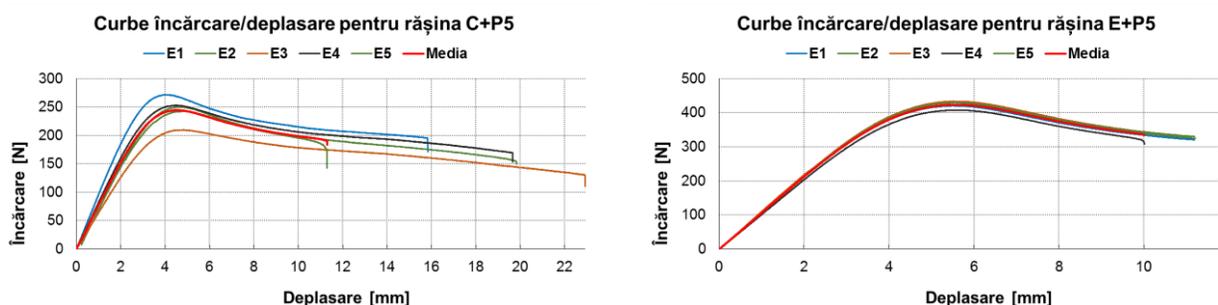


Fig. 17 Load/displacement curves of epoxy resin specimens – bending tests

Analyzing the average load/displacement curves (averages on the material) it can be found that the best response corresponds to epoxy resin E and the worst to epoxy resin C. In the case of three-point bending tests, the errors are generated by possible sliding of the specimens on the supports (which are also cylindrical and therefore there are only two contact points between the test piece and the supports). We did not observe deformations of the specimens in the support areas, but it can be seen that the displacements are appreciable - almost twice the diameter of the specimen.

As a first observation, it can be noticed, analyzing the average load/displacement curves, that in the area of small displacements (up to 2mm) epoxy resins C and H have practically the same response and epoxy resin E has the best elastic response.

In fig. 21. the individual curves (corresponding to each specimen) of the binary mixtures with 5%, volume fraction, modified vinyl ester epoxy novolac resin are shown. The responses of the materials, although less elastic, also respect for these mixtures, the situation in the case of epoxy resins.



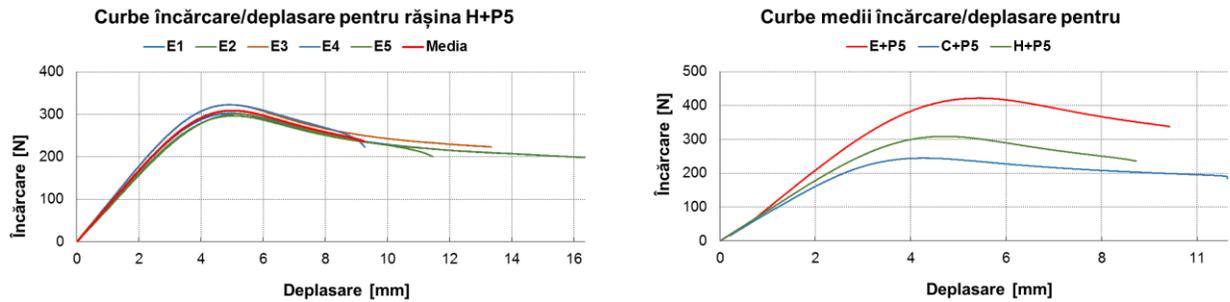


Fig. 18 Load/displacement curves of binary mixtures (5%) – bending tests

Resin mixture E responds best, followed by resin mixture H and, finally, resin mixture C. Compared to epoxy resins, it is easy to see that equal displacements of the punch correspond to lower specimen loads – in the case of mixture E+P5 this decrease in loading is almost imperceptible, compared to epoxy resin E.

For the mixtures with 10% epoxy novolac modified vinylester resin the individual responses – fig. 22. – are more dispersed, especially in the case of the H+P10 mixture, which confirms the results obtained in the other two types of tests, namely the fact that, somewhere between 5% and 10% volume fraction of the vinylester resin, the H epoxy resin mixtures no longer have elastic response. As for the other two mixtures, it is obvious that the range of elastic responses decreases with the increase in the volume fraction of the epoxy novolac modified vinylester resin.

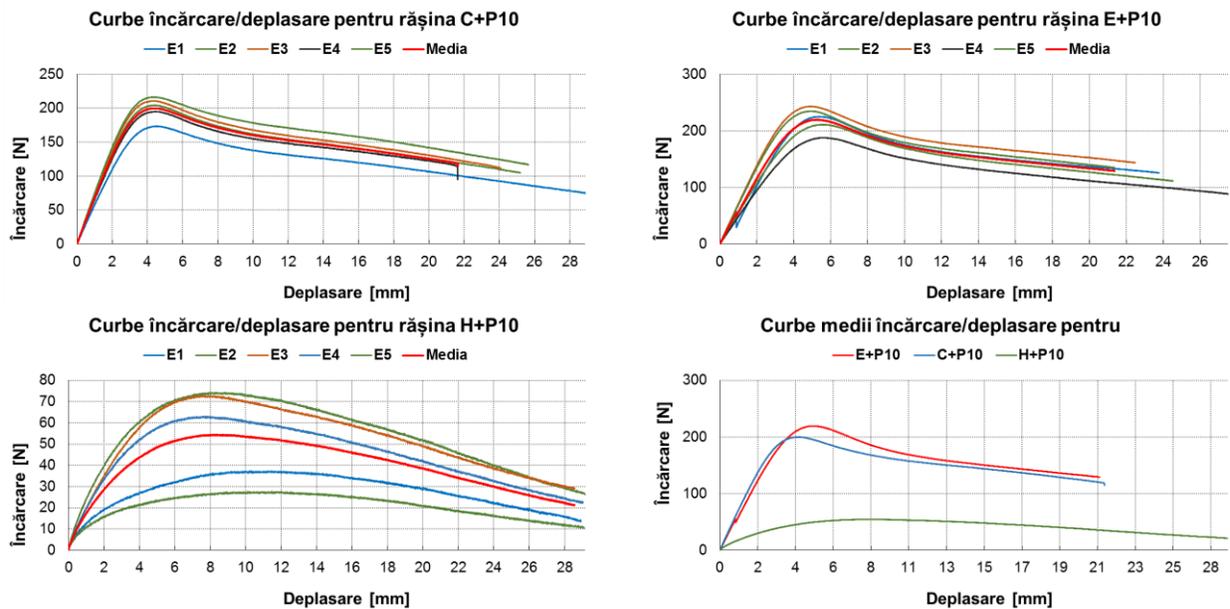


Fig. 19 Load/displacement curves of binary mixtures (10%) – bending tests

For the mixtures with 15% volume fraction of epoxy novolac modified vinylester resin the recorded results are shown in fig. 23. Except for the C+P15 mixture, the other mixtures show significant dispersions of the individual load/displacement curves.

It can be observed that the elastic response of the C+P15 mixture is superior to the elastic response of the E+P15 mixture – a reversed situation compared to the other materials tests results analyzed so far. In the case of compression, the situation was reversed.

Capitolul 4

The situation presented above also occurs in the case of the materials with the highest value of the volume fraction of the epoxy novolac modified vinylester resin in the mixture - fig. 24. In this case, the same perturbation of the response can be observed in the case of the E+P20 mixture. The only material whose response remains stable is C+P20.

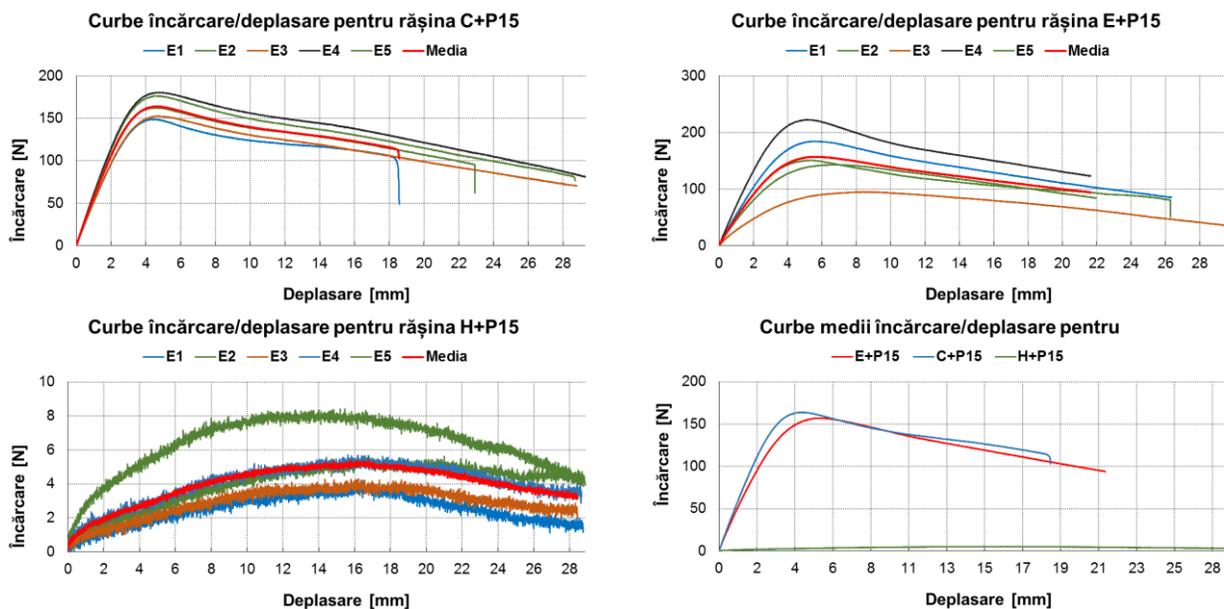


Fig. 20 Load/displacement curves of binary mixtures (15%) – bending tests.

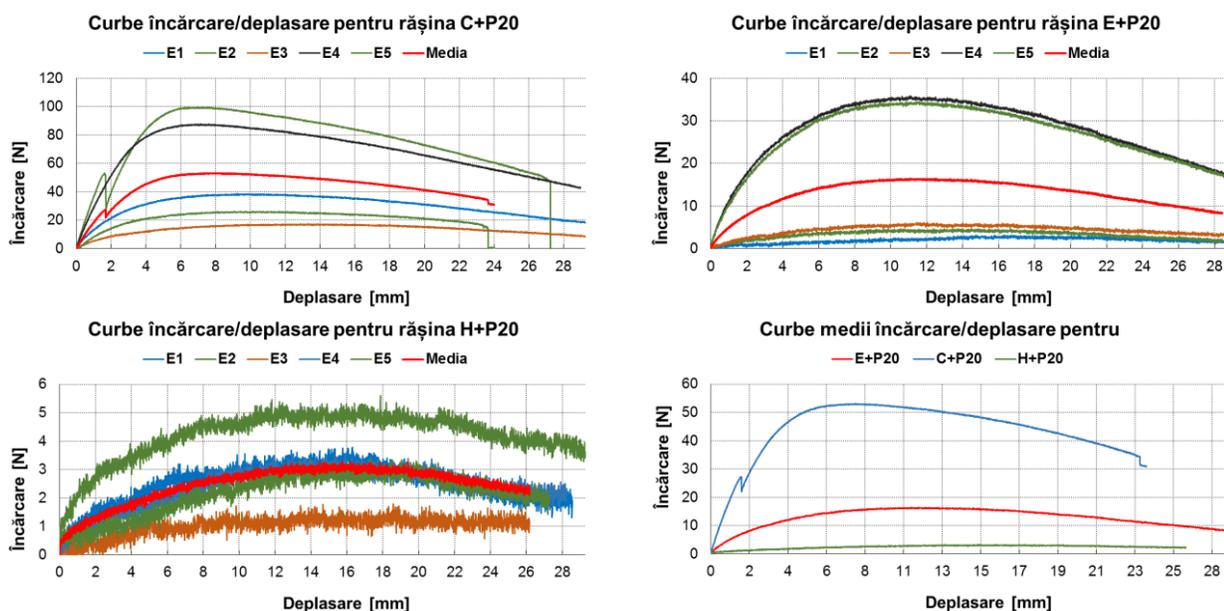


Fig. 21 Load/displacement curves of binary mixtures (20%) – bending tests

4.6. Three-point bending tests – partial conclusions

- at small volume fractions (5%) of the epoxy novolac modified vinylester resin, the mixtures with the three epoxy resins show elastic bending responses similar to epoxy resins - this means that the presence of the vinylester resin does not change (at this fraction) the properties of the epoxy resins;

- at higher volume fractions (10%), as in the case of compression and tensile tests, the mixture with epoxy resin H no longer has an elastic response, while the mixtures made with the other two epoxy resins show a reduced elastic response;
- for the mixture made with epoxy resin H, starting with 10% volume fraction of epoxy novolac modified vinylester resin, an instability of the responses of the samples is observed, non-periodic instability, which can lead to the conclusion that the response of the material is a superposition of elastic responses.

4.7. Tribological test results

După cum am arătat în capitolul 3 testele tribologice au fost realizate în geometria știft pe disc, cu discul din oțel și știftul realizat din materialul de analizat. Am stabilit trei regimuri tribologice (F,v) astfel încât produsul valorilor forței de încărcare și modulului vitezei de alunecare să fie același. Cele trei regimuri au fost prezentate în capitolul 3.

As we showed in chapter 3, the tribological tests were carried out in the pin-on-disk geometry, with the steel disk and the pin made of the material to be analyzed. We set three tribological regimes (F,v) so that the product of the values of the loading force and the sliding speed is the same. The three regimes were presented in chapter 3.

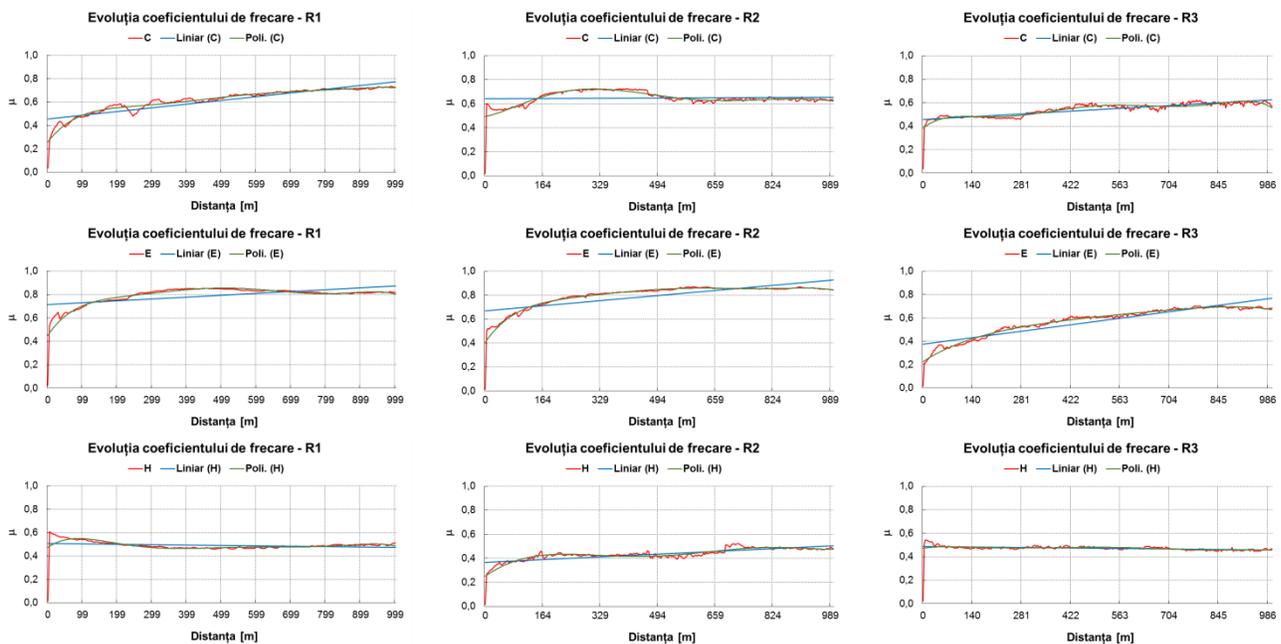


Fig. 22 The evolution of the sliding friction coefficient – epoxy resins

In fig. 26. the average evolutions of the friction coefficient of epoxy resins according to the friction distance are presented. It can be seen that, for each epoxy resin, the high values of the sliding friction coefficients correspond to the regime with the lowest load of the sample (R1). For epoxy resin C there is an increasing trend, for epoxy resin E the trend is slightly increasing and finally for resin H the trend is very slightly decreasing. For regime R2, epoxy resin C shows a very slightly decreasing tendency of the sliding friction coefficient, for epoxy resin E an increasing tendency (from 0.64 to 0.9) and for epoxy resin H a slightly increasing tendency (from 0.38 to 0.49).

Capitolul 4

For regime R3, the evolution of the value of the sliding friction coefficient is slightly increasing for epoxy resin C, increasing for epoxy resin E and slightly decreasing for epoxy resin H.

For a better understanding of the evolution of the friction coefficient, it would be more useful to strictly present the average evolution (average of the three tests) of the sliding friction coefficient without loading the representations with linear and polynomial trends - fig. 27.

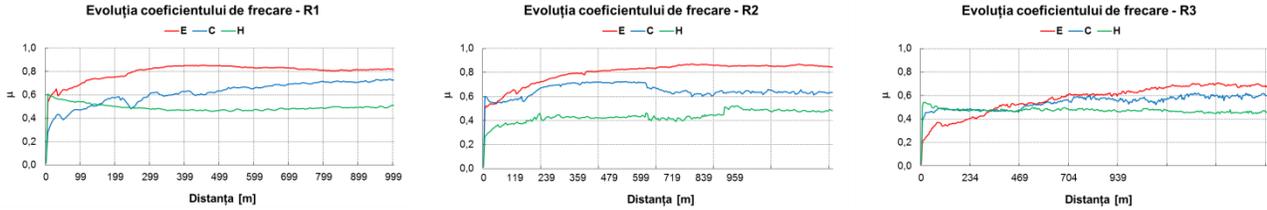


Fig. 23 Evolution of the coefficient of sliding friction – epoxy resins

Everything described above (based on the linear trend) can also be observed in the case of the representations in fig. 27. It should be noted that data acquisition has a certain speed and for this reason, apparently, at R2 and R3 regimes (lower speeds) the tests continue beyond the distance of 1000m.

In the case of binary mixtures of epoxy resin with epoxy novolac modified vinylester resin, the average evolution of the sliding friction coefficient values are given in fig. 28.

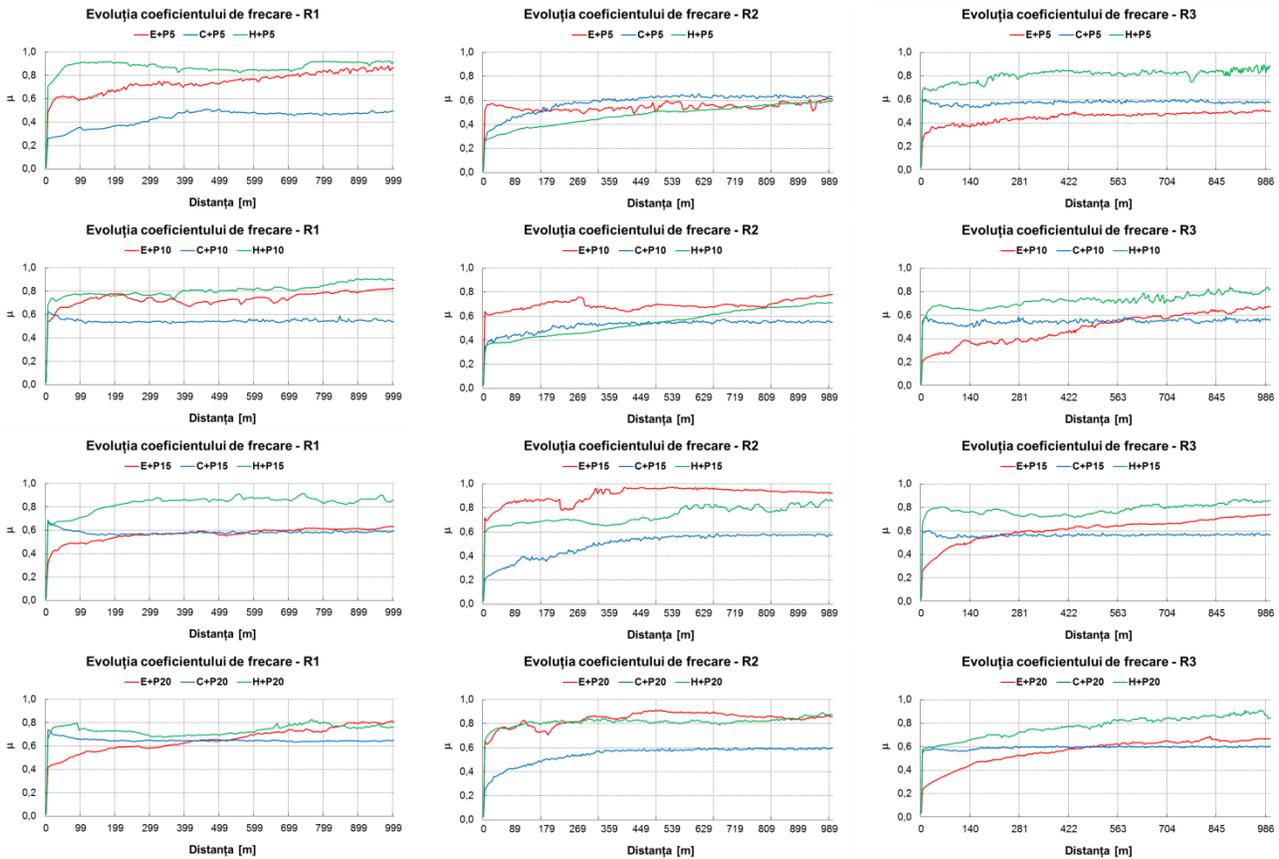


Fig. 24 Evolution of sliding friction coefficient – binary mixtures

4.8. Tribological tests – partial conclusions

- we performed tribological tests, in three different tribological regimes, in the pin on disc geometry, with the pin made from the binary mixture and steel disc;
- the evolution over time of the sliding friction coefficient value was recorded for three samples from each material, for each tribological regime;
- the binary mixtures of epoxy resin H usually present the highest values of the coefficient of sliding friction on steel - for any volume fraction of the vinylester resin and thus confirm the observations made following mechanical tests (material instability);

4.9. Thermal test results

The thermal tests aimed to determine the specific heat of binary mixtures and, as we showed in chapter 3, they were carried out on DSC 1 (Mettler Toledo). The test program included two heating-cooling cycles, each consisting of: isothermal maintenance, at -50°C , of the material for three minutes to establish thermal equilibrium; heating at a rate of $10^{\circ}\text{C}/\text{min}$ from -50°C to 150°C ; holding isothermally for three minutes at 150°C and finally cooling from 150°C to -50°C at the same rate of $10^{\circ}\text{C}/\text{min}$. The second cycle is, as I stated, made up of the same transformations.

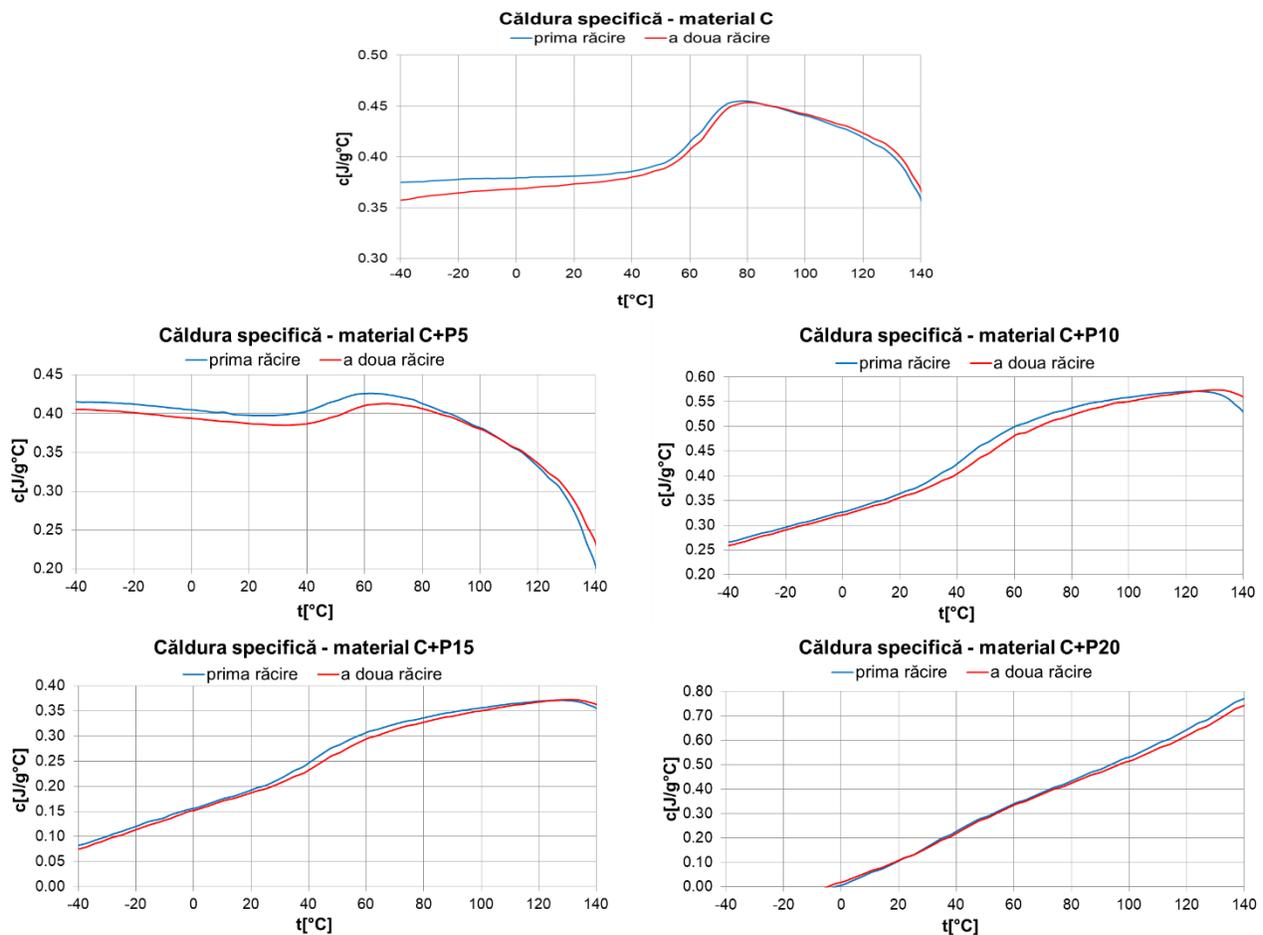


Fig. 25 The $c(t[^{\circ}\text{C}])$ function for binary mixtures of epoxy resin C

In fig. 30. Graphical representations of the dependence of specific heat on temperature are shown. How the specific heat is determined by relating the amount of heat given off (or absorbed,

Capitolul 4

when heated) by the sample to the product of the mass of the sample and the width of the temperature range ($c=Q/m\Delta t$) is immediately the fact that the functions $c(t)$ and $c(T)$ are identical (t denotes the empirical temperature – Celsius scale; T denotes the absolute scale – Kelvin).

What can be immediately observed in relation to the binary mixtures of epoxy resin C with epoxy novolac modified vinylester resin is that the appearance of the specific heat dependence on temperature changes with the introduction of epoxy novolac modified vinylester resin. In addition, it can be observed, in all cases, that the value of the specific heat is higher in the case of the first heating (the amount of heat is lower and the reference is made to the initial mass of the sample).

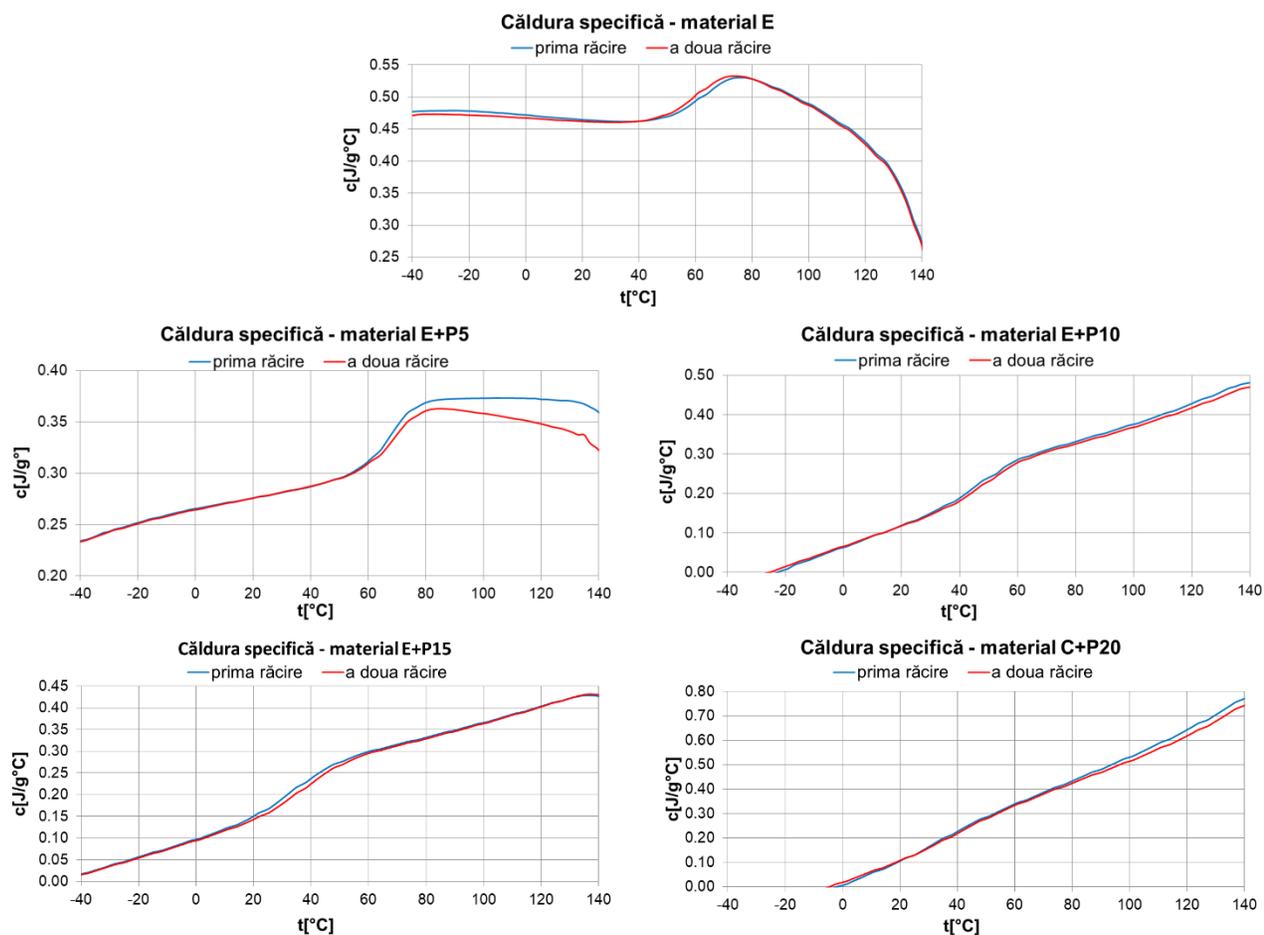


Fig. 26 $c(t^{\circ}\text{C})$ function for binary mixtures of epoxy resin E

It can be seen that the two epoxy resins analyzed so far show the same profile of the $c(T)$ curve. The same observation is valid for binary materials with 5% epoxy novolac modified vinylester resin. There are, on the curve profiles, maxima corresponding to values of 72-76°C (the value of the glass transition temperature of the epoxy resin). For the other concentrations of the binary mixtures, inflection points can be observed at temperature values of 40-45°C, which can be associated with epoxy novolac modified vinylester resins.

The similar profile of the binary mixtures of the three epoxy resins with the epoxy novolac modified vinyl ester resin indicates that the presence of the vinylester resin changes the thermal response of the base resin without, however, producing chemical changes (in which case the profiles would have been different).

Mass losses were also recorded during DSC analyses, a sign that some volatile components still exist in the mixture even though all materials have been thermally consolidated (this is true at a maximum temperature of only 90°C). And the mass losses were proportional to the volumes of epoxy novolac modified vinylester resin added to the epoxy resins so that the conclusion related to the existence of volatile substances is justified.

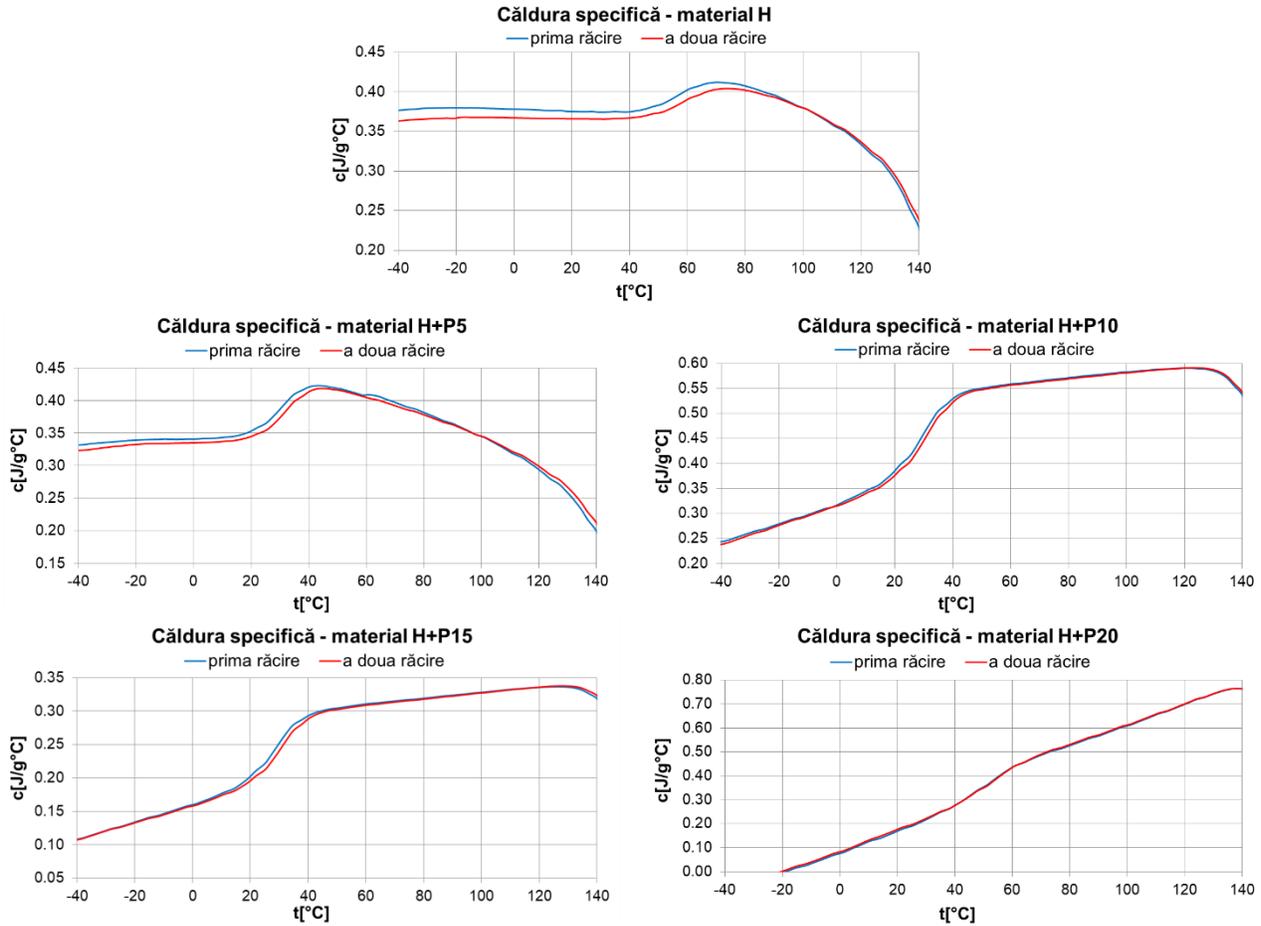


Fig. 27 The $c(t^{\circ}\text{C})$ function for binary mixtures of epoxy resin H

In this context, it would certainly be interesting to study the analysis of the mechanical properties of these materials after a thermal cure at a temperature equal to the maximum temperature reached during the DSC analysis. The decision to limit this temperature to 150°C was also made knowing that vinylester resins soften at relatively low temperature values.

The fastest alteration of the thermal behavior of the epoxy resin can be observed in the case of the binary mixtures of the E resin, while the slowest is observed for the binary mixtures of the H resin. It is interesting that if the epoxy modified vinylester resin fraction -novolac is 20%, all binary materials have practically the same thermal behavior.

4.10. Thermal tests – partial conclusions

- the presence of epoxy novolac modified vinylester resin in the studied epoxy resins, changes (in proportion to the volume fraction) the thermal behavior of the epoxy resins;
- the substance losses found after the end of the tests are proportional to the concentration of epoxy-novolac modified vinylester resin in the epoxy resin;

- the highest specific heat values correspond (regardless of the type of epoxy resin in the binary mixture) to a 20% concentration of vinylester resin in the epoxy resin.

4.11. Conclusions – Binary mixtures

- în urma testelor de tracțiune am constatat că răspunsul elastic al materialelor este redus odată cu creșterea fracției volumice a rășinii vinilesterice modificată epoxi novolac;
- în cazul rășinii epoxidice H deteriorarea răspunsului elastic este mult mai rapidă decât în cazul materialelor formate cu celelalte două rășini epoxidice studiate (C și E), constatare rezultată în urma analizei rezultatelor testelor de tracțiune;
- în cazul rezultatelor testelor de tracțiune există o dispersie destul de mare a evoluției individuale a fiecărei epruvete, pentru fiecare material, care poate fi explicată prin momentul în care a fost formată proba (funcție de vâscozitatea amestecului polimerizabil) și existenței unor foarte mici intruziuni gazoase;
- following the tensile tests, we found that the elastic response of the materials is reduced with the increase in the volume fraction of the modified novolac epoxyvinyl ester resin;
- in the case of epoxy resin H, the deterioration of the elastic response is much faster than in the case of the materials formed with the other two epoxy resins studied (C and E);
- in the case of tensile test results, there is quite a large dispersion of the individual evolution of each sample, for each material, which can be explained by the time when the sample was formed (depending on the viscosity of the polymerizable mixture) and the existence of very small gaseous intrusions;
- for the samples of epoxy resins and for those of resins modified with 5% epoxy novolac modified vinylester resin, there is a possibility that cracks may have appeared when the samples were tightened in the grips, but this hypothesis must be checked;
- for possible applications of binary mixtures - with the exception of verifying the hypothesis of nanostructuring - E+P5 and C+P5 materials are susceptible (possibly also those with +P10);
- the others could be used for impact-resistant materials (energy distribution in the material is much better). In this sense, a study on the adhesion of these binary mixtures to the different types of reinforcing fibers is important. If the adhesion properties of epoxy resins are also preserved for binary mixtures, then they could even be used for impact-resistant reinforced materials;
- the mixtures made with epoxy resin H no longer show any kind of elastic response to compression for vinylester resin volume ratios starting at 10%;
- for these mixtures, a study with a smaller step of variation of the volume rate of the vinylester resin would be interesting, in order to identify the exact volume rate at which the behavior changes;
- the errors recorded in the case of compression tests are lower than those recorded in the case of tensile tests because the samples are much smaller and the probability of the existence of defects is reduced;
- at higher volume fractions (10%), as in the case of compression and tensile tests, the mixture with epoxy resin H no longer has an elastic response, while the mixtures made with the other two epoxy resins show a reduced elastic response;
- for the mixture made with epoxy resin H, starting with 10% volume fraction of vinyl ester resin modified novolac epoxy, an instability of the responses of the samples is observed, non-periodic instability, which can lead to the conclusion that the response of the material is a superposition of elastic responses.

Chapter 5

Binary mixtures modified with organic and inorganic agents

5.1. Tensile test results

With all the inconveniences related to what I called the inconsistency of the materials above, I performed the tensile tests under the same conditions as the tests for the binary mixtures presented in the previous chapter.

The results of these tests are shown in fig. 34. and it can be seen that the results are comparable to those obtained for the binary mixtures (except for the M3 material). This means that there is an important contribution of inorganic ingredients to the properties of binary materials modified with organic and inorganic agents.

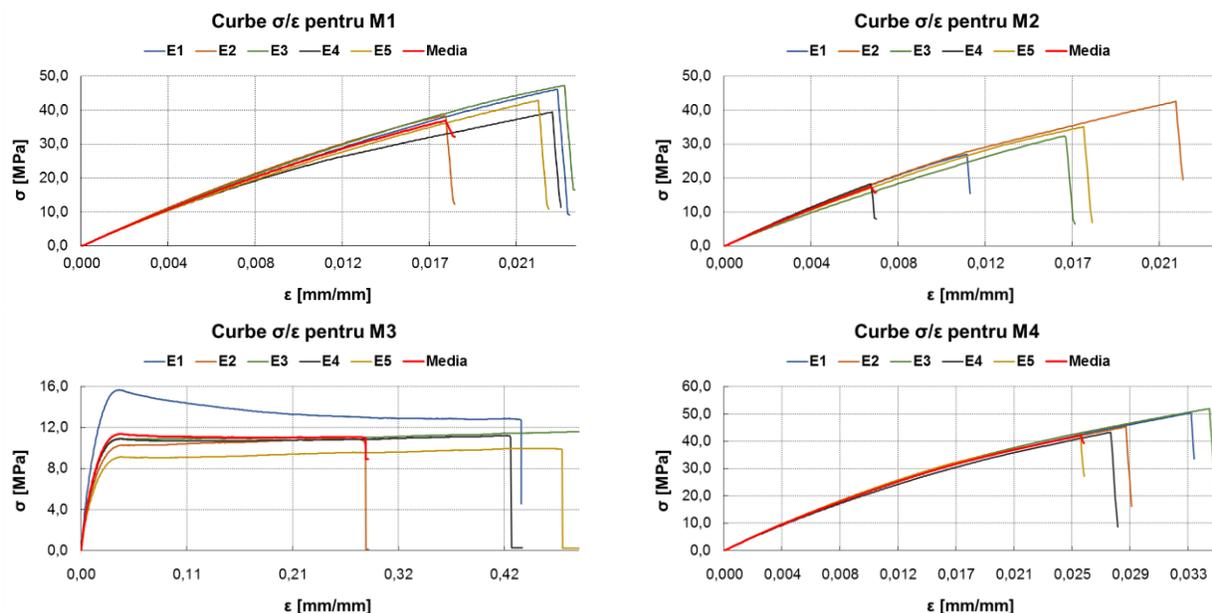


Fig. 28 Stress/strain curves for M materials - tensile tests

5.2. Tensile tests – partial conclusions

- unexpectedly, the materials formed (although they have a very high volume fraction vinyl ester modified epoxy novolac resins) behave similar to the E+P10 materials;
- the M3 material does not have a very consistent response and an elastic modulus value comparable to that of the E+P15 material;
- there seems to be a link between the presence of inorganic compounds and the polymerization of the samples (except M5 and M6 materials) as long as the properties of M materials (with 50% volume ratio) behave like E+P10 or E+P15 materials.

5.3. Three-point bending test results

Three-point bending tests were performed under the same conditions as for the binary

mixtures. The results of these tests are shown in fig. 36.

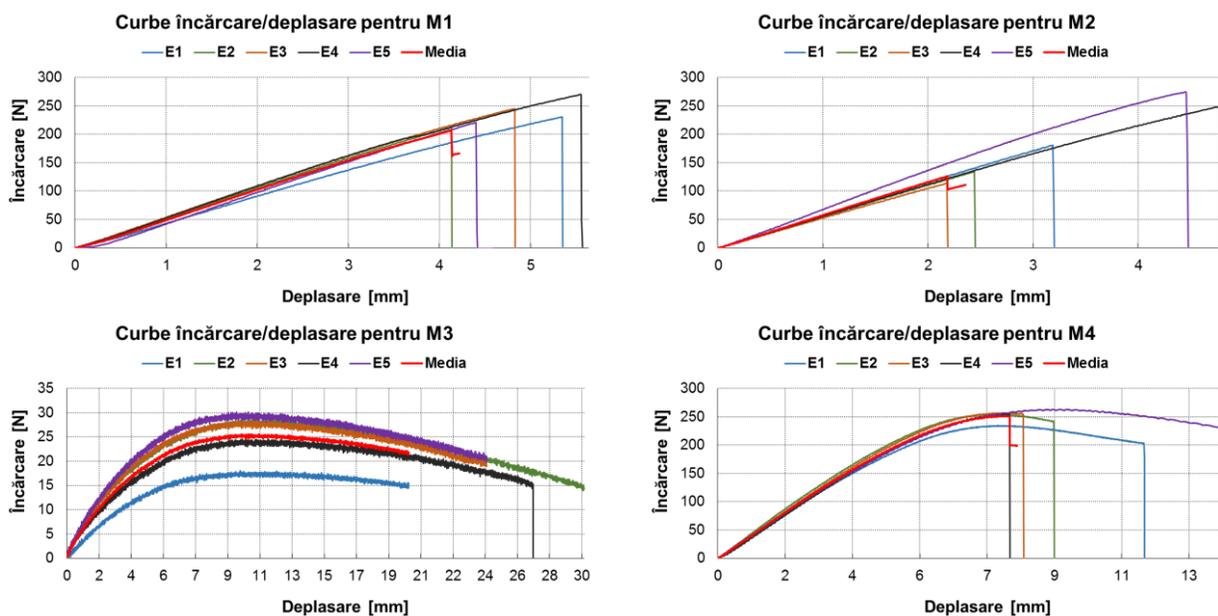


Fig. 29 Individual load/displacement curves – three-point bending tests

The first observable fact is related to the shaky appearance of the curves in the case of the M3 material, similar to the curves of the E+P20 material (paragraph 4.5.). For the materials M3 and M4 the profiles of the load/displacement curves resemble those of the curves obtained for E+PX materials, for materials M1 and M2 the responses (at three-point bending) are different from all those obtained at three-point bending for the binary mixtures .

This can only mean that the presence of some of the organic compounds contributes to a better polymerization of the mixture. As for the elastic modulus M materials - they are presented in fig. 37., along with the average load/displacement curves for these materials. For the tensile tests we could not make a representation of the average curves because the differences between the deformations corresponding to the materials are very large.

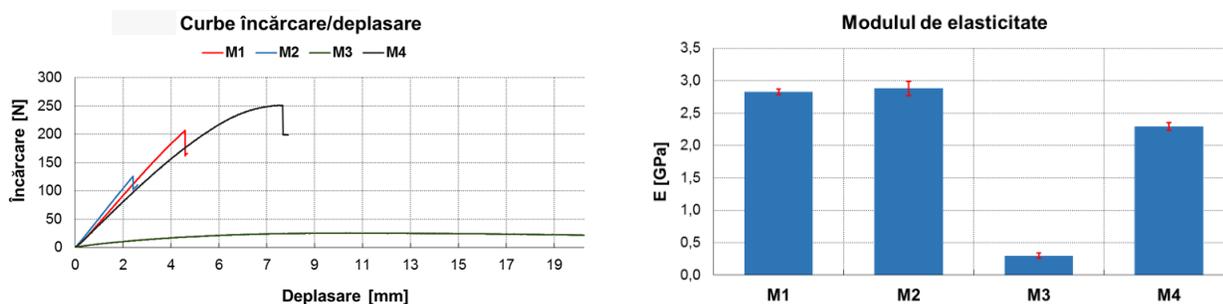


Fig. 30 Average load/displacement curves and flexural moduli of M materials

5.4. Three-point bending tests – partial conclusions

- three of the materials (M1, M2 and M4) present a profile of the load/deformation curves different from those of the curves obtained for any E+PX material;

- the individual load/displacement curves for the M3 material are similar to those obtained for the E+P20 material (perturbed appearance);
- the values of the flexural modulus are comparable to those obtained for the E+P5 mixture in the case of M1 and M2 materials, but for the M3 and M4 materials there is no correspondence between the E+PX materials.

5.5. Conclusions

- although they have the appearance of incompletely polymerized materials, the binary mixtures modified with organic and inorganic agents were tested for tensile and three-point bending;
- the other tests were not performed because it was impossible to cut the samples;
- the tensile tests reveal the fact that the materials behave like binary mixtures (epoxy resin - epoxy novolac modified vinylester resin) with a small volume ratio of the vinyl ester resin, which means that the presence of inorganic agents influences the polymerization of the mixture;
- in the case of M3 material – the three-point bending test looks similar to the three-point bending test of the binary mixture E+P20;
- the tensile elastic modulus is higher in the case of M1, M2 and M4 than the values of the same modules for E+P5, for M3 the value of the tensile modulus of elasticity is comparable to the value recorded for E+P15;
- in the case of the flexural modulus, the values for M1 and M2 are comparable to those for E+P5.

Chapter 6

Ternary mixtures modified with inorganic and organic agents

6.1. Tensile test results

The addition of other thermosetting polymers had two purposes: on the one hand to support (in suspension) the inorganic agents (or possible nanostructures) by increasing the viscosity of the mixture, and on the other hand to try to identify the effect of their presence compared to a reference material which in this case could be P1_1E or E+P10.

The results of the tensile tests for the ternary mixtures (three polymers) modified with organic (collagen) and inorganic agents (like all other results) will be presented in three groups: in the first group P1_1E and P9_1P; in the second group all materials to which we added polyurethane resin (P2_1M1, P3_1M2, P4_1M6 and P5_1M12); in the third group the materials in which we added silicone resins (P6_1S1, P7_1S2, P8_1S3).

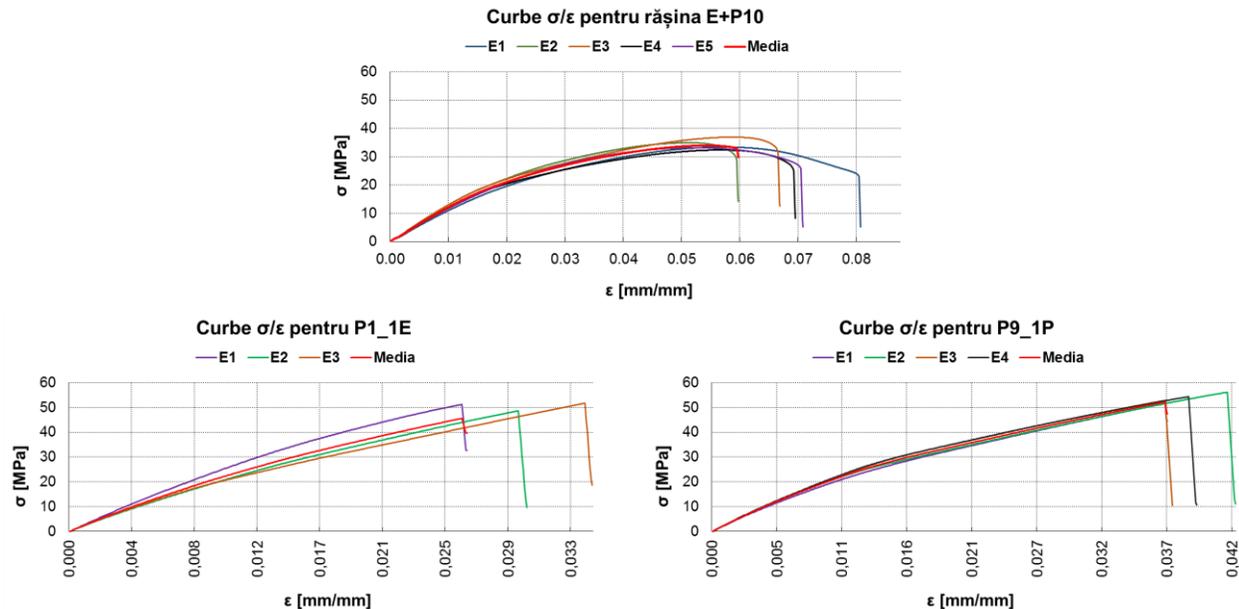
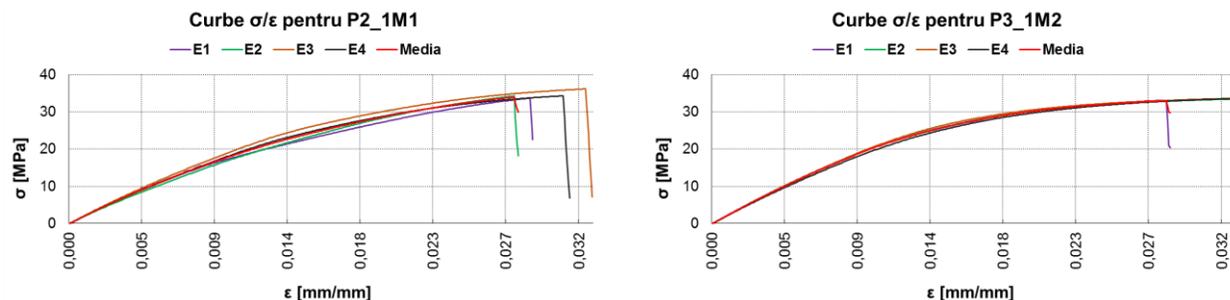


Fig. 31 Stress/strain curves for ternary mixtures (P1_1E and P9_1P) – tensile tests

Compared to the reference material (E+P10) a stiffer response (fractures of the specimens) of both ternary materials can be observed - fig. 37. The response of the latter materials is much more linear than the reference material (higher stiffness) probably due to the presence of modifying agents.



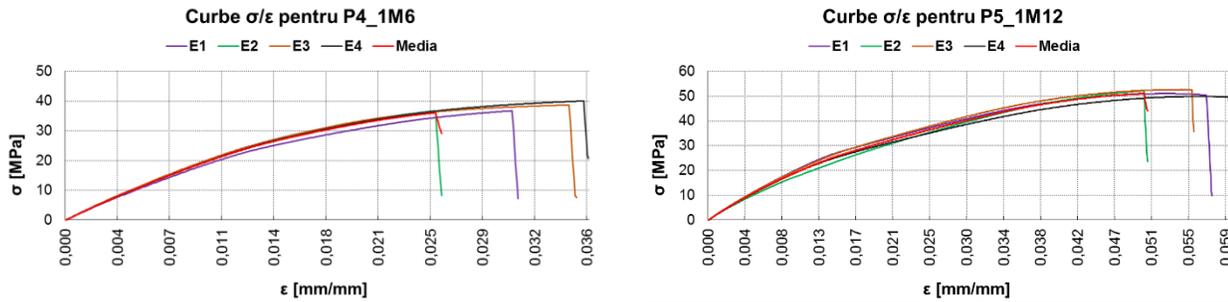


Fig. 32 Stress/strain curves for ternary mixtures with polyurethane resins – tensile tests

It can be seen that in the case of using polyurethane resins - fig. 38. – the elastic responses of the materials are close to the same level as the reference material (E+P10) for polyurethane resins P2_1M1, P3_1M2 and P4_1M6 (almost the same tensile strength). For the material P5_1_M12 the tensile strength is higher than that of the reference material (I mean the breaking stress value for the average of the curves which obviously corresponds to the breaking of the first specimen).

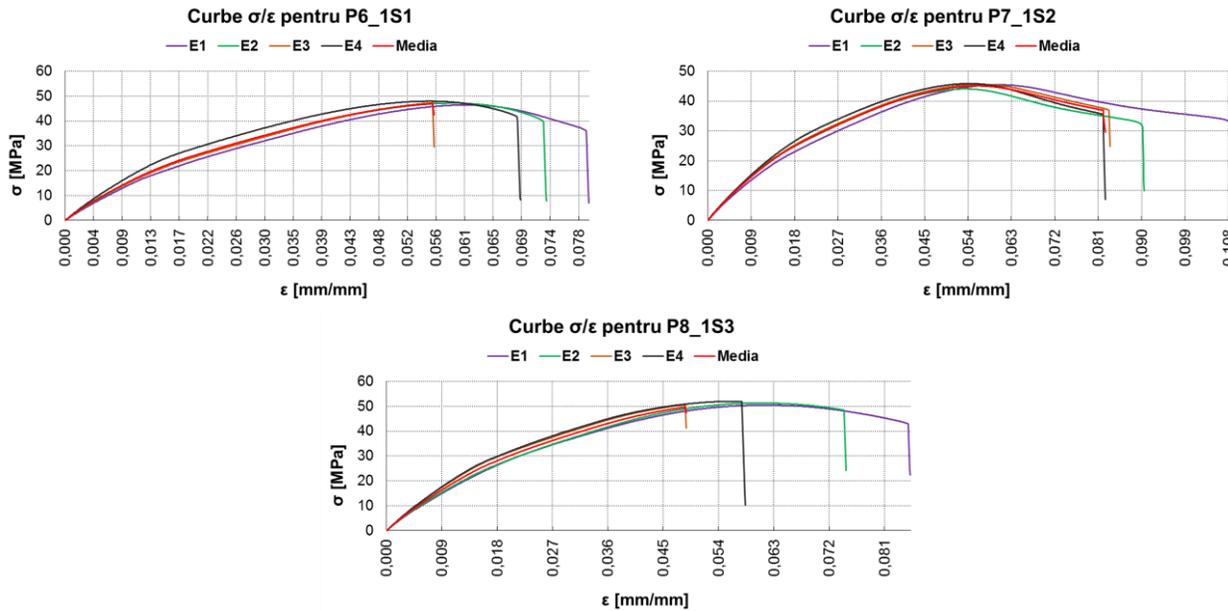


Fig. 33 Stress/strain curves for ternary mixtures with silicone resins – tensile tests

In fig. 39. the individual stress/strain curves of the ternary materials with silicone resins are shown and the more plastic response of the samples which are very little dispersed can be observed. more plastic means that all the individual σ/ϵ curves (and by implication the average curve) are not linear (they are similar to the E+P10 material curve profiles) but the fracture toughness of any of these materials is greater than the tensile fracture toughness of the reference material.

6.2. Tensile tests – partial conclusions.

- the tensile test results indicate that the ternary materials modified with organic and inorganic agents have a tensile strength higher than the reference (E+P10) and certainly higher than E+P15 which would be the binary equivalent (the initial binary mixture from which they are made these materials have 10% mass fraction vinylester resins modified novolac epoxy);

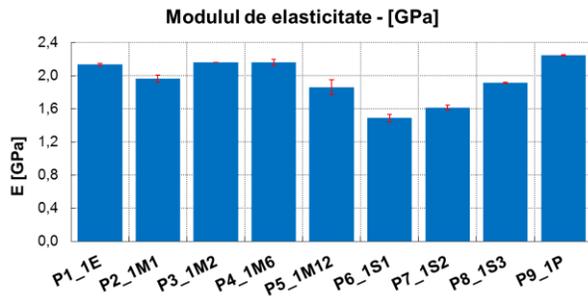


Fig. 34 Elastic modulus of modified ternary materials – tensile tests

6.3. Compression test results

As the tensile tests also the compression tests were carried out under the same conditions as those carried out for all the materials analyzed so far (epoxy resins and binary mixtures), with the same settings of the testing machine and also on cylindrical specimens with a height of 16mm and a base radius of 4mm. The results of these tests for materials P1_1E and P9_1P are shown in fig. 42. – as in the case of the tensile tests, we also reproduced the result of the compression tests on the reference material to facilitate the interpretation of the results.

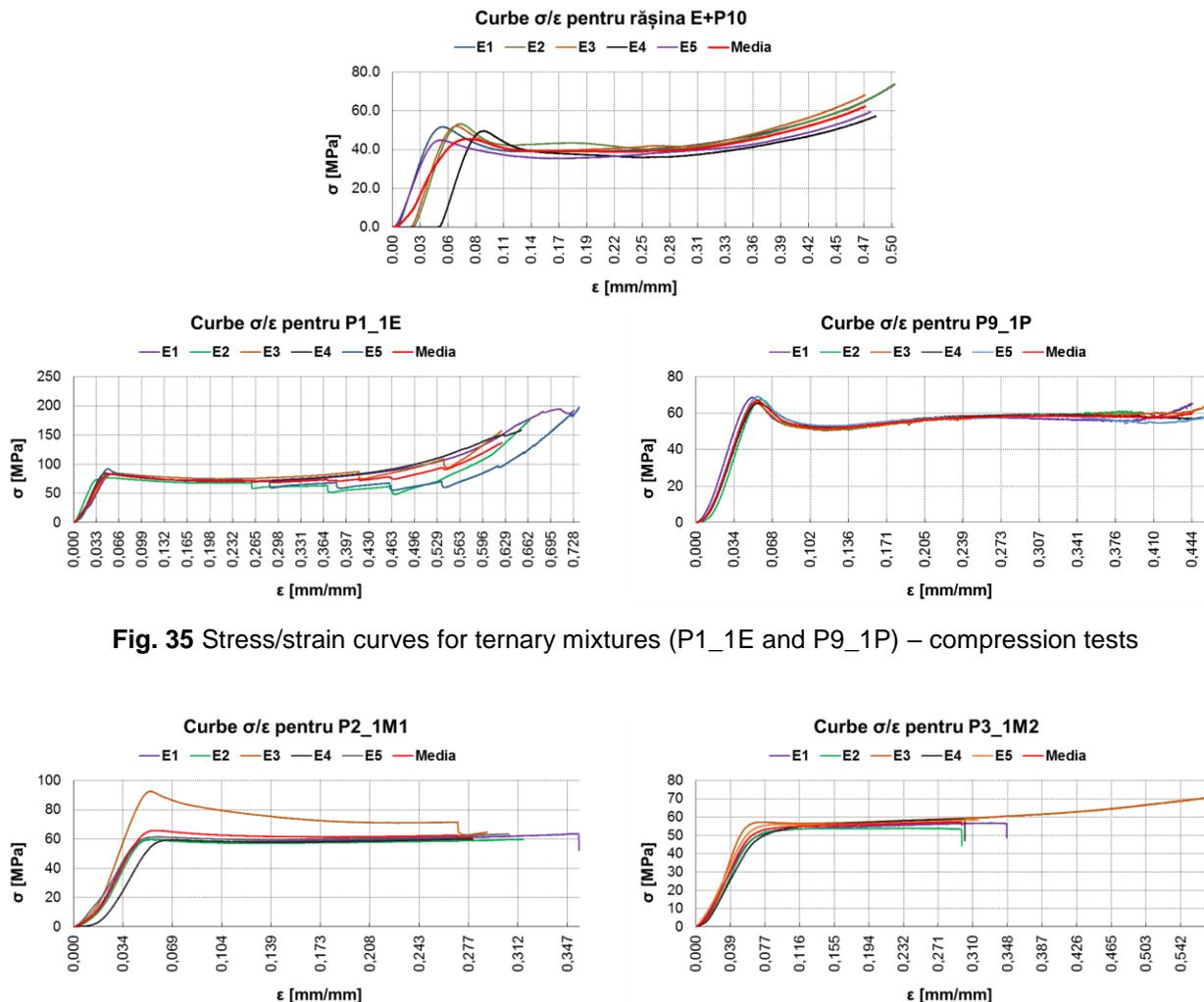


Fig. 35 Stress/strain curves for ternary mixtures (P1_1E and P9_1P) – compression tests

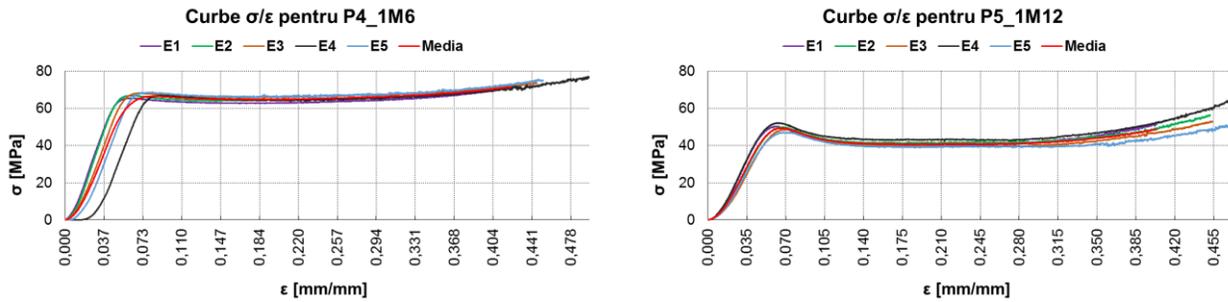


Fig. 36 Stress/strain curves for ternary mixtures with polyurethane resins – compression tests

For the ternary mixtures with polyurethane resins, the σ/ϵ curves are shown in fig. 43. It can be seen that for materials P3_1M2 and P4_1M6 the breaking stress is slightly higher than for the reference material. For P2_1M1 the same breaking stress is comparable to that of the reference material. Ternary materials modified with polyurethane resins are less brittle than the first material of this series (P1_1E) and in the cases of P4_1M6 and P5_1M12 a crumbling process can be observed (at high strains).

In fig. 44. curves for ternary materials with silicone resins are shown.

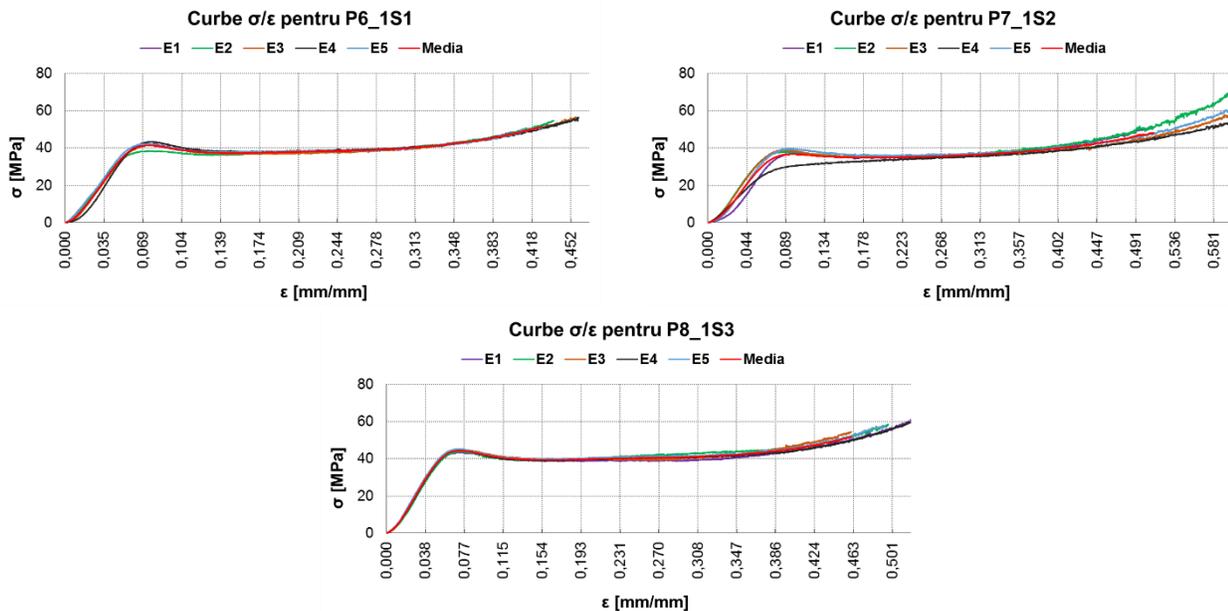


Fig. 37. Stress/strain curves for ternary mixtures with silicone resins – compression tests

6.4. Compression tests – partial conclusions

- the material P1_1E is brittle (it is equivalent to the binary material E+P5) and has a compression behavior similar to it (successive fractures appearing on the individual σ/ϵ curves);
- for the same material the stress at the elastic limit has a value comparable to that of the binary material E+P5 which means that the organic and inorganic agents used to modify the material have no effect on the compression properties (at least);
- the only exception is the P1_1E material which has a modulus of elasticity of 2.4GPa compared to 1.6GPa for the E+P10 material;
- ternary materials with polyurethane resins have compressive (as well as tensile) responses that

seem to depend on the added polyurethane resin;

- ternary materials with silicone resins have lower compressive elastic modulus in compression than the corresponding value for the reference material.

6.5. Three-point bending test results

For ternary materials with polyurethane resins - fig. 46. – it can be easily seen that in the case of the P5_1M12 material, the samples are reset on the supports, signaling the fact that the material is softer – as we also found in the tensile and compression tests.

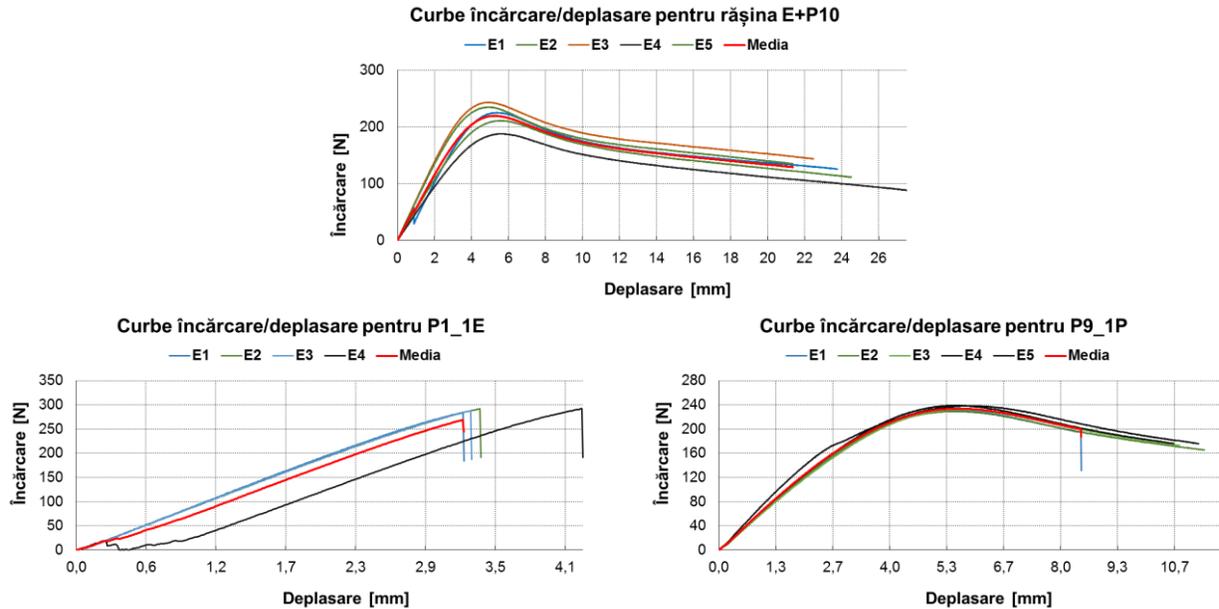
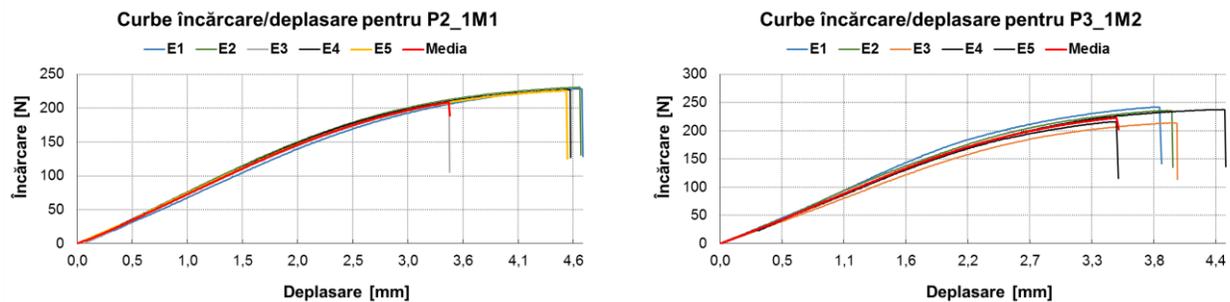


Fig. 38 Load/displacement curves for ternary mixtures (P1_1E and P9_1P) – bending tests

For the other three materials the response is elastic and the specimens break, which means that we have rigid materials. The maximum forces (at break) are lower than in the case of material P1_1E. From this point of view, no comparison can be made with the reference material E+P10 because the presence of polyurethane resins changes the bending response of the material.



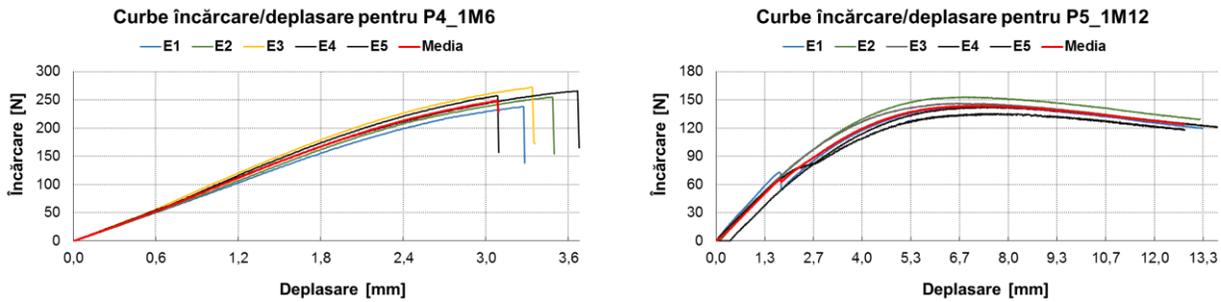


Fig. 39 Load/displacement curves for ternary mixtures with polyurethane resins – bending tests

In the case of ternary materials with silicone resins - fig. 47. – the situation is slightly different in the sense that the materials have a plastic behavior (the specimens do not break but remain deformed after the end of the test. The maximum loads of these materials are lower than the maximum loads of the other ternary materials and lower than the maximum load (average) of the reference material.

6.6. Three-point bending – partial conclusions

- compared to the reference material, the behavior of the ternary materials modified with inorganic and organic agents is completely changed for P1_1E, P2_1M1, P3_1M2 and P4_1M6;
- for the other materials the answer is similar to the answer of the reference material;
- flexural modulus - fig. 48. – have very low values for materials in which silicone resins have been added;
- the material with the highest value of the bending elastic modulus - as for the other tests performed - is P4_1M6;

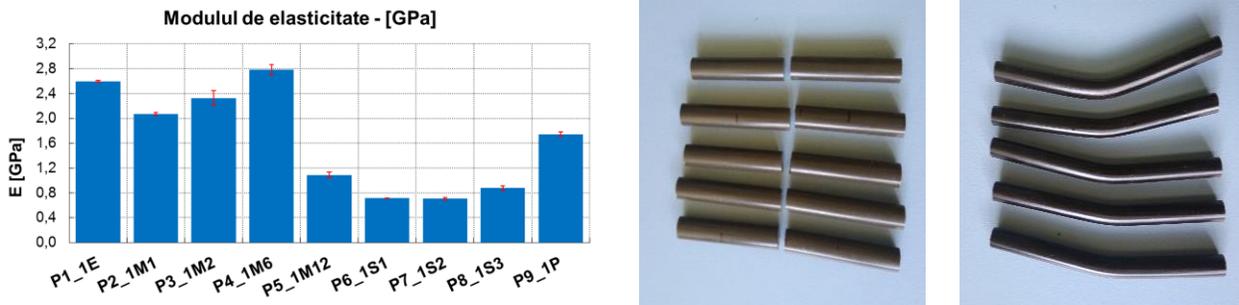


Fig. 40 Moduli of elasticity of modified ternary materials – bending. Images of test specimens P3_1M2 (left) and P4_1M6 (right)

6.7. Tribological test results

As in the case of the binary mixtures, the tribological tests were carried out on steel discs with the pin made of the material to be analyzed and in the same three tribological regimes. The responses of the materials should, in this case, also depend on the presence of the third polymer in the mixture.

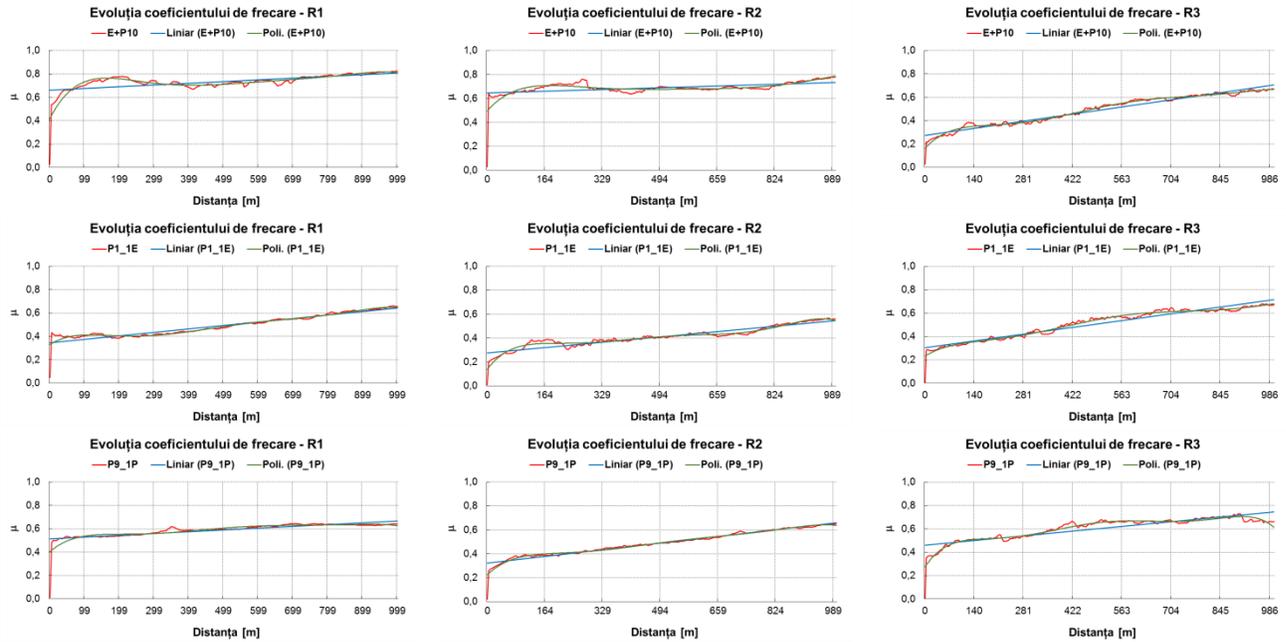
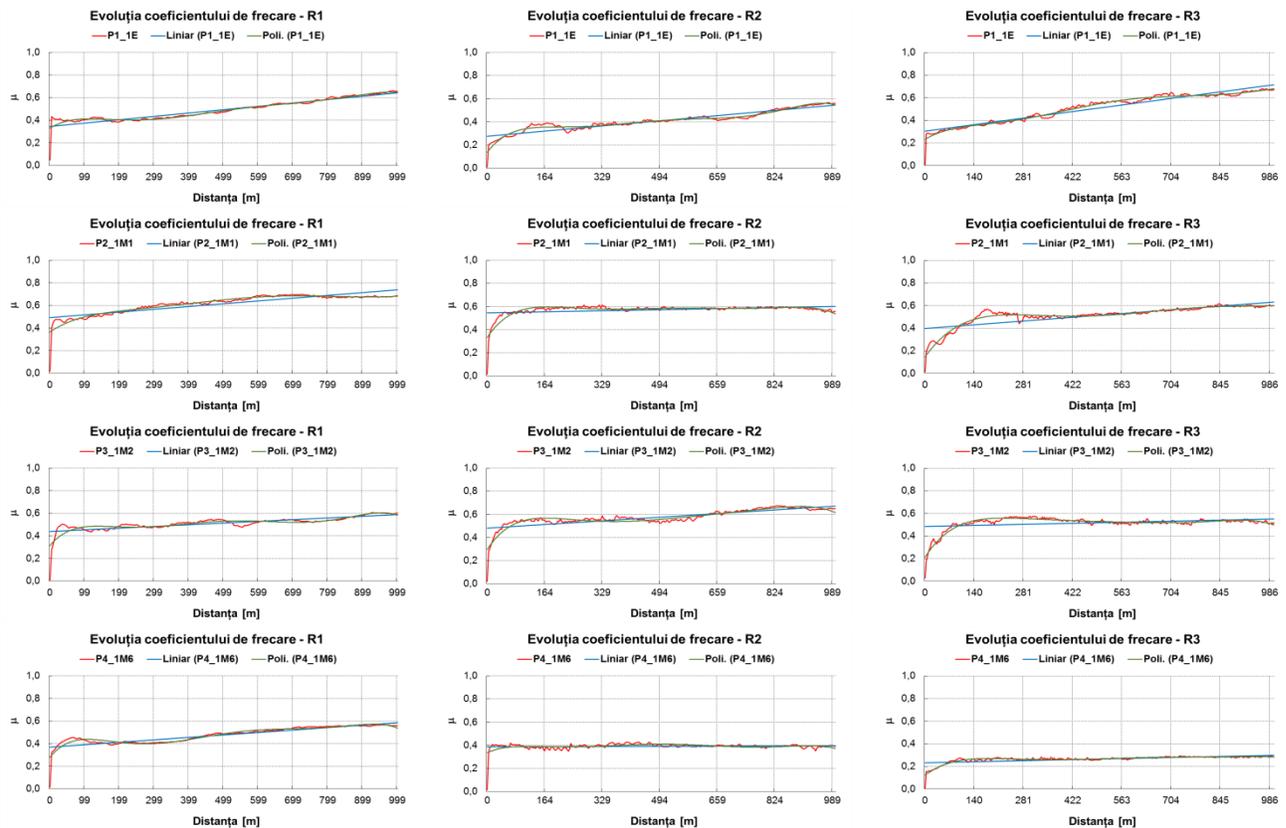


Fig. 41 Evolution of sliding friction coefficient – ternary mixtures

The first observation is related to the fact that, in the case of the tribological regime R1, the coefficient of sliding friction of the ternary materials is lower than that corresponding to the homologous binary mixture. In the case of the P1_1E material this behavior can only be explained by the presence of the mixture of collagen and inorganic compounds. In the R3 regime, the tribological behavior of this material is identical to that of the reference material.



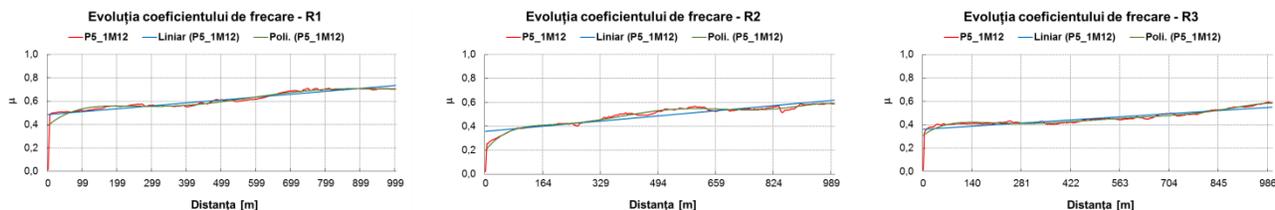


Fig. 42 Evolution of sliding friction coefficient – ternary mixtures with polyurethane resins

For the analysis of tribological responses of ternary materials with silicone resins, the reference material is P1_1E, the others being obtained by replacing the same volume of epoxy resin with polyurethane resin - fig. 50.

As in the case of the other tests carried out, the P4_1M6 material has the best tribological response, similar to the response of the reference material in the R1 regime and clearly superior to it or the responses of other materials in the R2 and R3 regimes.

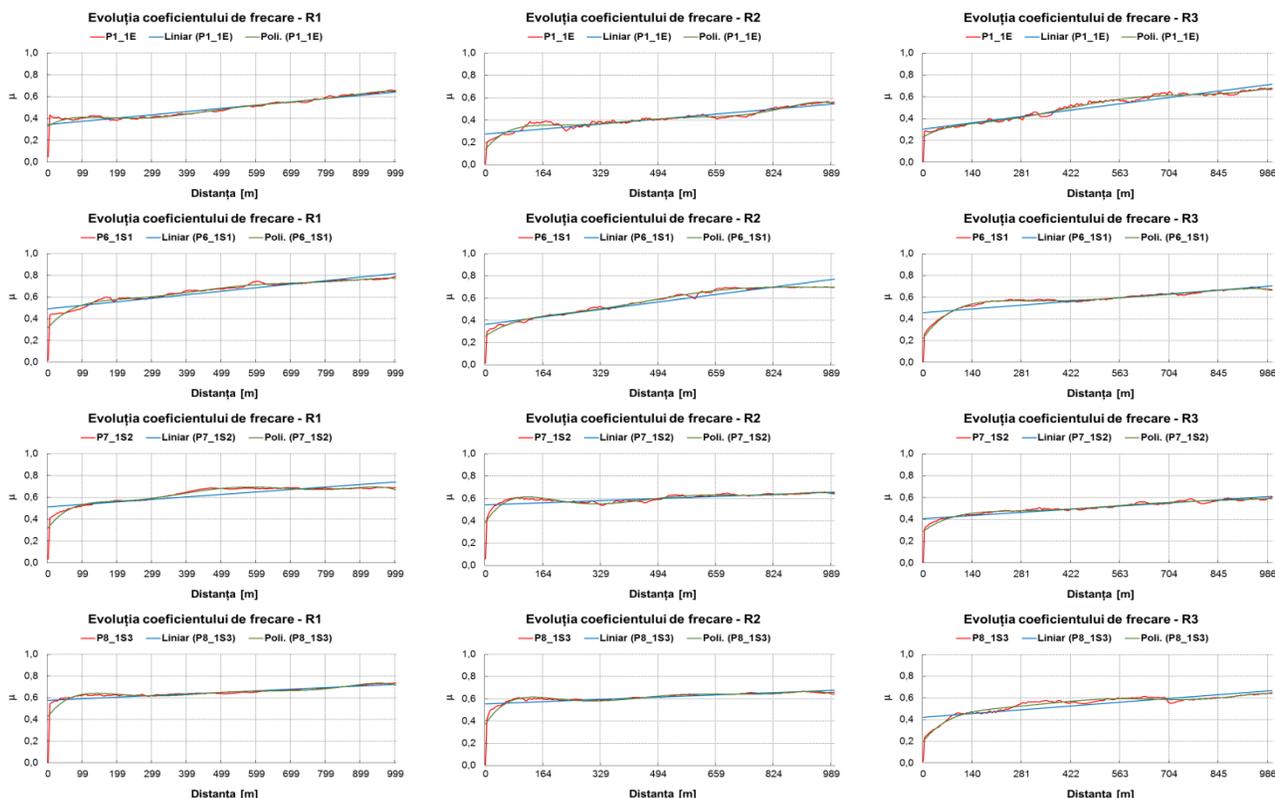


Fig. 43 Evolution of sliding friction coefficient – ternary mixtures with silicone resins

And in the case of these materials it can be observed that the tribological responses of the ternary materials with silicone resins are smoother than those corresponding to the reference material, P1_1E. Unlike ternary materials with polyurethane resins, in the case of materials in this category but with silicone resins, the friction coefficient values are higher than the corresponding values for the reference material and, of course, those recorded for ternary materials with polyurethane resins.

A more effective analysis - for a strictly tribological study - would be the one in which the friction coefficient variation curves would also be associated with the associated thermal fields (the changes in the tribological contact temperature values depending on the sliding distance) because, in this case, the events recorded as random oscillations of the sliding friction coefficient could also

be associated with other phenomena (detachment of fragments from the sample, for example).

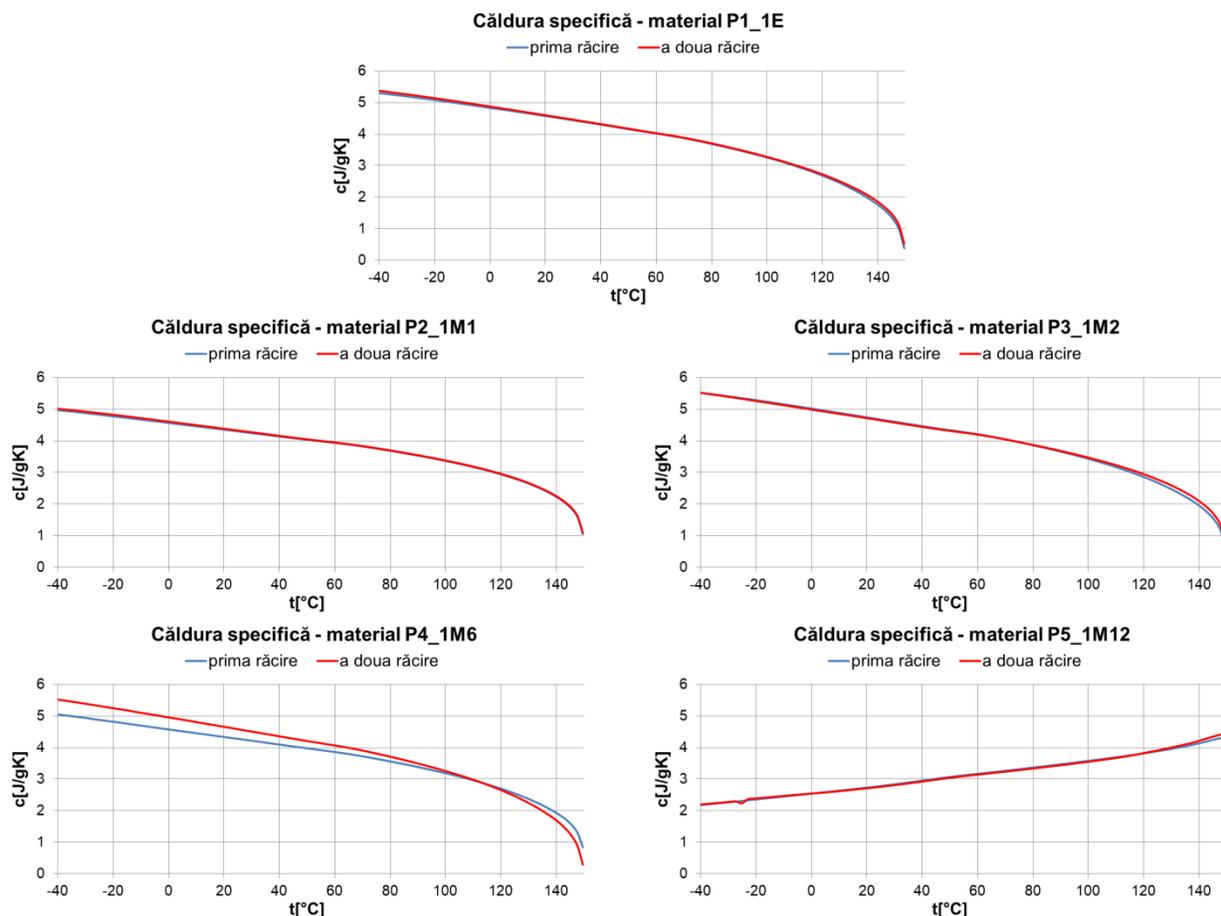
As at CCDCOMT we try to fully characterize any formed material, this tribological analysis of ternary materials was deemed necessary.

6.8. Tribological tests – partial conclusions

- the material P1_1E (immediate homologue of the reference material E+P10 presented in chapter 4) has a better tribological behavior (lower and more stable sliding friction coefficient) than the reference material which leads to the conclusion that the addition of collagen and inorganic agents contribute to the improvement of tribological behavior;
- ternary materials modified with collagen and inorganic agents with polyurethane resins as the third component of the ternary mixture, have superior tribological behavior to the reference material which, in this case, is the first material in the series, i.e. P1_1E and this can be explained by the properties of polyurethane resins;
- a complete analysis of some epoxy resin - polyurethane resin mixtures (similar to the one carried out in chapter 4 for binary mixtures epoxy resin – epoxy novolac modified vinylester resin) could lead to favorable conclusions for the use of these types of mixtures;

6.9. Thermal test results

As with the binary materials we used an analysis based on two heating-cooling cycles and the $c(T)$ curve was analyzed only on the cooling segments – the reasons were explained in Chapter 4.



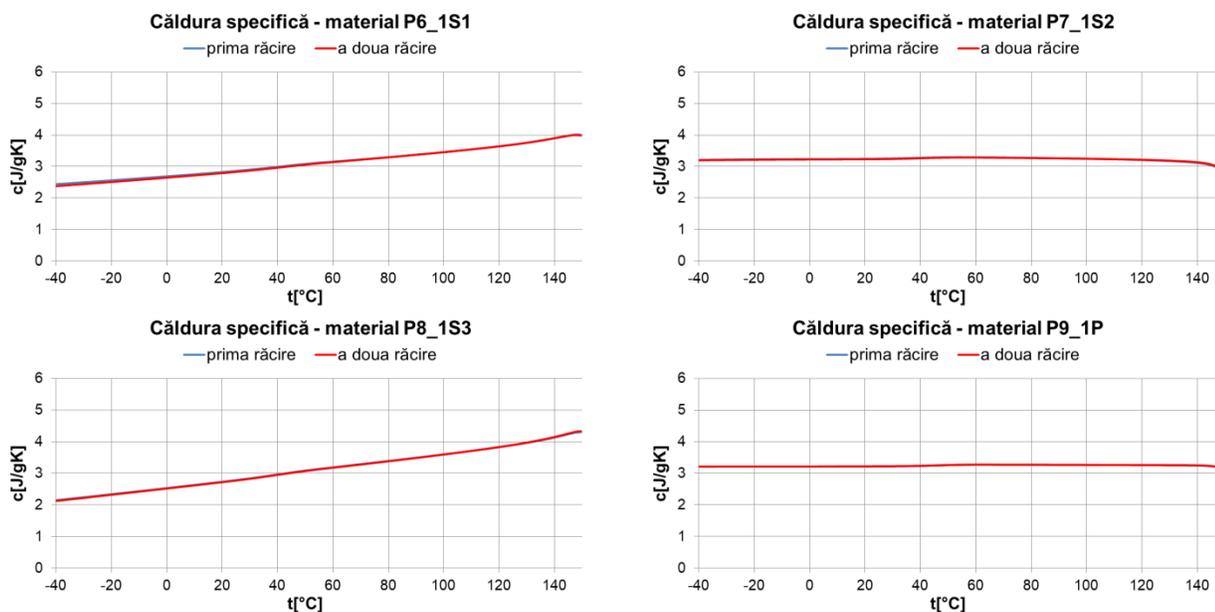


Fig. 44 The $c(T)$ functions for modified ternary materials

Se poate constata un comportament diferit al materialului P5_1M12 relativ la comportamentul materialelor ternare cu al treilea polimer rășină poliuretanică. Analizând și datele obținute în cazul testelor mecanice acest comportament nu mai pare ciudat, dat fiind faptul că și răspunsurile mecanice ale acestui material au fost diferite de cele ale omologilor săi.

Sunt surprinzătoare, de asemenea, curbele obținute pentru materialele P7_1S2 și P9_1P (primul cu al treilea polimer rășină siliconică și al doilea cu al treilea polimer poliuree) în sensul că valorile căldurii specifice practic nu depind de temperatură ceea ce ar putea semnaliza o stabilitate chimică ridicată a lanțurilor polimerice rezultate.

A different behavior of the P5_1M12 material relative to the behavior of the ternary materials with the third polyurethane resin polymer can be observed. Analyzing the data obtained in the case of mechanical tests, this behavior no longer seems strange, given the fact that the mechanical responses of this material were also different from those of its counterparts.

Also surprising are the curves obtained for P7_1S2 and P9_1P materials (the first with silicone resin as the third polymer and the second with polyurea as the third polymer) in the sense that the specific heat values practically do not depend on temperature, which could signal a high chemical stability of the resulting polymer chains.

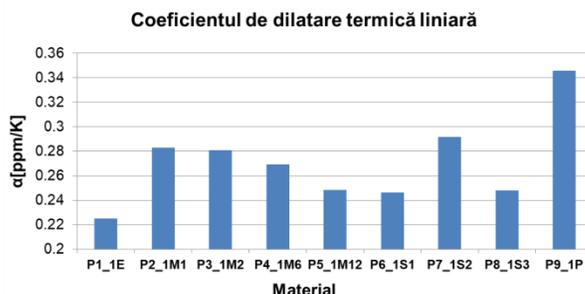


Fig. 45 Coefficient of linear thermal expansion of modified ternary mixtures

The material with the highest dimensional stability is P1_1E while at the opposite pole is the material P9_1P for which the third polymer is polyurea. In fact, polyurea was used out of curiosity knowing that it is self-healing (for this reason in the analysis it could only be compared with E+P10 and P1_1E, respectively).

P7_1S2 and P9_1P show the highest values of the coefficient of linear expansion and, I remind you, they also show a different behavior from the point of view of the specific heat (in their case, the value of the specific heat practically does not depend on the temperature). And from this point of view, an exhaustive analysis of ternary mixtures would be necessary.

6.10. Thermal tests – partial conclusions

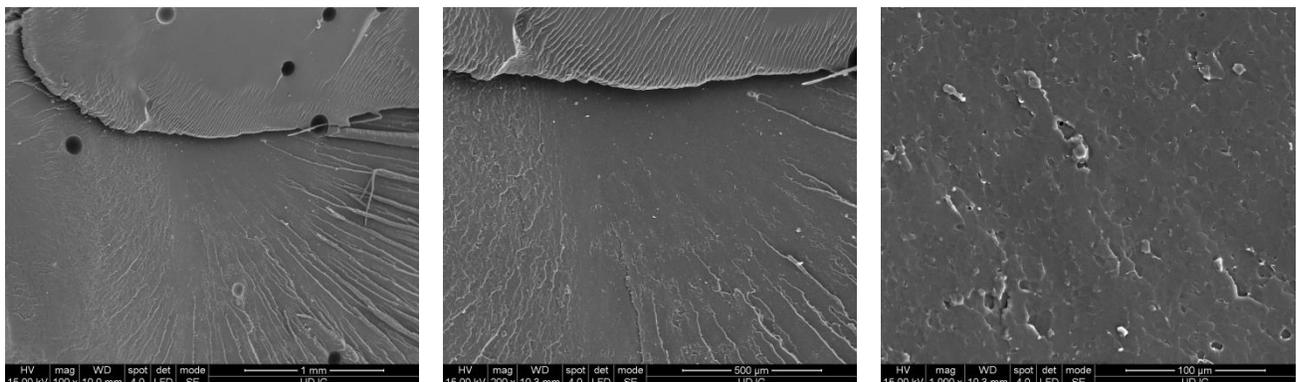
- for the reference material of the class – P1_1E and for three of the ternary materials with polyurethane resin the specific heat decreases with increasing temperature – the exception is the material P5_1M12 which also has a different mechanical behavior from its counterparts with silicone resin and this could mean a different chemical formulation of the M12 polymer compared to M1, M2 and M6 (presented in Chapter 3);
- for the materials made with silicone resins S1 and S3 (presented in chapter 3) and for the previously mentioned material, P5_1M12, the specific heat value increases with increasing temperature;
- for the other two materials (P7_1S2 and P9_1P) the specific heat value does not depend on the temperature value;
- the most dimensionally stable material is P1_1E and the least stable are the two materials whose specific heat does not depend on temperature;
- the specific heat values were obtained as averages of the experimental results obtained on five samples, while the coefficient of linear thermal expansion was obtained as an average of the results obtained for three samples.

6.11. SEM analysis of modified ternary mixtures

To avoid obtaining very soft materials (like those presented in chapter 5) we decided to use a third polymer and formed the nine materials presented in this chapter.

The results of the SEM analysis of the above materials are presented in the following.

The SEM analysis of the P1_1E material is shown in fig. 54. In the first image you can see some gas intrusions of very small diameter and the fact that the fractured surface corresponds to a rigid fracture. In the images with higher magnification (the second line) the continuous structure of the polymer is observable, interrupted by very small voids (gaseous intrusions).



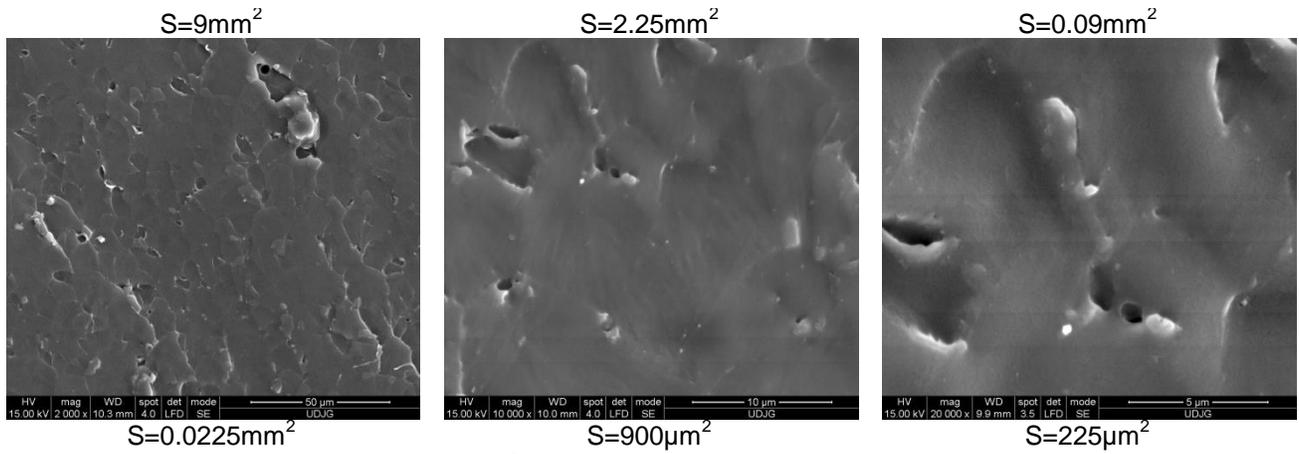


Fig. 46 SEM analysis of P1_1E material

Regarding the P2_1M1 material, the SEM analysis is shown in fig. 55. It can be easily seen that the fracture no longer has the same appearance as the fracture of material P1_1E. In addition, the polymer matrix is no longer as homogeneous as in the case of the reference material of the class. Agglomerations of relatively large sizes can be observed that could correspond to the third polymer or a compound resulting from its interaction with the epoxy novolac modified vinylester resin or the epoxy resin.

Again a study of the unmodified ternary blends could provide some clarification alongside, obviously, an EDAX analysis of the blend – the areas that would contain high nitrogen concentrations could correspond to the agglomeration areas of the polyurethane resin. An elemental distribution map could be revealing.

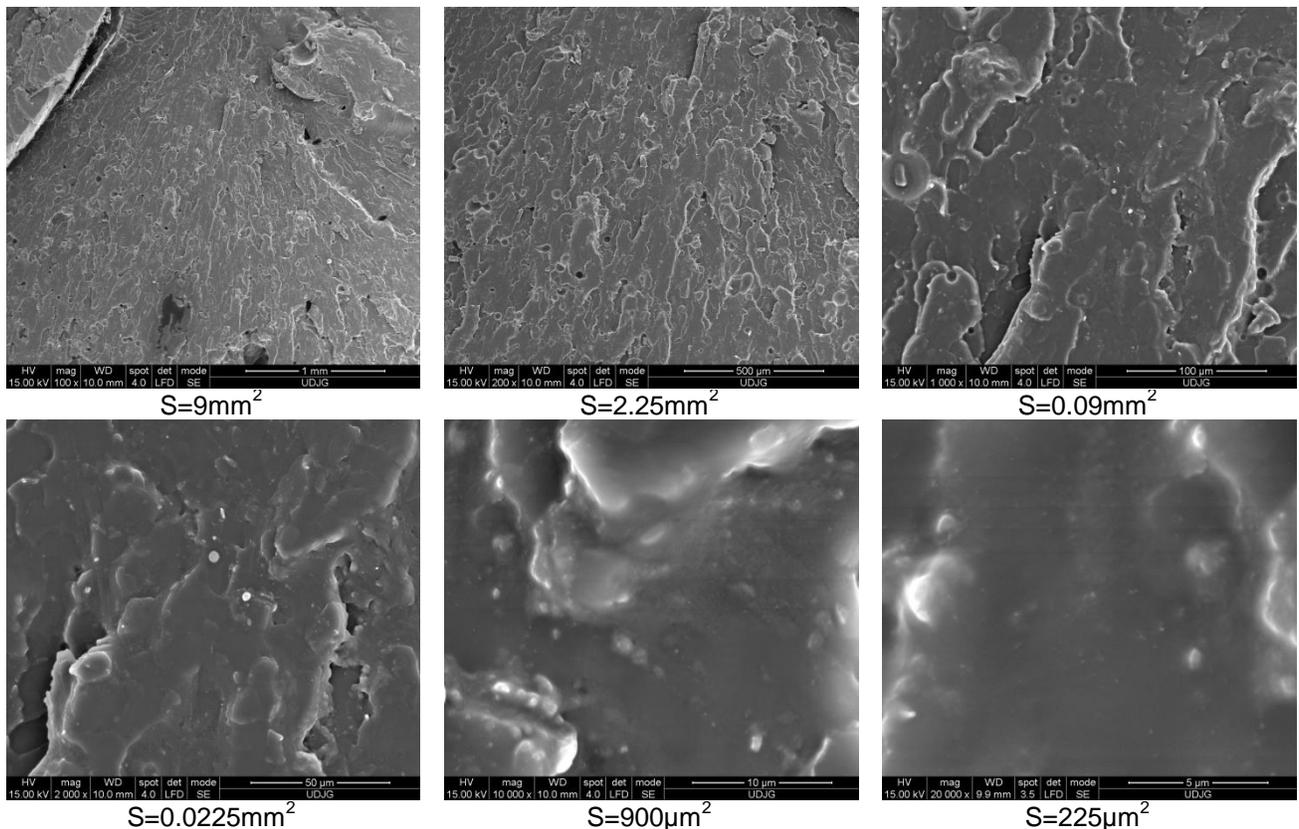


Fig. 47 SEM analysis of P2_1M1 material

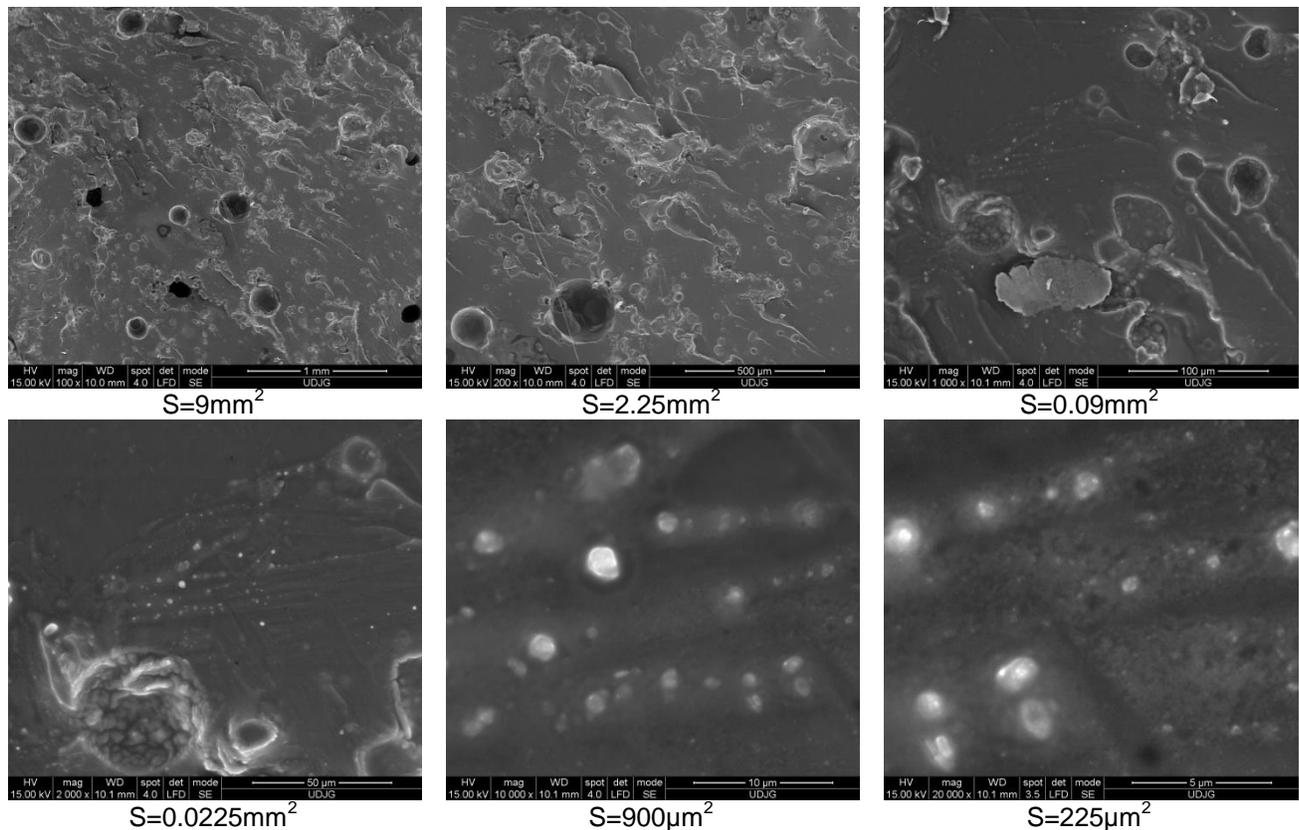


Fig. 48 SEM analysis of P3_1M2 material

The results of the SEM analysis of the third material are shown in fig. 56.

Structural differences can be observed both compared to P1_1E and compared to P2_1M1 – more gaseous and larger size intrusions. A globular formation in which structures are found (bottom left image), along with an apparent ordering of some structures along some lines. These could come from the casting or from a too short mixing time before pouring into the mold.

The fracture surface of material P3_1M2 (fig. 57.) does not resemble either that of material P1_1E or that of material P2_1M1, but the presence of gas intrusions and their sizes provide an explanation of the fracture position. The aspect of the matrix is much more inhomogeneous than in the first two cases and this also explains the different mechanical behavior of this material, as identified during the previous analysis.

For the P4_1M6 material, the SEM analysis results are presented in fig. 58. and a similarity of the appearance (morphology) in the case of the P1_1M1 material can be observed, although it would be more correct to specify that the appearance of the fracture of this material is placed between the appearance of the fracture of P1_1M1 and that of the fracture of P3_1M2.

The appearance of the fracture of the P5_1M12 material - fig. 59. – is one of a rigid fracture and the appearance of the fracture is similar to the appearance of the fracture of the material P2_1M1 as well as the morphology so that the hypothesis of the different formulation of this polyurethane resin (M12) can be an explanation of the different mechanical behavior. Another difference, this time with the P3_1M2 and P4_1M6 materials, is that there are apparently fewer gaseous intrusions. This could be a consequence of more effective mixing before pouring into the polypropylene tubes.

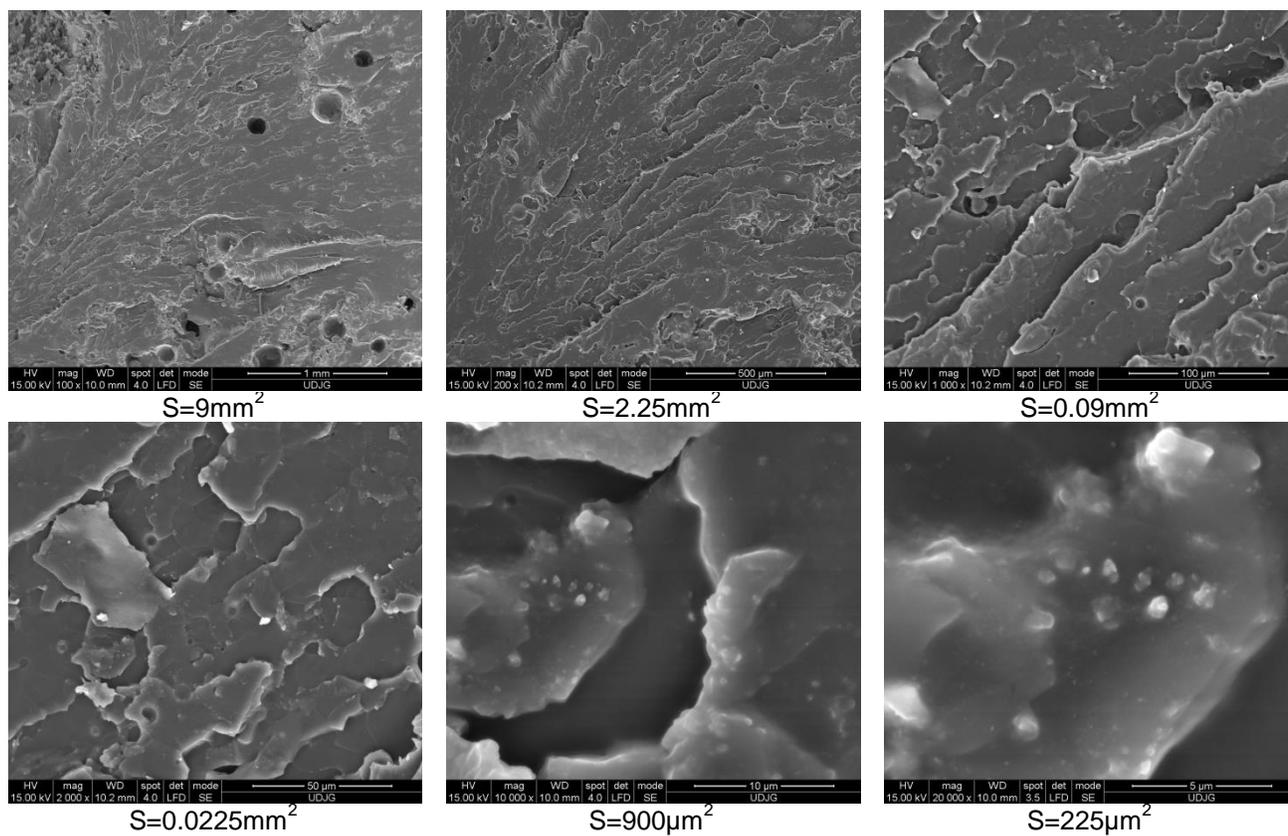


Fig. 49 SEM analysis of P4_1M6 material

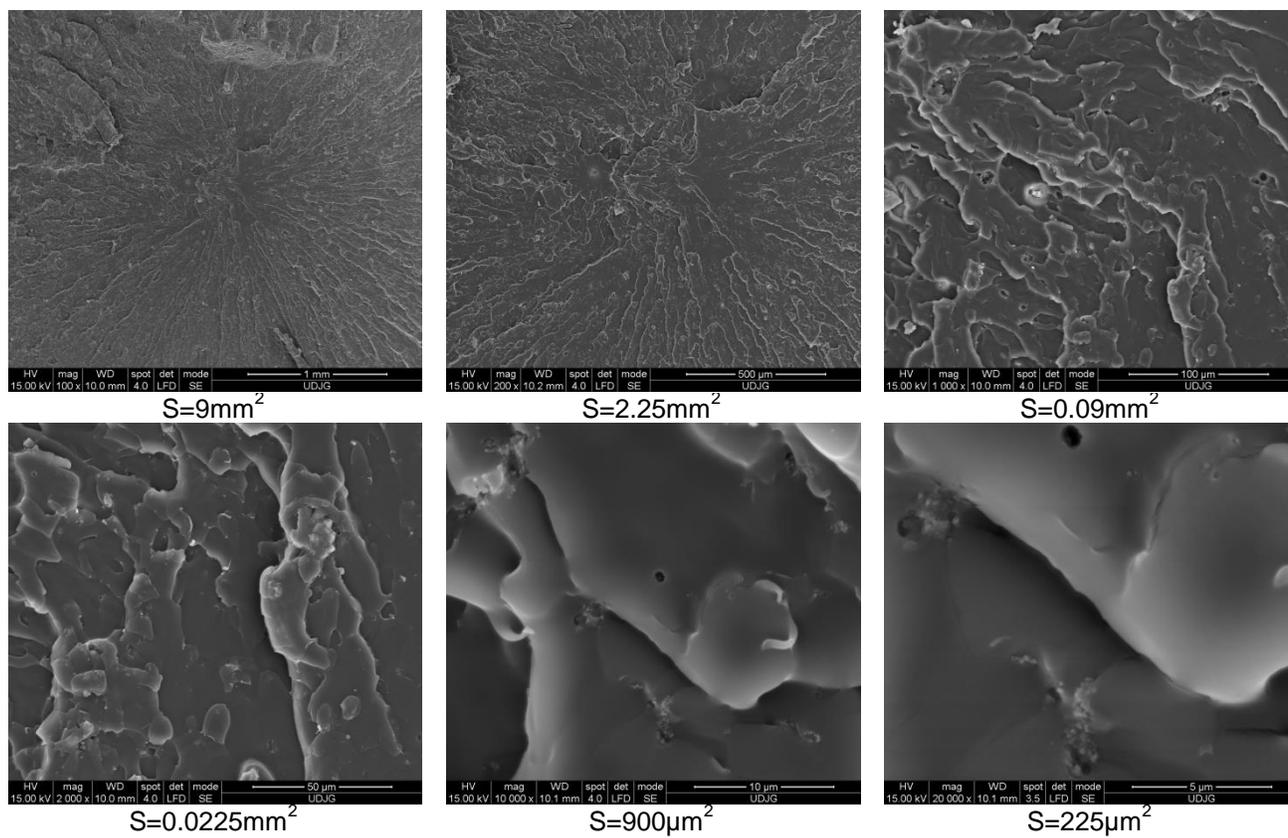


Fig. 50 SEM analysis of P5_1M12 material

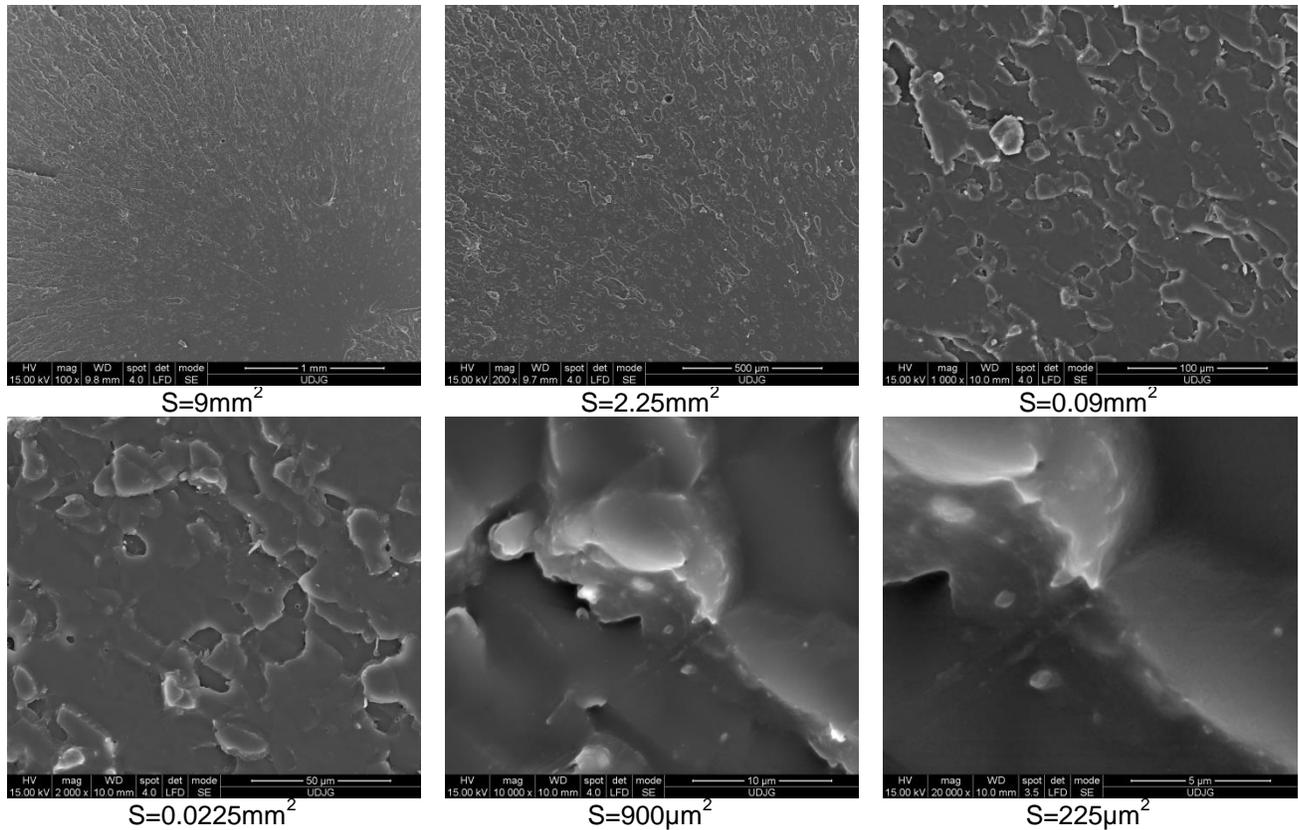


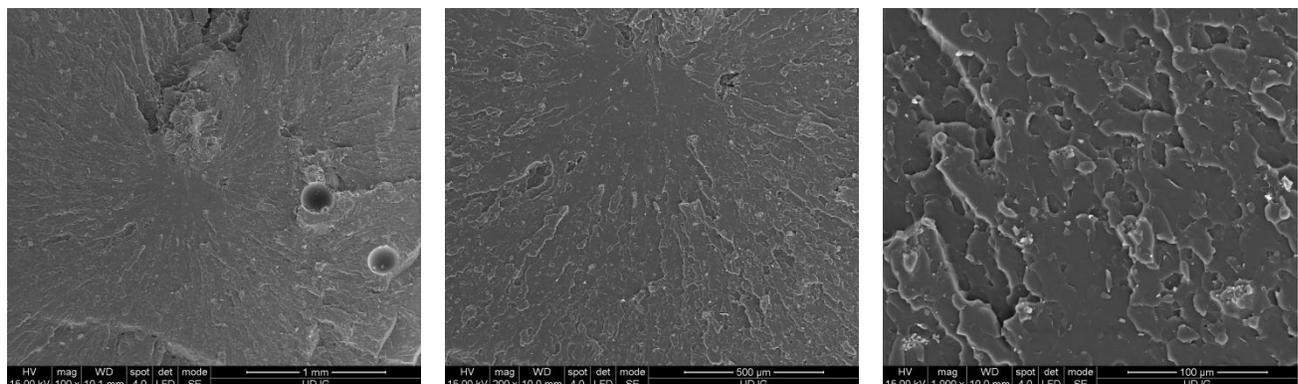
Fig. 51 SEM analysis of P6_1S1 material

The P6_1S1 material is the first in the series where the third polymer of the ternary blend is a silicone resin and the SEM analysis is shown in fig. 60.

The morphology is different than those encountered and discussed so far, the appearance of the fracture is one of a plastic fracture. The material seems more homogeneous than those in the class made with polyurethane resin and the number of gaseous intrusions is reduced.

Structures that seem to be made of polymers can also be observed (much less numerous than in the case of the P3_1M2 material) and for the higher magnifications, granules can be observed that can also be observed in the other materials. These granules are not on the surface of the material but appear to be trapped in the polymer matrix.

The second silicone resin material as the third component of the ternary mixture, is the P7_1S2 material and the SEM analysis results are shown in fig. 61.



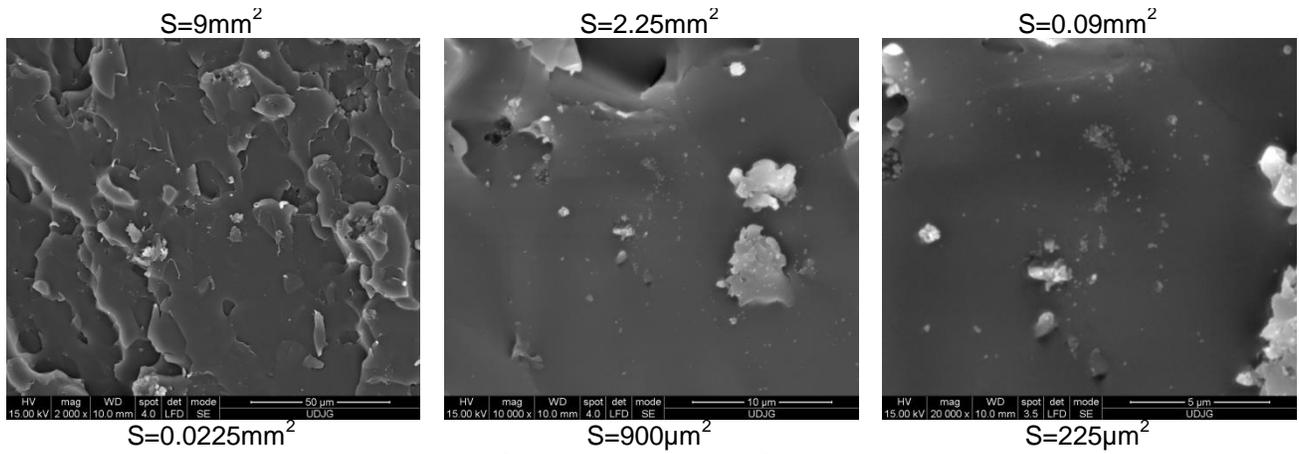


Fig. 52 SEM analysis of P7_1S2 material

For this material the appearance of the fracture surface is similar to that of the fracture surface of the previous material. What is different is that, at the highest magnification, nanometric structures are visible on the fracture surface (until now they were trapped in the polymer matrix). Also visible are two structures that appear crystalline (very strong glow) and have dimensions of approximately 5 µm (could be constituted by inorganic agents).

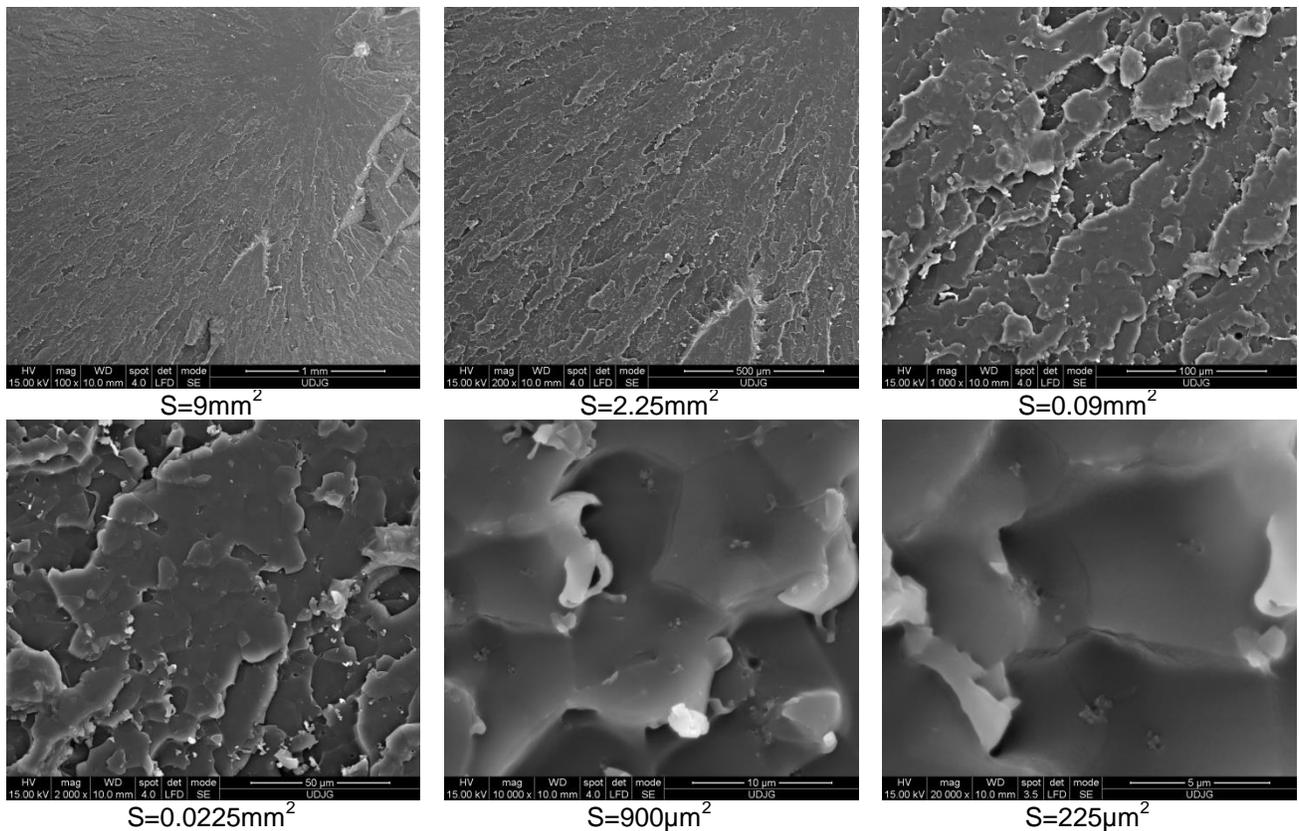


Fig. 53 SEM analysis of P8_1S3 material

The SEM analysis of the P8_1S3 material is shown in fig. 62. the appearance being similar to that of the other two materials which have silicone resin as the third component of the ternary polymer mixture. In this case, nanostructures are no longer visible on the surface of the material (as in the previous case), but trapped in the surface of the polymer. Unlike ternary mixtures with

polyurethane resins, in the case of ternary mixtures with silicone resins the similarities are much greater and this means chemical formulations with only small variations between the three silicone resins.

The last analyzed material is the P1_1P material which is made with polyurea as the third polymer in the blend and it is hard to believe that there could be any similarities to those seen so far. The SEM analysis of this last material is presented in fig. 61.

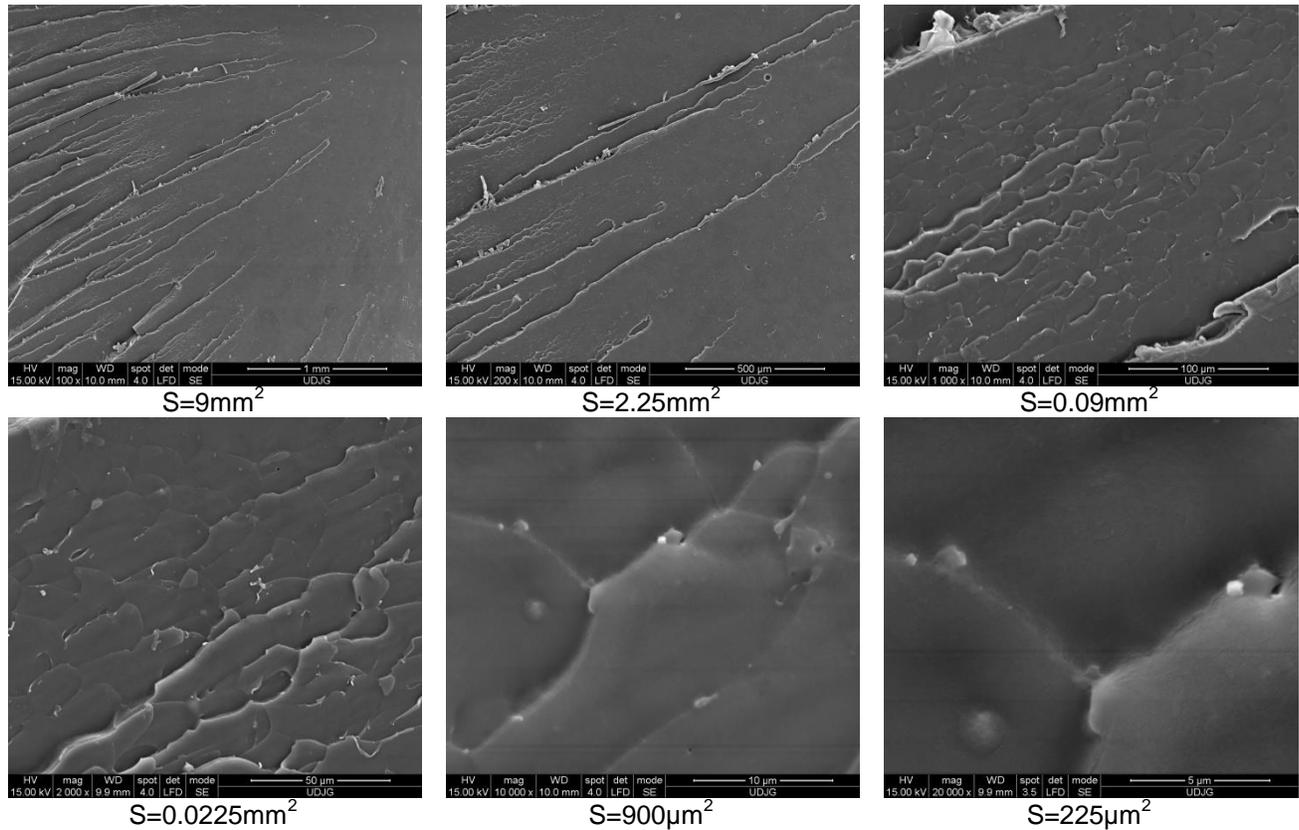


Fig. 54 SEM analysis of P9_1P material

The aspect of the matrix of this material is very homogeneous, similar to the reference material of this class – P1_1E, and not many small-sized structures are observable (compared to the other materials).

The sample analyzed under the electron microscope has a thickness of approximately 4-5mm. A single cast sample could yield 20 fragments that could be studied, but the results would not be very different. In a certain sense, the way the samples were obtained by breaking the sample at room temperature, is beneficial because it reveals aspects that must be taken into account in future studies (the method of mixing the components and the duration of the mixing, in such a way that avoid gaseous intrusions but that the time is not exceeded either where the mixture can be poured into moulds).

As I mentioned, the chemical formulation of commercial resins is not public information (I might even say secret) so gaseous intrusions could be the consequence of local chemical reactions between two or more substances in the mixture. At the macroscopic level, no effects of chemical reactions were observed.

It is possible that the observed nanostructures are, in fact, recrystallizations of the precursors in the mixture. These recrystallizations could be caused by the occurrence of local chemical

Capitolul 7

imbalances generated by the polymerization reaction (the chemical reaction between the epoxy resin and the epoxy resin hardener). We cannot know the exact nature of these nanostructures in the absence of an EDAX analysis.

The dimensions of the nanostructures are given in fig. 64.

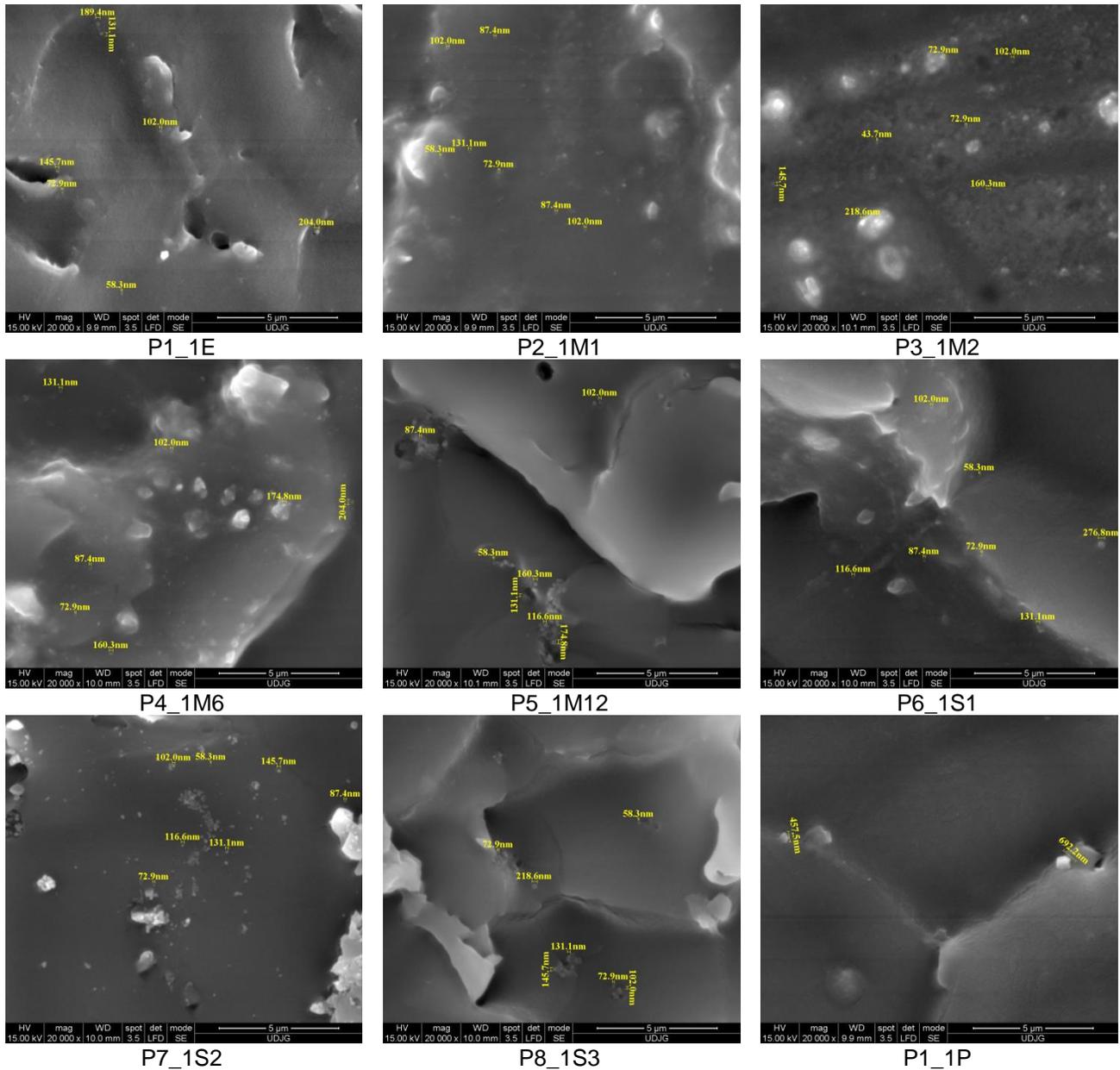


Fig. 55 Dimensions of the nanostructures

The collagen-stabilized inorganic agent solutions were complete solutions and despite varying laboratory conditions and accidental cessation of mixing never showed instabilities leading to precipitation. The mixture of epoxy resin and epoxy novolac modified vinylester resin is transparent enough (has a slight yellowish tinge) to allow visualization of any precipitates.

6.12. SEM analysis – partial conclusions

- SEM analysis highlights the existence of some nanostructures even if there is no certainty about their chemical structure;
- the existence of these nanostructures confirms the validity of the hypothesis of nanostructuring through localized chemical reactions in the volume of the polymer;
- morphological changes of the polymer matrix are observable (mainly due to the addition of the third polymer) and these completes the information obtained in the mechanical tests.

6.13. Conclusions

- considering the conclusions of the SEM analyses, this part of the work should be called the Analysis of the properties of nanostructured materials;
- the tensile test results indicate that the ternary materials modified with organic and inorganic agents have a tensile strength higher than the reference (E+P10, the reference for P1_1E) and certainly higher than E+P15 which would be the binary equivalent (the binary mixture initially from which these materials are made has 15% mass fraction of vinyl ester resin modified epoxy novolac);
- the modulus of elasticity of the modified ternary materials have higher values than the values corresponding to the reference material (E+P10), i.e. 1.37GPa;
- except for materials P6_1S1 and P7_1S2, all modified ternary materials have values of the elastic modulus higher than the value of the elastic modulus of the epoxy resin measured under the same conditions (chapter 4.1.);
- the material P1_1E is brittle (it is the equivalent of the binary material of E+P10) and has a compression behavior similar to it (successive fractures appearing on the individual σ/ϵ curves);
- for the same material the stress at the elastic limit has a value comparable to that of the binary material E+P10 which means that the organic and inorganic agents used to modify the material have no effect on the compression properties (at least);
- the compressive elastic modulus has lower values than the compressive elastic modulus of the reference material (E+P10);
- the only exception is the P1_1E material which has a modulus of elasticity of 2.4GPa compared to 1.6GPa for the E+P10 material;
- the compressive elastic modulus of the material P1_1E is also higher than the elastic modulus of of its counterpart E+P10 (2.25GPa);
- ternary materials with polyurethane resins have compressive (as well as tensile) responses that seem to depend on the used polyurethane resin;
- ternary materials with silicone resins have lower compressive elastic modulus than the corresponding value for the reference material;
- regarding the P9_1P material, it was formed to test the self-healing capacity of polyurea, but the study in this direction must be continued;
- compared to the reference material, the behavior of the ternary materials modified with inorganic and organic agents is completely changed for P1_1E, P2_1M1, P3_1M2 and P4_1M6;
- for the other materials the answer is similar to the answer of the reference material;
- the flexural modulus has very low values for materials in which silicone resins have been added;
- the material with the highest value of the bending elastic modulus - as for the other tests performed - is P4_1M6;

Capitolul 7

- a study would be necessary regarding the materials obtained by mixing the epoxy resin with the corresponding fractions of the other resins, in order to understand what is the effect of their presence and what is the effect of the presence of inorganic compounds (collagen was only used to isolate the ions of inorganic substances and to ensure the stability of the solutions);
- with the exception of material P5_1M12, all the other obtained materials with polyurethane resins show a rigid response to bending, along with P1_1E which is the counterpart of the binary mixture E+P10.

Chapter 7

Personal contributions, conclusions and future research directions

The SEM analysis of the materials presented in chapter 6 confirms the existence of some nanostructures, even if their chemical structure is not known.

The continuation of the study could be constituted by an analysis of the chemical structure of the nanostructures (EDAX, or X-ray diffraction, for the case where YBCO was formed whose crystalline structure is known).

The presented study was carried out in order to verify the hypothesis of the nanostructuring of epoxy matrices by developing some local chemical reactions, between specially chosen precursors, in the prepolymer mixture. This study started from the observation that the precursors (anorganic substances) are very little soluble or insoluble in epoxy resin or its hardener but are soluble in epoxy-novolac modified vinylester resin diluted with styrene.

In a future study it should be verified that the inorganic salts are soluble in styrene to be able to truly analyze the solubility in vinylester resin. However, its presence stabilizes the solution and allows the isolation of ions whose interaction is desirable for the creation of nanostructures.

With these, the first stage of the study was directly related to the choice of the epoxy resin (having three such polymers available) and the analysis of the properties of the binary mixtures – epoxy resin/vinylester resin – with different volume ratios of the vinylester resin. The materials produced had vinylester resin volume ratios between 5% and 20% in 5 percent increments.

A future study should continue with the epoxy resin E and with a lower step of the volume rate of the vinylester resin because the results obtained have jumps that can only be explained by a continuous evolution of the analyzed parameters values with the volume rate of the two components of the mixture.

The results of the mechanical tests showed that higher than 5% volume ratios of epoxy novolac modified vinylester resin in the epoxy resin (any of them) fundamentally change the elastic response of the formed materials (for all types of tests performed - tensile, compression, three-point bending).

The materials become softer – which for some applications could be beneficial – in the sense that the response is no longer rigid and for fabric reinforced composites this is an advantage, provided, however, that the adhesion of the mixture to the fibers is equal to that of epoxy resins, to ensure a quality interphase.

The results of the tribological tests indicate different types of behavior of the materials which, this time, depend on the epoxy resin (the volume ratios of the vinylester resin being equal) or on possible chemical reactions (unknown and which we did not observe at the macroscopic level) between the different chemical substances present in the resins formulations.

For resin H (second in stiffness) the results of mechanical tests at fractions of vinylester resin of 15% and 20% are relevant – it no longer shows elastic response. For the other two epoxy resins the results are different, in the sense that even at high concentrations from the side of the binary mixtures there is a small elastic response of the specimens.

From a thermal point of view, the DSC analysis shows that the presence of the vinyl ester resin changes the aspect of the dependence of the specific heat on temperature, that is, the profiles of the $c(T)$ curves are different and also depend on the volume fraction of the vinyl ester resin. In this case, the changes in the profiles of the $c(T)$ curves are similar, which means that the variations in the chemical formulation of the three resins are not very significant.

A future study should aim to analyze the properties of epoxy resin- epoxy novolac modified vinyl ester resin binary blends but at a finer vinyl ester volume fraction variation rate (with a step of 1%).

The materials presented in Chapter 5 were, in fact, failures of the nanostructure approach – six different combinations of inorganic agents were tested that did not lead to viable materials (some of which did not polymerize). Of course, in the beginning the mixture of E-epoxy resin with epoxy novolac modified vinyl ester resin was equivolumic (which certainly could not lead to a solid material). Furthermore, although four materials polymerized the other two remained very viscous liquids and I attributed this to the presence of Lanthanum (used in place of Barium).

The mechanical properties of these materials (tensile and three-point bending tests) are very low compared to even those of the binary materials studied in Chapter 4. Because they were very soft (from the mold release) and remained soft and after thermal consolidation no specimens could be obtained for compression tests or for tribological tests.

As a last resort, starting from the knowledge that the compound YBCO is formed, we used only the precursors necessary to obtain it and, in order to prevent obtaining samples that cannot be tested mechanically, we decided to add to the modified binary polymer mixture, a third polymer. This is also an opportunity to expand knowledge and can be a good starting point for a study of the properties of ternary polymer blends. Certainly, such a study should start with low rates of the two added components, in order to accurately understand the effect of each of them.

The conditions in which the ternary mixtures modified with collagen and inorganic agents were made were also determined by the need to completely solvate some stoichiometrically determined amounts of inorganic agents (to allow obtaining the desired compound – YBCO) and, although these amounts are small, their degree of solvation in the vinyl ester resin did not allow any significant reduction in its volume.

It should be noted that the binary mixture (epoxy resin plus vinyl ester resin in which the agents were solvated – including collagen) was mixed (on a magnetic mixer) at constant temperature for weeks before being mixed with the third polymer and, later with the epoxy resin hardener.

The materials obtained have properties that depend, in general, on the third component of the ternary mixture, as indicated by the analysis of the mechanical properties. Changes in the thermal behavior of the formed materials are also observed and these changes are not necessarily related to the nature of the third polymer but can also be attributed to the presence of inorganic agents - the amount of collagen used for the whole mixture - 5g - was so small that it cannot be taken into account.

For a rigorous study it would be necessary to keep laboratory conditions for each mixture formed, which, in the case of CCDCOMT, is impossible. It would also be important for all tests to be conducted under the same conditions.

The mechanical properties of nanostructured materials are not extraordinary, but they provide the conditions for using these materials for the formation of multifunctional composites. They can also be used as a matrix for the formation of fabric-reinforced composites with superior properties (especially from electrical and electromagnetic point of view).

Bibliography

- [19] C. Li, Q. Li, X. Lu, R. Ge, Y. Du, și Y. Xiong, „Inorganic salt based shape-stabilized composite phase change materials for medium and high temperature thermal energy storage: Ingredients selection, fabrication, microstructural characteristics and development, and applications”, *Journal of Energy Storage*, vol. 55, p. 105252, nov. 2022, doi: 10.1016/j.est.2022.105252.
- [176] Y.-C. Shi *et al.*, „Rational design of a functionalized silicone polymer for modifying epoxy-based composites”, *Journal of Materials Research and Technology*, vol. 19, pp. 3867–3876, iul. 2022, doi: 10.1016/j.jmrt.2022.06.086.
- [177] B. Hemanth, H. G. Hanumantharaju, K. P. Prashanth, și B. K. Venkatesha, „Investigation of wear characteristics of collagen fiber reinforced polymer matrix composites used for orthopaedic implants”, *Materials Today: Proceedings*, vol. 54, pp. 498–501, 2022, doi: 10.1016/j.matpr.2021.11.429.
- [178] O.-L. Petrașcu, R. Manole, și A.-M. Pascu, „The behavior of composite materials based on polyurethane resin subjected to uniaxial tensile test”, *Materials Today: Proceedings*, vol. 62, pp. 2673–2678, 2022, doi: 10.1016/j.matpr.2022.05.308.
- [179] L. Xu, X. Li, F. Jiang, X. Yu, J. Wang, și F. Xiao, „Thermosetting characteristics and performances of polyurethane material on airport thin-overlay”, *Construction and Building Materials*, vol. 344, p. 128252, aug. 2022, doi: 10.1016/j.conbuildmat.2022.128252.
- [180] N. H. Nash, A. Portela, C. I. Bachour-Sirerol, I. Manolakis, și A. J. Comer, „Effect of environmental conditioning on the properties of thermosetting- and thermoplastic-matrix composite materials by resin infusion for marine applications”, *Composites Part B: Engineering*, vol. 177, p. 107271, nov. 2019, doi: 10.1016/j.compositesb.2019.107271.
- [181] R. Tu și H. A. Sodano, „Additive manufacturing of high-performance vinyl ester resin via direct ink writing with UV-thermal dual curing”, *Additive Manufacturing*, vol. 46, p. 102180, oct. 2021, doi: 10.1016/j.addma.2021.102180.
- [182] F. J. Barbon, R. R. Moraes, C. P. Isolan, A. O. Spazzin, și N. Boscato, „Influence of inorganic filler content of resin luting agents and use of adhesive on the performance of bonded ceramic”, *The Journal of Prosthetic Dentistry*, vol. 122, nr. 6, p. 566.e1-566.e11, dec. 2019, doi: 10.1016/j.prosdent.2019.09.013.
- [198] K. Takahashi, K. Yaginuma, T. Goto, T. Yokozeki, T. Okada, și T. Takahashi, „Electrically conductive carbon fiber reinforced plastics induced by uneven distribution of polyaniline composite micron-sized particles in thermosetting matrix”, *Composites Science and Technology*, vol. 228, p. 109642, sep. 2022, doi: 10.1016/j.compscitech.2022.109642.
- [199] D. Chen, H. Wu, J. S. Wei, S. L. Xu, și Q. Fang, „Nonlinear visco-hyperelastic tensile constitutive model of spray polyurea within wide strain-rate range”, *International Journal of Impact Engineering*, vol. 163, p. 104184, mai 2022, doi: 10.1016/j.ijimpeng.2022.104184.
- [201] P. Xu *et al.*, „Pre-use interfacial shear strength prediction for fiber-reinforced thermosetting composites based on stress-impedance effect of ferromagnetic microwires”, *Composites Part A: Applied Science and Manufacturing*, vol. 152, p. 106684, ian. 2022, doi: 10.1016/j.compositesa.2021.106684.

- [203] Y. Fu și X. Yao, „A review on manufacturing defects and their detection of fiber reinforced resin matrix composites”, *Composites Part C: Open Access*, vol. 8, p. 100276, iul. 2022, doi: 10.1016/j.jcomc.2022.100276.
- [204] X. Wang *et al.*, „Static and dynamic compressive and tensile response of highly stretchable polyurea”, *International Journal of Impact Engineering*, vol. 166, p. 104250, aug. 2022, doi: 10.1016/j.ijimpeng.2022.104250.
- [205] <https://www.r-g.de/art/120300>
- [206] <https://www.r-g.de/en/art/105100>
- [207] <http://www.polydis.ro/wp-content/uploads/2014/08/Epiphen-4020.pdf>
- [208] <http://sirindustriale.com/wp-content/uploads/2020/10/VE-64M140.pdf>
- [209] <https://btools.ro/shop/Altropol/Multicast-1>
- [210] <https://btools.ro/shop/Altropol/Multicast-2>
- [211] <https://btools.ro/shop/produse-btools/Rasini/Rasina-Poliuretantica-Multicast/Multicast-6>
- [212] <https://btools.ro/shop/produse-btools/Rasini/Rasina-Poliuretantica-Multicast/Multicast12-Kit2kg>
- [213] <https://btools.ro/shop/produse-btools/Cauciuc-Lichid-Silicon-RTV-Zhermack/Cauciuc-Lichid-Silicon-RTV2-Zhermack-Aditie/Silicon-Aditie-RTV2-ZA13>
- [214] <https://btools.ro/shop/produse-btools/Cauciuc-Lichid-Silicon-RTV-Zhermack/Cauciuc-Lichid-Silicon-RTV2-Zhermack-Aditie/cauciuc-siliconic-lichid-rtv-za22>
- [215] <https://btools.ro/shop/produse-btools/Cauciuc-Lichid-Silicon-RTV-Zhermack/Cauciuc-Lichid-Silicon-RTV2-Zhermack-Aditie/cauciuc-siliconic-lichid-rtv-HT33>

List of figures

Fig. 2 Electronic balance (left), mixed solutions in novolac epoxy modified vinyl ester resin, heat setting oven (right).....	18
Fig. 3 Mechanical tests	19
Fig. 4 TRM1000 tribometer	19
Fig. 5 DSC 1 (<i>Mettler Toledo</i>)	20
Fig. 6 TMA – SDTA 810 (<i>Mettler Toledo</i>)	20
Fig. 7 σ/ϵ curves of epoxy resin specimens - tensile	21
Fig. 8 σ/ϵ curves of binary mixtures (5%) – traction.....	22
Fig. 9 σ/ϵ curves of binary mixtures (10%) – traction.....	22
Fig. 10 σ/ϵ curves of binary mixtures (15%) – traction.....	23
Fig. 11 σ/ϵ curves of binary mixtures (20%) – traction.....	23
Fig. 12 Moduli of elasticity of binary materials - traction	24
Fig. 14 σ/ϵ curves of epoxy resins - compression.....	25
Fig. 15 σ/ϵ curves of binary mixtures (5%) – compression	25
Fig. 16 σ/ϵ curves of binary mixtures (10%) – compression	26
Fig. 17 σ/ϵ curves of binary mixtures (15%) – compression	26
Fig. 18 σ/ϵ curves of binary mixtures (20%) – compression	27
Fig. 20 Load/displacement curves of epoxy resin specimens - bending	28
Fig. 21 Load/displacement curves of binary mixtures (5%) – bending.....	29
Fig. 22 Load/displacement curves of binary mixtures (10%) – bending.....	29
Fig. 23 Load/displacement curves of binary mixtures (15%) – bending.....	30
Fig. 24 Load/displacement curves of binary mixtures (20%) – bending.....	30
Fig. 26 The evolution of the sliding friction coefficient – epoxy resins.....	31
Fig. 27 Evolution of the coefficient of sliding friction – epoxy resins	32
Fig. 28 Evolution of sliding friction coefficient – binary mixtures	32
Fig. 30 The $c(t^{\circ}C)$ function for binary mixtures of epoxy resin C.....	33
Fig. 31 $c(t^{\circ}C)$ function for binary mixtures of epoxy resin E	34
Fig. 32 The $c(t^{\circ}C)$ function for binary mixtures of epoxy resin H.....	35
Fig. 34 Stress/strain curves for M - tensile materials	37
Fig. 36 Individual load/displacement curves – three-point bending.....	38
Fig. 37 Average load/displacement curves and flexural moduli of M materials	38
Fig. 38 Stress/strain curves for ternary mixtures (P1_1E and P9_1P) - tensile.....	41
Fig. 39 Stress/strain curves for ternary mixtures with polyurethane resins - tensile.....	42
Fig. 40 Stress/strain curves for ternary mixtures with silicone resins - tensile.....	42
Fig. 41 Moduli of elasticity of modified ternary materials - tensile	43
Fig. 42 Stress/strain curves for ternary mixtures (P1_1E and P9_1P) - compression.....	43
Fig. 43 Stress/strain curves for ternary mixtures with polyurethane resins - compression	44
Fig. 44. Stress/strain curves for ternary mixtures with silicone resins - compression.....	44
Fig. 46 Load/displacement curves for ternary mixtures (P1_1E and P9_1P) - bending	45
Fig. 47 Load/displacement curves for ternary mixtures with polyurethane resins - bending.....	46
Fig. 49 Moduli of elasticity of modified ternary materials – bending. Images of test specimens P3_1M2 (left) and P4_1M6 (right)	46

Fig. 50	Evolution of sliding friction coefficient – ternary mixtures	47
Fig. 51	Evolution of sliding friction coefficient – ternary mixtures with polyurethane resins	48
Fig. 52	Evolution of sliding friction coefficient – ternary mixtures with silicone resins	48
Fig. 53	The $c(T)$ functions for modified ternary materials	50
Fig. 54	Coefficient of linear thermal expansion of modified ternary mixtures	50
Fig. 55	SEM analysis of P1_1E material	52
Fig. 56	SEM analysis of P2_1M1 material	52
Fig. 57	SEM analysis of P3_1M2 material	53
Fig. 58	SEM analysis of P4_1M6 material	54
Fig. 59	SEM analysis of P5_1M12 material	54
Fig. 60	SEM analysis of P6_1S1 material	55
Fig. 61	SEM analysis of P7_1S2 material	56
Fig. 62	SEM analysis of P8_1S3 material	56
Fig. 63	SEM analysis of P9_1P material	57
Fig. 64	Dimensions of the nanostructures	58

