**IOSUD – „DUNĂREA DE JOS” UNIVERSITY OF GALAȚI**
**Doctoral School of Mechanical and Industrial Engineering**

# ABSTRACT
# DOCTORAL THESIS

## Researches regarding the hybrid methods utilization to nanostructure polymers matrix. Mechanical effects

**Ph.D,**
**ing. Rodica CHIHAI (PEȚU)**

**Scientific coordinator,**
**prof. univ. dr. habil. Adrian CÎRCIUMARU**

**Series I6 Mechanical Engineering No. 7x**
**GALAȚI**
**2023**

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**Ph.D,**
**ing. Rodica CHIHAI (PEȚU)**

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**Series I6 Mechanical Engineering No. 7x**
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# DECISION

## ***Gratitudes***

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***P.h.D Rodica Chihai (Pețu),***
***Galați 2023***

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## Introduction

Since the beginning, the 21st century has shown signs of a crisis with raw materials and energy (a crisis felt since the previous millennium) superimposed on the crisis of the environment (global warming). In this context, research has evolved rapidly in search of more reliable, more economical and more protective engineering solutions in terms of the environment. The gradual transition from propulsion based on internal combustion engines to propulsion based on electric motors (but aimed at hydrogen-based propulsion) required finding technical solutions (engineering materials) with special performances. Among these, composites stand out in the effort of researchers and the amounts invested in research, given the fact that their properties can be designed based on the use to be given to them.

Thus, the published results of research in the field of composite materials cover an extremely wide area of applications starting with those related to the manufacture of lighter benchmarks (automotive industry, aerospace industry, sports equipment industry) and more resistant than those made from traditional materials, up to radiation protection, in the case of cancer teletherapy.

There are many sources of information (written or electronic) which give as an example of the famous (in Romania) adobe composite. Building material obtained from the mixture of straw (or other plant residues) with wet soil and fermented cattle manure (containing resistant fibers) together with other organic components that increase the malleability of the mixture (before drying) and ensure a better link (now we would say interphase) between the mixture of wet substance and straw. Then, another often used example, is reinforced concrete - a material that generated a revolution in the field of construction, allowing the construction of skyscrapers. Research, as far as concrete is concerned, is also of great interest in the world of the 21st century given the need for housing and, above all, the needs for transport and production.

According to most current classifications of composite materials, they can be included in three large groups. The classification criterion is the nature of the matrix of the composite material – metal matrix composites (MMC), ceramic matrix composites (CMC) and polymer matrix composites (PMC).

Composite materials emerged in the middle of the 20th century as a promising class of engineering materials that offer us new perspectives on modern technology. So, the idea of combining several components has been used by man for thousands of years to produce a material with properties that are not possible to achieve with individual components. Composites can be treated as natural materials that have emerged as a result of a process of prolonged evolution.

The advantages and properties of these unique materials were quickly understood, being used to obtain a material by combining two or more constituents with different physicochemical characteristics. These represent a benefit to creating a better standard of living and to advance human life.

Polymer composites stand out due to their excellent properties such as corrosion resistance, high stiffness, good fatigue properties, as well as good impact properties, low density, good damping properties (all of which, obviously, depending on the nature of the polymer). Due to their applicability in most different fields and simple processing methods, these materials have become more attractive and susceptible to be used in other fields as well. Modern technologies require composite materials with special properties that can be obtained by joining some of the most diverse components (phases). These materials, required by industries whose products are required in aerospace applications, transportation, electricity production from renewable sources, must present, apart from extraordinary properties, a long life or the possibility of cheap and fast repair.

*Introduction*

Particular attention is paid, in the last decade, to nanocomposites (regardless of the nature of the matrix) as long as, in most cases, the nanophases added or formed in the matrix are ceramic materials (most of them having melting temperatures higher than those of metals). The techniques for obtaining nanophases (powders whose grains are of nanometric size) have also evolved a lot and, as a consequence, their prices have decreased, making them accessible to an increasing number of researchers or engineers. The best example is carbon nanotubes or graphene.

The intrinsic properties of these nanophases are those of the material from which they are made (ceramic, metal, polymer, biopolymer), but the properties of the materials obtained by dispersing them into different types of matrices are significantly different from those of the respective matrices. The main characteristic of nanophases is the very large specific surface area, which determines the formation of an interphase (matrix – nanophase) of very large size and this interphase, or rather the transport phenomena occurring at its level, determines the properties of the nanocomposite formed, modifying the responses matrix.

More or less recent studies have shown that it is possible to form nanophases - metallic or ceramic - with uses in biotechnology, medicine and a variety of other industries, based on the use of plant extracts. These nanophases have also been investigated from the perspective of their use as alternatives to conventional biocontrol agents. In the synthesis of these nanostructures, plant extracts function as reducing, stabilizing and coating agents.

Polymer nanocomposites can be used in a wide range of electronic devices, including transistors, solar cells, sensors, various detectors, diodes and laser diodes, as well as to make anticorrosive and antistatic coatings. The considerable advantage of polymer nanocomposites is given by the ease with which materials that combine strength with stiffness (polymers) can be obtained and the remarkable properties induced by the presence of nanostructures in the matrix.

The nanostructuring of a polymer matrix is, in the first sense, the result of the uniform dispersion of a nanophase in a polymer matrix. The approach is not a simple one, because nanoparticles tend to form agglomerations and this fact leads to an uneven structure of the material. In order to obtain uniform dispersions of nanoparticles in a matrix (especially a polymer matrix), strategies have been proposed for ultrasonication of mixtures, functionalization of nanoparticles (carbon nanotubes), the use of surfactants, each of which leads to more or less results satisfying. In recent years, at the Thermoset Matrix Composites Research and Development Center (CCDCOMT), methods of obtaining nanostructures directly in an epoxy matrix using solutions (in various organic solvents) of nanostructure precursors (inorganic substances) have been tested.

The nanostructures used for the formation of nanocomposites generally have a crystalline structure and can act as crystallization seeds in a (liquid) prepolymer causing, in this way, a local crystallization of the polymer (around the nanometer grain) with obvious effects on the behavior of the nanocomposite. Thus, a nanocomposite material is a mixture of amorphous and crystalline, the transition from one to the other being made through the interphase. Obviously, at high concentrations of the nanophase in the matrix, it is possible to obtain a material with qualities inferior even to those of the polymer (from a mechanical point of view), because the presence of each nanometric grain means a discontinuity of the polymer chains and, therefore, a concentrator of effort.

On the other hand, at low concentrations of the dispersed nanophase, the effect of its presence in the matrix is not intense enough and the designed properties (these are physical properties – electrical conductivity, thermal conductivity, dielectric permittivity, magnetic permeability) cannot be achieved, despite theoretical predictions based on either mixing models or percolation theory.

The current methods of nanostructuring are the methods in which nanometer-sized powders are used that are dispersed in the polymer. The best example is the example of nanotubes dispersed in PMMA (polymethylene methacrylate). The process takes place during extrusion, and granules of PMMA modified with nanotubes are obtained from carbon. Theoretical studies indicate a significant increase in the electrical conductivity of the nanocomposite material, which is not confirmed by experimental determinations (an explanation being given by the different electrical conductivity of the carbon nanotubes – in the axial direction and, respectively, in the transverse direction, along with the completely random orientation of them in the polymer matrix.

In a study carried out at CCDCOMT, starch was used to increase the viscosity of the prepolymer (epoxy resin) in order to limit the aggregation tendency of carbon nanoturbs, and the result was to obtain a starch-modified epoxy matrix with a concentration of 5% (mass fraction) of carbon nanotubes. The findings of the electrical tests showed no appreciable increases in electrical conductivity. In contrast, in another work, an epoxy resin was modified with carbon black to produce a material with great electrical conductivity.

Along with the two crises mentioned above (that of resources and that of energy), there is another one that we must refer to in the context of finding sustainable solutions. This is the food waste crisis. Most of these can be turned into compost, others can be used to produce biogas or liquid biofuels. Research has shown, however, that much of this waste contains really valuable substances - in the case of red tomatoes - lycopene, in the case of grapes - polyphenols, and the list can go on with other examples. The extraction of these (valuable) substances is an expensive process, but the use of powders obtained by lyophilization (which preserves most of the valuable substances) seems to be a path that we should follow. There are many studies on the use of powders obtained by lyophilization to obtain nanostructures. Of course, the separation of the nanostructures from the *soup* in which they are produced is, again, an approach that involves very high expenses.

We know from various studies carried out by those dealing with the use of natural resources that there is the possibility of obtaining nanostructures using different plants, parts of plants or plant extracts. The question is whether we could utilize another plant extract in place of starch (which was stated earlier in regard to the synthesis of polymer nanocomposites), which would allow a somewhat uniform dispersion of some nanostructures that would be placed in a polymer matrix.

This means that it should be known, on the one hand, what is the effect of adding these plant extracts to the polymer and, on the other hand, the possibility should be tested that a polymer modified with such powders of plant nature could be used to disperse nanostructures that could lead to interesting effects not only mechanically, but also thermally or electrically.

These nanostructures could be ferrites, carbides of various metals (silicon carbide or tungsten, with extraordinary properties), clays, because being ceramic materials, have very good dielectric permittivity and can be used to obtain electrical capacitors.

In the literature, thermosetting polymers (and unfortunately not only them) are referred to as resins - epoxy resins, polyurethane resins, polyphenolic resins, etc. On the other hand, these (solid) resins are obtained by mixing two substances that lead to polymerisation - one of them (the base) is called *resin* and the other (the one that triggers the chemical polymerisation reaction) is called *hardener* for most commercial materials.

At the outset, in order to avoid certain ambiguities, it should be specified that the polymer that is obtained is a resin, the material formed is resin, but when we make the mixture, one liquid component is called resin and the other hardener. Disambiguation must be done from the beginning. A formed material is a modified resin, a thermoset polymer modified with various organic and/or inorganic agents.

*Introduction*

Freeze-dried vegetable powders retain the most valuable substances in terms of action in the human body (as evidenced by research carried out at Bioaliment) and it is natural to wonder whether they could interact with the chemicals contained in the formulation of an epoxy resin (either resin or hardener). The fundamental component of the formulation of an epoxy resin is the diglycidester of bisphenol A (derived by esterification from bisphenol), and most vegetable residues resulting from the processing of grapes contain phenols. It is natural to ask what would be the result of adding a powder (obtained by lyophilization) from grape processing residues to an epoxy resin.

Under these conditions, the study was oriented towards this direction, that of dispersing vegetable powders in the epoxy matrix to identify the effects of their presence on the mechanical properties of the final material, as a first step. The second one was related to the dispersion of nanometric powders in polymer modified with vegetable powders in order to analyse the stability of such mixtures, on the one hand, and to analyse the dispersion quality of nanostructures in such a modified polymer, on the other hand.

The field of composite materials has fascinated me ever since I was studying in the first cycle (undergraduate studies) specialising in *Materials Processing Engineering*. Then, for the first time when I entered the laboratory, I was presented with polymeric materials formed by other students at the CCDCOMT (Centre of Research and Development for Thermoset Composites) research centre of excellence, which impressed me greatly. This prompted me to do my first research in this area for my undergraduate thesis on *Protein Modified Composite Materials.*

At that time, with only a one month gap, I also finished my bachelor studies at Bogdan Petriceicu Hasdeu University in Cahul, Republic of Moldova, majoring in *Accounting*, with the subject of *Income Tax Accounting*. I liked this field, but I decided to continue my advanced studies in the field of *Materials Science*.

This stage of life was very important, because for the first time we worked in a laboratory to form polymeric materials, which were designed from scratch and, therefore, we obtained a polymer matrix composite.

I continued my studies in the second cycle (Master's degree) in the *Advanced Materials Engineering* program. The dissertation topic was entitled *Influence of mode of formation on the properties of wheat gluten-gelatin modified epoxy systems*. In the work I analysed how modifying agents, in different amounts, as well as the mode of formation of the composites, influence the properties of wheat gluten and gelatin modified epoxy systems.

The supervisor of the studies that resulted in the bachelor's thesis, the dissertation and the present work was and is Prof. Dr. Phys. Adrian Cîrciumaru, who patiently guided me and helped me to understand what epoxy resin is, how to work with this material, all the rules that must be known and respected in a laboratory and especially at the Research and Development Centre for Thermoset Composites (CCDCOMT).

# 1. Nanostructuring of polymeric matrices

Nanotechnology refers to the manipulation of matter on an atomic or molecular scale, using nano-sized materials and structures, from 1 to 100nm [1], [2], [3]. Due to its small size, nanoparticles have unique physical and chemical properties, such as large surface ratios by volume or high interfacial reactivity. To date, (growing nanoparticles) have shown that they have specific interactions with contaminants in water, gas and even soils, and such properties that may mean, for the future, new improved green technologies [4], [5].

Therefore, the small particle size may involve problems related to mass transport and excessive pressure drop when applying permanent pressure or any other flow systems, as well as certain difficulties in separation and reuse, as well as possible damage to the ecosystem and human health, which can be caused by the potential release of nanoparticles into the environment [6].

Polymer-based nanocomposite retains the inherent properties of nano-particles, while polymer support materials provide stability, processability and some interesting improvements caused by nanoparticle-matrix interaction [7].

Nanoparticles generally used include metal oxides, biopolymers and nanoparticles with a single enzyme. These nanoparticles can be loaded into porous resins, cellulose or carboxymethylcellulose, chitosan, alginate and others [8].

The choice of polymeric materials is usually guided by their mechanical and thermal behavior. Other properties such as hydrophobic or hydrophilic balance, chemical stability, compatibility, optical or electronic properties and chemical functionalities, such as: solvation, wetability, modeling effect, must be considered [9].

Nanotechnology allows the intentional modification of the properties of the surfaces and their endowment with any desired function. Nanostructured surfaces, coatings and films have been important advances in controlling the properties of wetting, adhesion, mechanical, thermal, magnetic, electrical and optical properties and the ability to direct the behavior of cells [10], [11].

A number of promising approaches to the manufacture of functional nanostructured surfaces, coatings and films have been stimulated by opportunities to improve the properties of surfaces and interfaces through the combination of surface structure, morphology and their physical and chemical properties [12].

The ability to combine nanoscale (bio) organic and inorganic components allows the construction of intelligent natural materials that have found a compromise between different properties or functions (mechanical, density, permeability, color, hydrophobia).

Such a high level of integration associates several aspects: the miniaturization whose object is to host a maximum of elementary functions in a small volume, hybridization between inorganic and organic components optimizing possibilities, functions and complementary hierarchy.

With regard to artificial materials, the possibility of combining the properties of organic and inorganic components for the design and processing of materials is a very old challenge which probably started in the centuries (Egyptian circles, green ceramic bodies from China, prehistoric frescoes) [13].

## 1.1. Methods of nanostructuring by green synthesis

Silver nanoparticles can be produced by a light and safe process called green synthesis and are considered an effective antimicrobial agent. The antimicrobial effect of silver nanoparticles synthesized with *Euphorbia tirucalli* (aveloz) is described by Oliveira [14].

Black tea leaf extracts have been used to produce silver nanoparticles with various shapes, such as spheres, trapezoids, prisms and rods. Onitsuka S. et al. reported that polyphenols and flavonoids are responsible for the synthesis of these nanoparticles [15].

Recent studies [16], [17], [18] have reported that *Gelidiella* extract could be used as a reducing agent to produce spherical silver nanoparticles (22nm). The very stable dispersion of silver nanoparticles with a size of 16-40nm was formed by treating the solution of Ag salt with *Datura metal leaf* extract (*Solanaceae*) [19].

Sugars and reducing flavonoids were also responsible for the green synthesis of silver nanoparticles using *Cacumen placadi* extract. Therefore, the high temperature (90°C) is responsible for the formation of silver nanoparticles (18.4 ± 4.6nm) with small distribution [20].

Bouafia A., [21] presented a study in which he performed a rapid technique for the synthesis of silver nanoparticles using tannin extracted from grape pomace. Grape pomace tannin is involved in reducing and covering silver nanoparticles and leads to the formation of stable tannin nanoparticles [22].

The synthesis of iron nanoparticles was achieved by maintaining the reaction temperature at 50-60ºC. Aqueous sorghum bran extracts have been used to biologically synthesize iron nanoparticles at room temperature [23].

Palladium nanoparticles have been synthesized using an extract taken from the shell of *Cinnamomum zeylanicum* (cinnamon) [24]. Changing the concentration of cinnamon extract, reaction pH and temperature during the synthesis process was found not to influence the particle size (15-20nm) and morphology.

In another study, it was described that extremely catalytic palladium nanoparticles could be produced by bioreduction using mutant *Escherichia coli* strains [25]. Lloyd and his collaborators proposed earlier that *Escherichia coli* could be used to produce palladium nanoparticles using hydrogenases present in the bacterium [26].

### 1.2. Hybrid composite materials

Hybrid composite materials are formed in a typical matrix by combining more than two different types of fillings or fibers. They offer various features that cannot be achieved by using the reinforcement alone. Choosing fillers and fibers can reduce the cost of preparing the composite. The properties of the composites depend on the use of reinforcement in the composite materials. Fillers have often been used to reduce the amount of polymer used or to modify the general properties of the polymer, and the final characteristics of the materials depend on the density, the size and shape of the fillers mixed together with the polymer and the quality of the polymer-filling material interface. Naturally available fillings are the most cost-effective and also improve the performance of the composite [27], [28].

### 1.3. Applications of hybrid composites

Nanocomposites based on epoxy resin and clay can be used for reinforcement, sealing, adhesion, insulation and combustion resistance. For example, at Audi, Volkswagen and Chevrolet HHR, the ventilation of the foot heater and the central console are made of epoxy-argile laminates respectively. In addition, due to their high flammability, Pirelli tires are made of epoxy-argile nanocomposites. With regard to electronics and thin films, under the trade name Nanomer, Nanolokt and Durethan, polymeric clay nanocomposites have considerable properties related to insulation and barrier capacity [29].

The most commonly used matrix used as a basis for clay reinforcement is the epoxy matrix, which is widely used in the automotive industry. In this way, innovative epoxy argila-based matrices are accompanied by high-strength fibers such as carbon and fiberglass, taking a step towards commercial applications in the high-tech automotive and aviation industries. This is mainly due to the existence of a symbiosis with the aspects of reducing density, low costs, and remarkable mechanical properties. As another example, liquid helium storage tanks made of epoxy-argile nanocomposite consisting of carbon fibers as micro-hardeners showed a rate of helium leakage five times lower than that of cryotankments made without clay [30]. Moreover, the anti-corrosion feature of epoxy-argile nanocomposites makes them the ideal candidates for aircraft where anticorrosive coating is required [31].

Despite the growing commercial spectrum of biodegradable film production, some difficulties, such as the knowledge, cost, and performance of these materials compared to conventional resins, require an additional approach. Biodegradable films, mainly starch and fruit puree, have high permeability to water vapor and low mechanical properties, thus making it necessary to use plasticizers and curing materials [32].

However, many of these reinforcement materials result in poor adhesion to the interface with other matrix components [33].

Starch is one of the most prevalent components of natural biomass. Many plants store starch as an energy source, as a natural polymer, biocompatible, renewable and biodegradable. Starch is obtained from different classes of plants, such as cereals, roots, tubers, legumes and fruits. Cereals have the highest percentage of starch [34].

Starch is a biocompatible macromolecular carbohydrate consisting of a large number of glucose units that bind together by glycosidic bonds. The structure of this polymer can be divided into two sections of linear helical amylose and branched amylopectin (α-d-glucose monomers), which contain hydroxyl groups (–OH) [35], [36]. These groups have strong intermolecular interactions, which give, based on a closer arrangement, increased crystallinity and high melting temperatures. The presence of hydroxyl groups favors the rupture of hydrogen bonds, which causes disintegration into small fragments.

Of the different classes of adhesives, pressure-sensitive adhesives are one of the most common types and represent a potential application that would benefit from the use of renewable materials. Self-adhesive tapes, labels, stamps, and adhesive notes are present in everyday life (electronic industry, auto parts). They adhere by simply applying pressure to a wide variety of materials, and often the link is reversible.

The main advantage of pressure-sensitive adhesives compared to other types of adhesives is ease of use. There are no storage problems, no mixing or activation is required and no waiting periods. Pressure-sensitive adhesives are viscelastic materials that combine a liquid-like dissipator character necessary to form molecular contact under light pressure and a solid-like character to withstand macroscopic stress during the separation phase, properties that can be achieved with low *Tg* polymer networks easily crosslinked. The performance of the network adhesive can also be adjusted by incorporating functional groups. Fatty acid derivatives are an attractive resource for the development of bioadhesive due to their inherent low glass transition temperature. Methyl acrylate oleate was used in polymerization in aqueous emulsion, and the resulting polymer showed physical properties comparable to oil-based polymers and showed pressure-sensitive properties. Although both types of polymers have comparable adhesion, shear strength and elasticity, the detachment of oleate-based polymers was lower [37].

Self-adhesive coatings with controlled viscoelastic properties, containing carboxyl groups as adhesion promoters, are described. These adhesive gels were composed of hydroxyl-functional polyesters synthesized by volume polycondensation of dimeric fatty acids and dimeric fatty diols in combination with maleate triglycerides [38].

Thermal stability and optical transparency are important factors for flexible electronics and thermal applications of pressure sensitive adhesives. Soy oil-sensitive pressure adhesives are particularly good candidates for applications in modern flexible electronic devices such as displays, semiconductors and solar cells, due to their thermal properties, and for transparent labeling and packaging bands due to their high transparency. Pressure-sensitive adhesives from epoxy soybean oil/dihydroxyl soybean oil systems have been developed by balancing the resin ratio of sticky groups and the degree of crosslinking [39].

In addition, other properties, including chemical and heat resistance, as well as high mechanical properties, such as impact resistance, high strength and hardness and other applicable functional properties, including the high adhesion potential of different substrates and the electrical insulation properties, are assigned for this type of material [40], [41], [42], [43]. These properties mentioned above in epoxy resins can be manipulated to achieve the desired goals by incorporating different nanoparticles, which are so-called hardeners [44], [45], [46], [47], [48].

Therefore, materials reinforced with these reinforcing additives can find a wide application in various fields, including the aerospace, defense and automotive industries.

In principle, the production of renewable oils and monomers has been shown to be technologically feasible and able to replace petrochemical raw materials. Almost since the beginning of the renaissance started at the end of the last century, renewable oils have also been proposed as composite matrices, and this trend is constantly growing with promising results. Some of the biopolymers and precursors based on vegetable oil are currently commercially available and there are companies that offer organic-based polymeric derivatives (epoxy precursors, alkyd and polyurethane being the most common) for specific applications. In some cases, natural oil thermosetting opens up new possibilities in certain specific areas, such as biomedical applications, which have not been taken into account for oil-based materials.

### 1.4. Partial conclusions

So, unlike any other class of materials, durable plastics, with an attractive combination of low costs and high performance, are needed to meet the needs of a growing world population in terms of health, housing, clothing, communication, mobility, food and energy. Plastics play a key role in sustainable development. The development of new industrial products or commercial processes is the purpose of continuous research in both the public and private interest.

The high production of plastics worldwide increases the disposal of these materials and leads to a large accumulation of non-degradable waste, which results in a huge impact on the environment. The production of commercial plastics meets the requirements of ecological chemistry for poor and clean production through the use of solvent-free processes, with efficient use of resources, without training on by-products, waste management and even the use of renewable resources.

Organic-inorganic hybrid materials are not only a creative alternative for designing new materials and compounds for academic research, but their improved or unusual features allow the development of innovative industrial applications.

## 2. Objectives of research

Based on the bibliographic research presented above and in agreement with the doctoral supervisor and the members of the guidance commission, to continue the research activity started with undergraduate studies and undergraduate studies, I decided to broaden the horizons for agents to change the properties of an epoxy resin (Epiphen RE4020-DE4020) for the purpose of capitalizing on previous experience, from a personal point of view, but also to contribute to the development of the database on the results of the change (by using various powders) the properties of the resin mentioned developed at CCDCOMT over almost twenty years of activity.

Because powdery extracts of plant debris have been shown to be very useful in obtaining nanostructures, the proposed research aims to use some of these extracts to standardize the distribution of inorganic nanoparticles in epoxy resin, based on the fact that nanostructures could interact with plant powders, the latter ensuring the buoyancy of premiums in the pre-polymeric mixture. In other words, testing for a colloid (in pre-polymer) that, after polymerization, ensures uniform distribution of nanoparticles.

A decade ago there was a global trend in the study of polymers modified with clays (as shown in the previous Chapter). In addition, at CCDCOMT there was a precedent of the study of composites made with epoxy matrix (the epoxy system already mentioned above) and modified with clays for obtaining materials with tribological responses superior to those of resin epoxy. There is an advantage to the use of cosmetic clay for changing the properties of epoxy resins (and polymers, generally) due to the fact that they are organic-inorganic compounds. Thus, organic components (different from one clay to another) could interact with the organic epoxy matrix, facilitating the achievement of some balance in the inorganic component (generally silicates).

In this context, and based on the assumption that a chemical interaction between vegetable waste powders and the organic component of clay would be possible, there would be a good chance that a modified polymer with vegetable powder and clay would allow better results in the distribution of nanostructures.

Nanostructures used to modify the properties of epoxy resin were carefully chosen based on their intrinsic properties: nano-graphite, nano-silver, nano-therrite, strontic nano, and tungsten nanocarbide. Each of these agents was chosen after the analysis of their properties (and availability) thus, nano-graphite is a material with high electrical conductivity (and high thermal conductivity); nano-silver is an antioxidant agent that could stabilize a mixture of organic compounds; and strontic ferrite is a material with remarkable magnetic properties. The success of such a composite would mean obtaining a multifunctional material, especially if it retains the adhesive properties of epoxy resin.

The main purpose of this research was, from the very beginning, to identify changes in the properties of an epoxy resin (highly studied in CCDCOMT) in the presence of lyophilized vegetable powders used as agents to prevent the aggregation of nanoparticles.

The first part of the study was to obtain information on the modification of epoxy resin with clays (three clays of cosmetic use) and in different mass fractions of them in the final composite. Epoxy-clays composites were designed for three values of the mass fraction of the clay, and it was established that the most advantageous way of formation is to obtain cylindrical samples using molds made of polypropylene (a method developed at CCDCOMT and used in previous studies).

The intermediate stages, in order to achieve this first objective, were:

- determining the exact masses of polymer and clay (for each type of clay and for each mass fraction of clay) to obtain a sufficient number of cylindrical specimens;

- establishing the strategy for making prepolymeric mixtures in order to avoid foaming the mixture, on the one hand, and to avoid the agglomeration of clay particles, on the other;
- effective formation of epoxy/clay composite materials;
- consolidation, by heat treatment, of the formed materials;
- extraction of specimens required for traction tests (stretching), three-point bending (bending), tribological and physical (water absorption);
- performing the above-mentioned tests, processing and interpreting the results obtained;
- the formulation of the conclusions and the choice of clay to be used in the following materials.

The second objective was to identify the induced changes in the properties of materials in the presence of vegetable powders. And this objective was achieved by going through some stages:

- determining the quantities of vegetable powders added to the prepolymeric mixture;
- the effective formation of materials, this time both in the cylindrical form (mentioned above) and in the form of plates with a thickness of 1mm;
- consolidation of materials (heat treatment) and extraction of specimens necessary for the mentioned tests and in the case of clay/epoxy composites to which tests have been added to determine the dielectric permittivity;
- statistical analysis of test results and their interpretation;
- formulation of partial conclusions.

As will be shown in the Chapter on materials used and methods of analysis, the addition of vegetable powders had (in some cases) unexpected effects – reduction of the viscosity of the prepolymer mixture with direct consequences on the decantation of added powders. For this reason, two categories of modified materials with starch and starch and clay, respectively, have been formed under this second objective, in addition to vegetable powders, in order to increase the viscosity of the prepolymer mixture in order to reduce the decantation. As in the above cases, the objective was achieved by going through the following steps:

- establishing the dust dispersion strategy in the prepolymeric mixture (the addition order to ensure the conditions for limiting the decantation);
- sample formation (cylindrical and flat);
- extraction of specimens, after consolidation by heat treatment;
- performing tests (listed and above);
- statistical analysis of the results obtained from the tests and their interpretation;
- formulating partial conclusions.

The steps taken to achieve this goal were:

- determining the required quantities of material to ensure the formation of the required number of specimens required for the intended tests;
- making the mixture of nanostructures (mechanical);
- establishing the nanostructure dispersion strategy;
- material formation (cylinders and plates) and their consolidation;
- extraction of specimens.

## 2.1. Partial conclusions

The beginning of the research starts from the correct establishment of the objectives, which is a first and very important stage. Clear and well-established objectives lead to qualitative research with results in line with expectations. Likewise, a very important stage is the documentation and study of as many articles and works in the field as possible.

## 3. Formation of polymeric composite materials

### 3.1. General observations

Epoxy resins have superior resistance, are very adherent, and have low contraction in formation. However, over 90% of the world's production of epoxy resins is represented by epoxy resins with polymerization by condensing reactions involving bisphenol A (BPA), which is considered to be an environmentally toxic and harmful material [49]. With this in mind, researchers have made many efforts to synthesize epoxy resins from biocomponent alternatives rather than BPA. Consequently, epoxy prepolymers were synthesized from other raw materials, such as epoxy cardanol [50], isosorbide [51], gallic acid [52], tannins [53] and vegetable oils (especially soybean oil) [54], [55].

### 3.2. Polymer formation stages

For this study the polymer used was epoxy resin – bi-component epoxy system – Epiphen RE4020-DE4020 (as mentioned, since the introduction, RE4020 is the base or resin and DE4020 is the hardener). The mixture of these two liquid substances (in the mass or volume rate recommended by the manufacturer) has a gel time of approximately forty-five minutes) is the prepolymeric mixture, in the volume of chemical reactions leading to polymerization (the manufacturer declares a complete polymerization time of approximately twenty-four minutes). After forty-five minutes ( gel time ) the mixture is very viscous and can no longer be handled for casting or other operations.

**Fig. 1.** Polypropylene tube molds with plasticine plugs

After closing them (at one end), the tubes were fixed with plasticine in a container in which molten wax was poured among them.

**Fig. 2.** Glass and rubber moldings

After twenty-four hours, the composite materials were extracted from the polypropylene tubes as well as from the glass sheet molds and subjected to a heat-consolidation treatment. It consists of the introduction of polymerized materials into the BINDER (circulating air) oven and the application of a controlled thermal program, consisting of heating the oven enclosure to a temperature of 60ºC, maintaining it for eight hours, raising the temperature to 80ºC, maintaining the temperature for two hours, and finally, the last stage, heating to 90ºC for one hour.

### 3.3. Modified polymeric materials

In order to form modified materials with three types of clay, the steps described above were completed. Epoxy resin E was modified with three types of clay (black clay, white clay, and red clay) in proportions of 5%, 10%, and 15% (mass fractions).

The clay used is for cosmetic use, but with a different origin: black clay is collected from the Dead Sea, red volcanic clay from Morocco and white clay from Jordan

To correctly identify modified and unmodified polymeric materials after extraction from the mold, they were encoded. Unmodified polymeric material, i.e., the control is M00. Polymer materials modified with black clay: 5% (M01), 10% (M02), and 15% (M03). After that, follow the modified polymeric materials with red clay, as specified above: M04, M05, and M06. And finally, the modified polymers with white clay: M07, M08, and M09.

Polymeric materials modified with clays (black, red, and white) were subjected to several tests: mechanical (traction, bending, and compression), tribological, and thermal. Next, in polymers modified with other additives, we used black clay. We are going to analyze what properties of the polymeric material have changed, but first of all, clay was used to prevent agglomerations in the polymeric material.

After the same working principle, but with other modifiers we formed a new set of materials, in which we added vegetable powders (pomegranate, grapes, sea buckthorn, kiwi), black starch and clay (from the Dead Sea) to the unmodified epoxy resin.

Polymeric materials modified with vegetable powders were encoded from M10 to M21. Therefore, M10 is modified epoxy resin with sea buckthorn powder, M11 is modified epoxy resin with sea buckthorn powder and starch, after which M12 is modified epoxy resin with sea buckthorn powder, starch and black clay.

With M13, M14, M15 I noted epoxy modified with kiwi powder, then kiwi and starch, then kiwi, starch and clay. Next, M16-M18 represents the modified epoxy resin with pomegranate powder and from M19-M21, represents the modified epoxy resin with grape powder according to the above process.

### 3.4. Partial conclusions

Thus, the beginning of the present research started from the idea of modifying the epoxy resin (Epiphen RE4020-DE4020) with an organic-inorganic component of three types, namely black, red and white clay (for cosmetic use). It was added to component A in different quantities, namely 5%, 10% and 15%.

In the second stage, I formed materials with vegetable powders (buckthorn, kiwi, pomegranate, grape,) to which I added black clay and potato starch. The role of the starch is to prevent the deposition of the added powder when the material is poured.

In the third stage of materials formation, I added black clay, starch, vegetable powders and a nano mixture (silver, tungsten carbide, strontium ferrite, graphite).

The introduction of these modifiers aimed at changing the properties of the polymer material obtained at the end. Tracking these changes will be done by testing the specimens of each material in mechanical tests (traction, bending), their structural analysis, water absorption, to finally get an overview of how modifying agents have influenced the reference.

## 4. Polymer materials modified with clays

### 4.1. General observations

There are a variety of mechanical tests that aim to determine the behavior of materials at compression, traction, bending, twisting, shear, wear, or contact pressure. They can be done in static or dynamic conditions, at ambient temperature, at high or low temperatures, as well as in corrosive environments.

### 4.2. Structural analysis

In the case of polymers, it is known that there are three types of mechanical responses: rigid behavior (fragile) corresponding to thermoset polymers, elastic behavior corresponding to elastomers (all thermoset polymers), and the behavior characteristic of thermoplastic polymers, an elasto-plastic behavior that is similar to the behavior of metals.

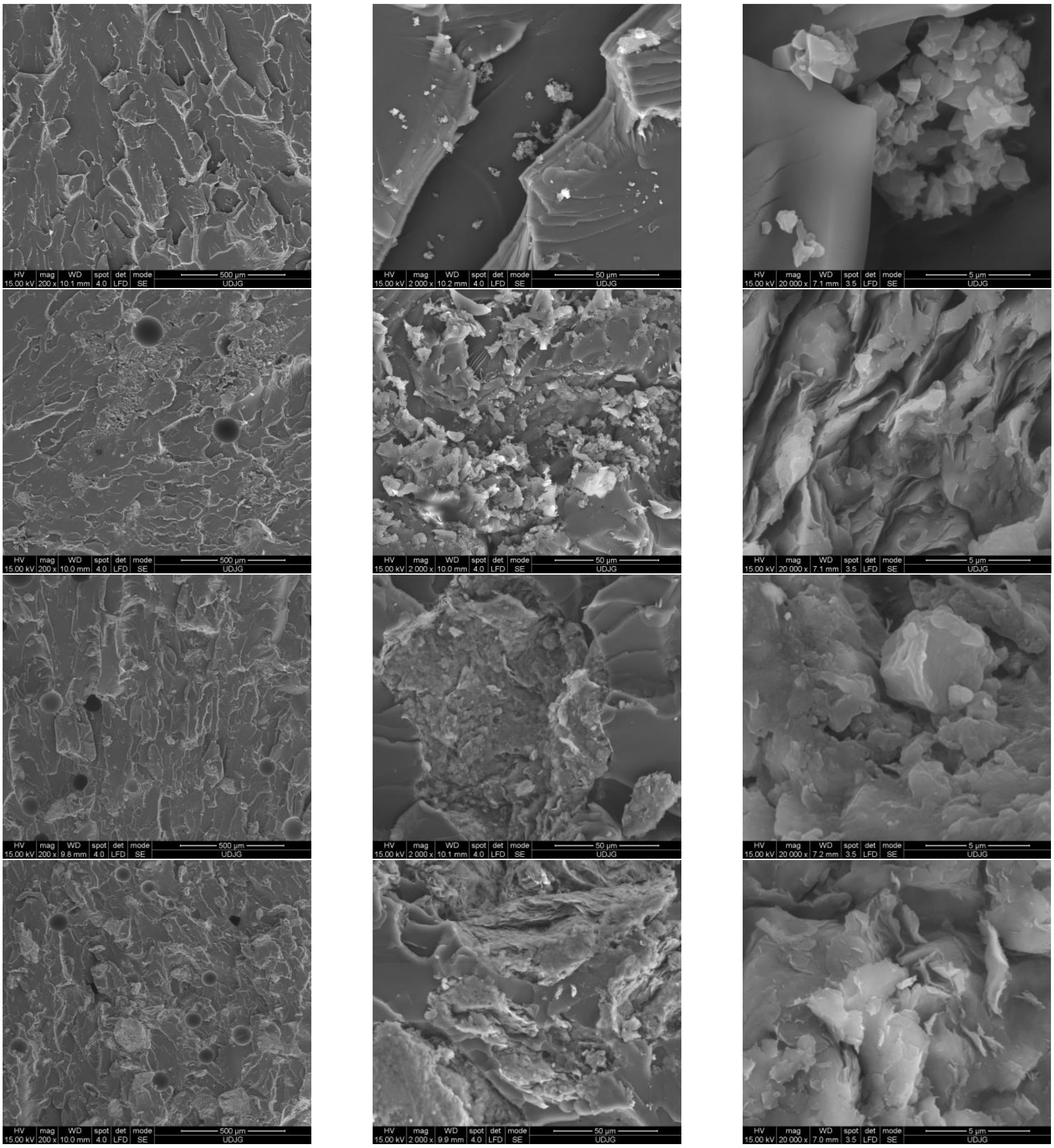

**Fig. 3.** Structural analysis of materials M00-M03

In Fig. 3., SEM micrographs of black clay-modified materials are shown at the three concentrations mentioned in the previous Chapter.

In the Fig. 4., keeping the previously established template (i.e., the SEM micrographs of the epoxy resin on the first line), are presented micrographs of modified materials with red clay, which, as specified in the previous Chapter, have the same values of clay concentration.

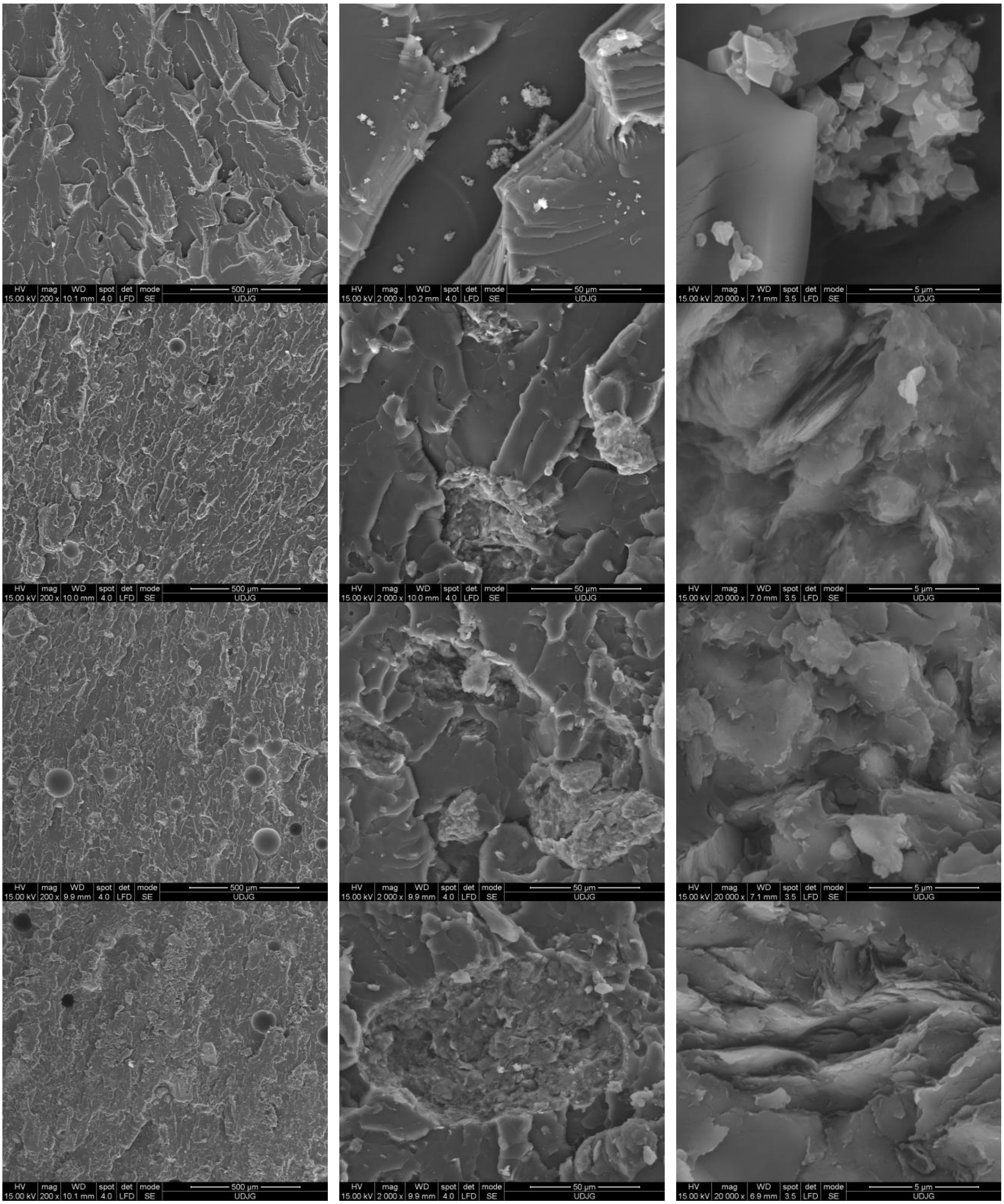

**Fig. 4.** Structural analysis of materials M00, M04-M06

At a first analysis, the different appearance of clay agglomerations (compared to the case of black clay – Fig can be observed. 3.). In the case of images with the lowest magnification (left-hand column) finer fragmentation of the polymeric islands (can be observed also compared to black clay composites), which means, or better dispersion of clay, or other chemical reactions of the organic phase of clay with the polymer matrix.

In Fig. 5., the structural analysis of modified polymeric materials with white clay (M07-M09) is rendered. SEM micrographs are presented for the same magnifications as for materials formed with the other two types of clay and on the first line is kept the sequence of SEM micrographs of the epoxy resin.

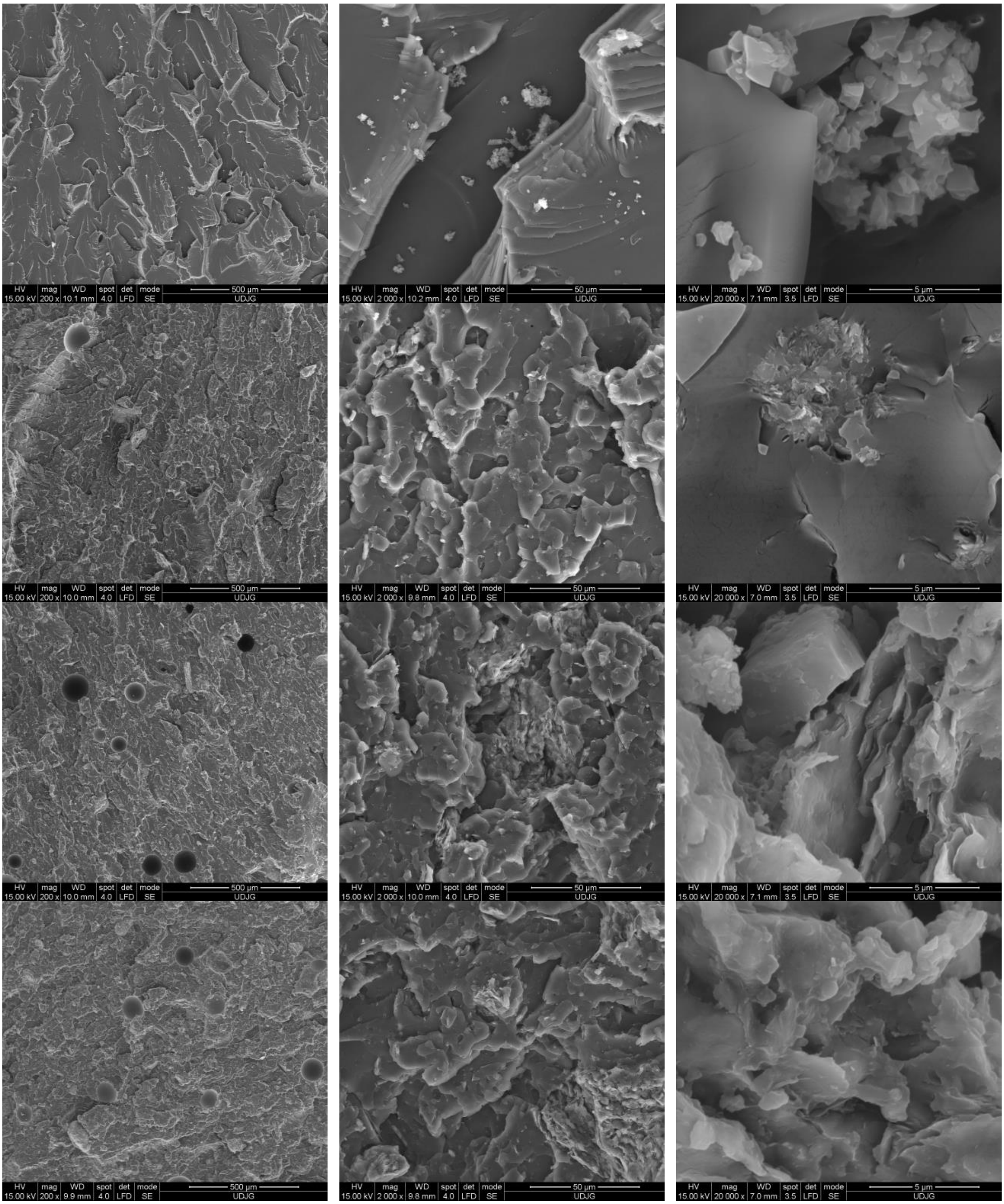

**Fig. 5.** Structural analysis of materials M00, M07-M09

### 4.3. Partial conclusions – structural analysis

- for SEM analysis, fractured specimens were selected following the bending in three points that have the fracture surface as flat as possible, in order to allow the identification of morphological differences;
- the fracture certainly occurs in the vicinity of the plan which includes the direction of load and depends on the number of defects in the plan or in the vicinity of that plan;
- the analysis reveals morphological differences of the polymeric matrix, similar in appearance but different in size depending on the type of clay used to change the properties of epoxy resin;
- there was no control of the choice of test piece from which samples for SEM analysis (for example, the same batch test for all materials) were obtained, because this control would have meant giving up the proximity of the analyzed surface to flatness;
- a choice of the type presented above, an analysis of surface morphology would also have been allowed depending on the time of casting the sample (we performed this type of analysis in the case of mechanical test results);
- the analyses presented above do not represent by far an accurate analysis of the materials formed, but only provide a statistical picture– a single sample of any specimen of a material– given that the area of the area under investigation is much smaller than the cross-sectional area of the specimen.

### 4.4. Analysis of the mechanical properties of polymeric materials modified with clays

#### 4.4.1. Tensile tests

Tensile strength can be defined as the voltage (maximum effort) that an object can tolerate before breaking. In fragile objects, the maximum value of tensile strength is close to the point of flow, but the value is higher in ductile materials.

In Fig. 6. effort-deformation curves are rendered for each epoxy resin test piece, as well as the mean curve of the epoxy resin behavior. What is very important to mention is that on the first part of the curve, all the specimens have the same answer, with the differences appearing only after the end of the linear regime.

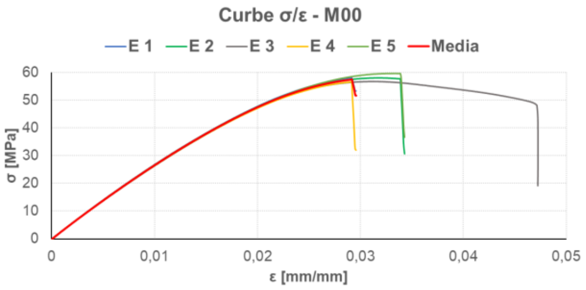

**Fig. 6.** σ/ε curves-unmodified polymeric material

As can be observed (for test piece 3), a significant decreasing passage of the modulus of elasticity before rupture also occurs. Epruvets 1, 2, and 5 break at the same deformation, while test piece 4 yields the lowest value of the deformation. These differences, which do not affect the elastic response, may be due to possible non-homogeneities of the specimens (gaseous intrusions, insufficient polymerization, small variations in the dimensions of the specimens – the polypropylene tubes being quite deformable). What is most important is the fact that in the elastic response regime, all specimens respond identically, and the maximum value of the effort is around 60MPa, which corresponds to a 3mm elongation of the specimens.

In the Fig. 7. the individual curves of the tests performed on the specimens made of the modified black clay composites are rendered. We kept the same scale (in terms of voltage) to facilitate comparison with the epoxy resin response. In terms of deformation, the scale is changed because these materials are more rigid.

As with epoxy resin specimens, (can be observed for all three materials) identical test piece response in the elastic regime area (with a small dispersion in the case of material M01). And, this time, the deformations at which the ruptures occur are different (not essentially) except for the M03 material at which the specimen 5 shows a significantly higher elongation. What is interesting is that for materials with 5% and 10% black clay the maximum voltage is about 30MPa, while for material with 15% black clay the value of this parameter is about 40MPa.

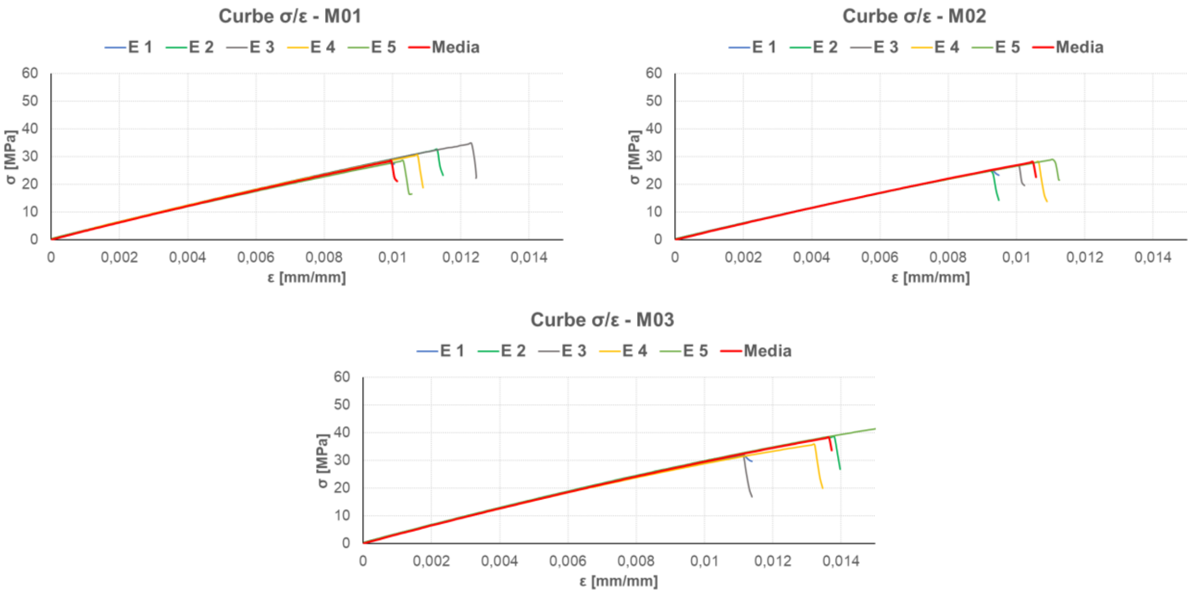

**Fig. 7.** σ/ε curves-polymer materials modified with black clay 5%, 10%, 15%

In Fig. 8. are presented (in the system used above) the individual stress-strain curves of the specimens from the materials M04-M06, i.e. the materials modified with red clay. And, in this case, because the dispersion of experimental data is very small (especially in the elastic regime), the differences in behavior appear in terms of rupture (deformation or elongation at break). As with modified black clay materials, the deformations are smaller than with epoxy resin.

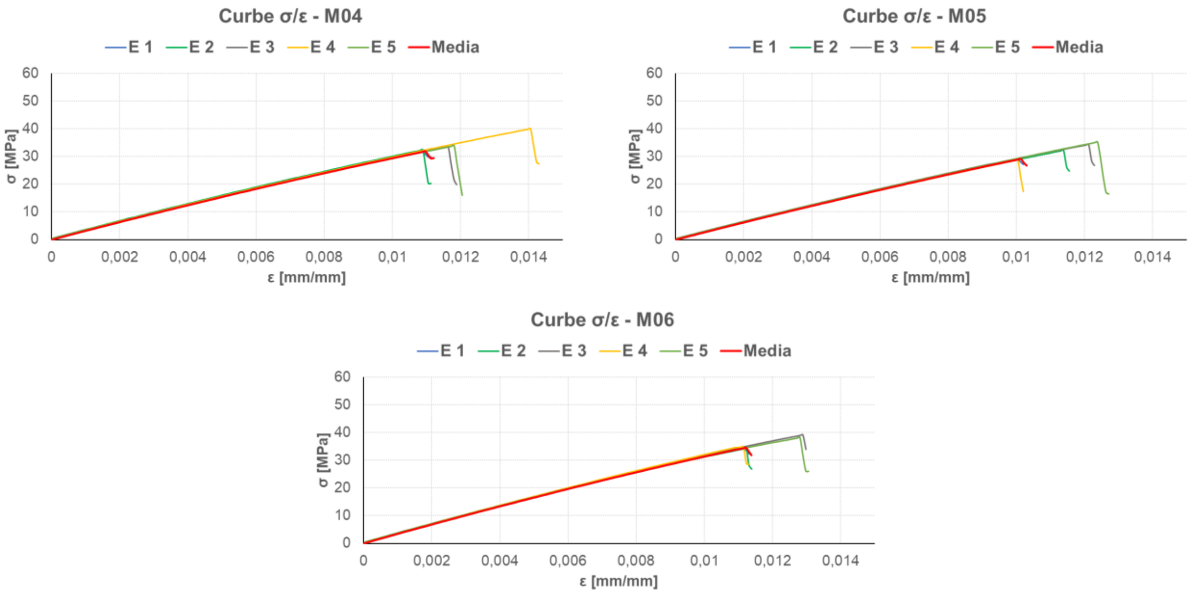

**Fig. 8.** σ/ε curves-polymer materials modified with red clay 5%, 10%, 15%

In the Fig. 9. the individual behaviors of the specimens tested for stretching of the modified materials with white clay are rendered. Thus, as we specify in the section dedicated to structural analysis, in the case of this clay the most important morphological changes of the polymer appear. It can be seen that, unlike the other two categories of materials analyzed, in this case, the responses for low concentrations are different, with the lowest average voltage value being recorded for the material with 10% white clay and the lowest recorded value for the analyzed materials.

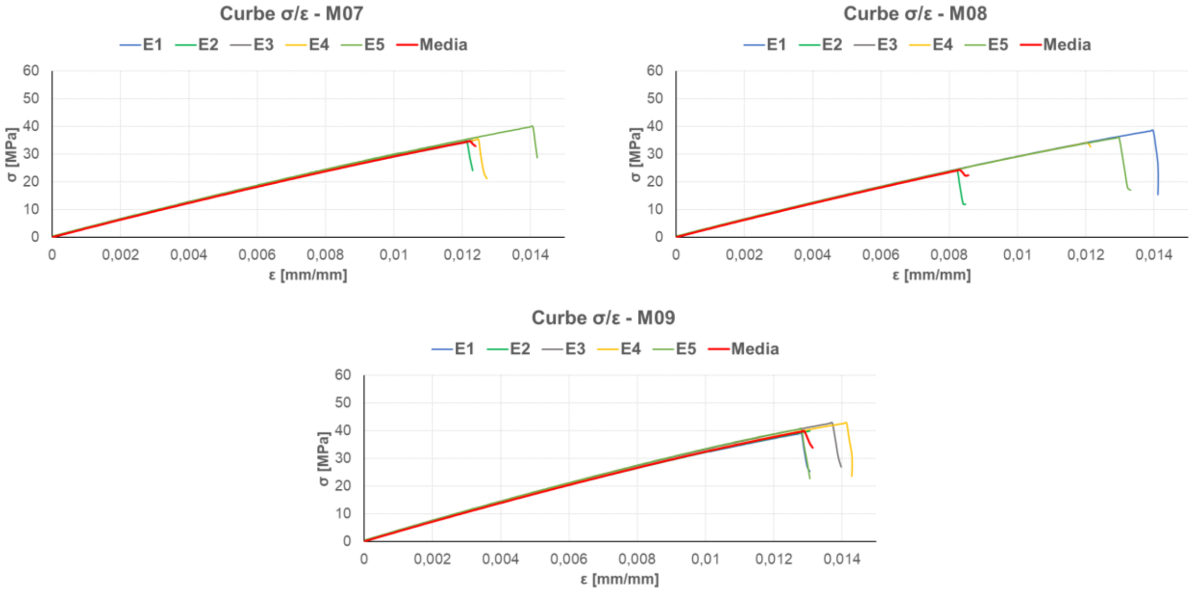

**Fig. 9.** σ/ε curves-polymeric materials modified with white clay 5%, 10%, 15%

Analyzing the data in the Fig. 10. it can be seen that, among the modified materials with clay, the best answers correspond to the highest concentration of the modifying agent, in all three cases.

Analyzing the data presented in the Fig. 7. – Fig. 9. it is obvious that the test specimens were broken at different times and a batch of five specimens cannot perform a thorough statistical analysis.

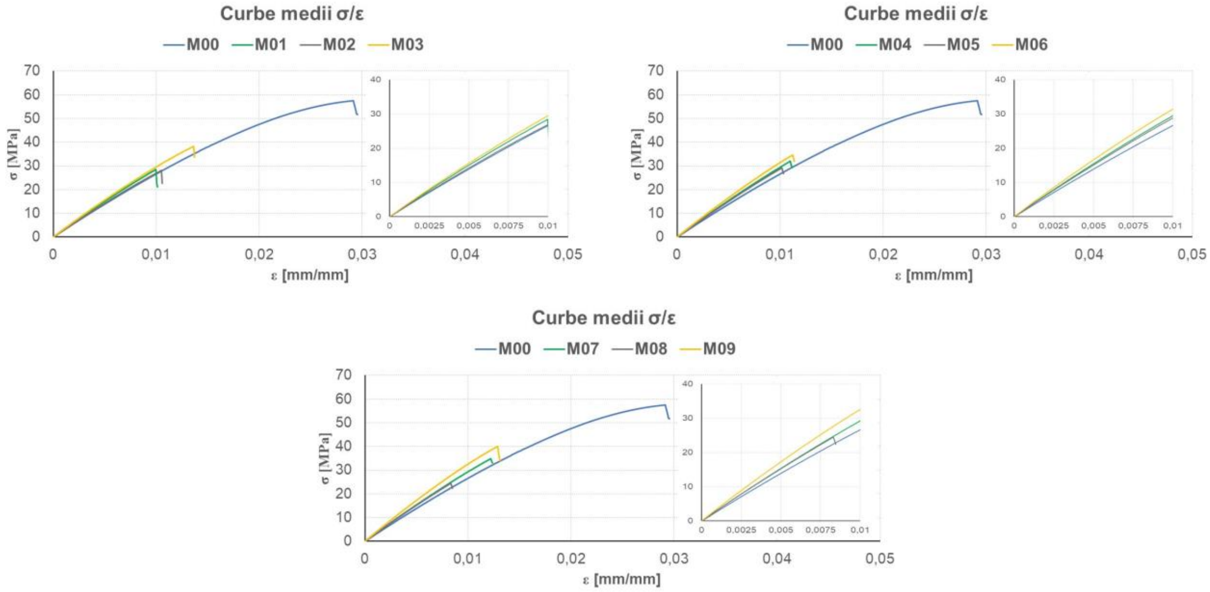

**Fig. 10.** Average σ/ε curves-polymer materials modified with clays

**Table 1.** Tensile modulus of elasticity of polymer materials modified with clays

| | M00 | M01 | M02 | M03 | M04 | M05 | M06 | M07 | M08 | M09 |
|---|---|---|---|---|---|---|---|---|---|---|
| **E[GPa]** | 2.76 | 3.07 | 2.89 | 3.18 | 3.14 | 3.07 | 3.39 | 3.13 | 3.10 | 3.52 |
| **E[%]** | 100 | 111.23 | 104.71 | 115.21 | 113.76 | 111.23 | 122.82 | 113.40 | 112.31 | 127.53 |

To continue the analysis, in Fig. 11., the average stress/strain curves for the formed and tested materials are shown, but this time the criterion is the concentration of the modifying agent – 5% for materials M01, M04, M07; 10% for materials M02, M05, M08; 15% for materials M03, M06 and M09.

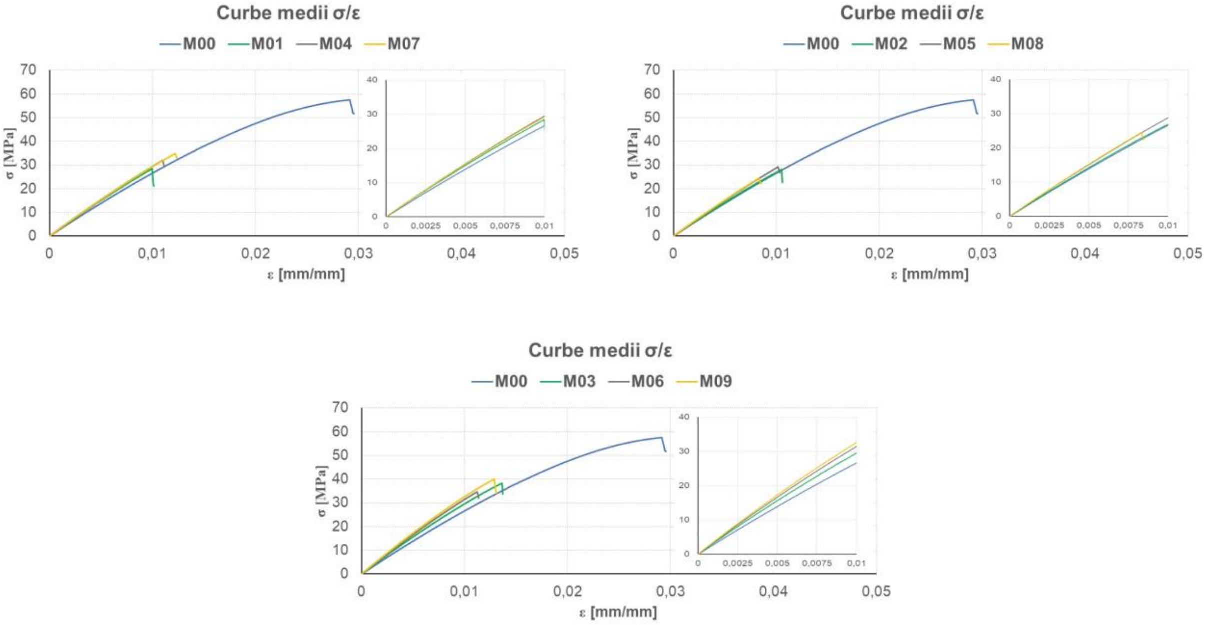

**Fig. 11.** Average σ/ε curves-polymer materials modified with clays

Compared to the matrix material, all clay-modified materials break earlier – the latter break when the deformation ε is about 0.01 or slightly higher, while, the epoxy resin has a deformation of about 0.03. In terms of elongation, for modified materials its value at break (average) is about 1mm, while for epoxy resin the value of elongation at break (average) is 3mm. Certainly, therefore, the modified materials are more rigid.

### 4.4.1.1. Conclusions – tensile tests

- materials modified with clays (composites) have an elastic behavior, in general, better than that of the epoxy resin, in conditions where the range of elongations is significantly reduced, even if the epoxy resin has an elasto-plastic behavior (after the elastic region);
- the best elastic responses of materials modified with clays (even better than the response of epoxy resin) are obtained in the case of the maximum concentration of the modifying agent (clay), regardless of its nature, as can be seen from Fig. 12.;
- the values of the modulus of elasticity given by the software application are slightly higher because these values are determined for each specimen over the entire domain (until failure) and this method of calculation leads to a greater dispersion of the averaged data;
- the values of the modulus of elasticity of the materials modified with 15% clay are higher than the values of the modulus of elasticity of all other materials – more than 15% for the black clay, more than 22% for the red clay and more than 27% for the white clay (all of which are evaluated in ratio of modulus of elasticity of epoxy resin);

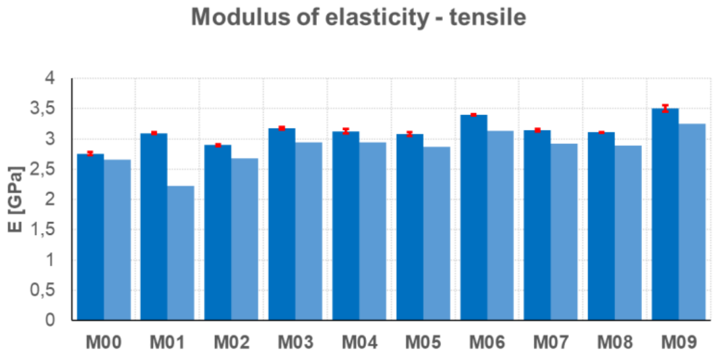

**Fig. 12.** Tensile modulus of elasticity of polymer materials modified with clays

- the fact that the values of the elasticity modules are high, although the clay concentration is high (in the materials mentioned above), which means a higher defect density (clay particles) may be associated with a matrix interface/better quality clay due to possible chemical reactions between the organic phase of the clay and the epoxy matrix.

### 4.4.2. Bending tests

Flexural modulus is calculated as the tendency of a material to resist bending [56]. The bending module is obtained from the slope of the load/displacement graph produced by a bending test and is measured as a consequence of voltage changes in relation to the deformation. In general, the bending module or the elasticity module is equivalent to the traction module or the Young module, but these values may be different in the case of polymeric materials. Bending resistance is defined as the ability of a material to withstand the forces of bending, which are applied perpendicular to the longitudinal axis [57].

Each unmodified and clay-modified polymeric material tested for bending will be analyzed in more detail below. In Fig. 13. the curves corresponding to the five tested specimens for the material M00 (epoxy resin) are shown. It can be seen that for all the tested specimens, the load/displacement curves show a linear area (elastic regime), followed by an area similar to an elasto-plastic behavior. Only one specimen (E3) breaks in the elastic regime. The maximum bending load is 350N, with a maximum displacement of up to 7mm, at the E4 and E5 specimens. However, the average recorded displacement between the five test specimens is 3mm and the average load is 250N. As with stretching tests (tensile), the average is calculated in relation to the first rupture of a specimen.

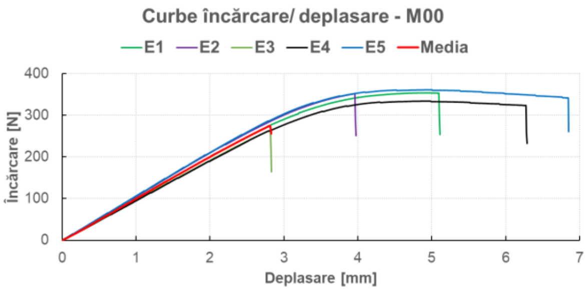

**Fig. 13.** Load/displacement curves-unmodified polymer material M00

Epoxy resin is not without defects (as we have shown in the section dedicated to structural analysis); crystalline structures may occur, either due to natural crystallization or the pre-existence of impurities in the mixing vessels.

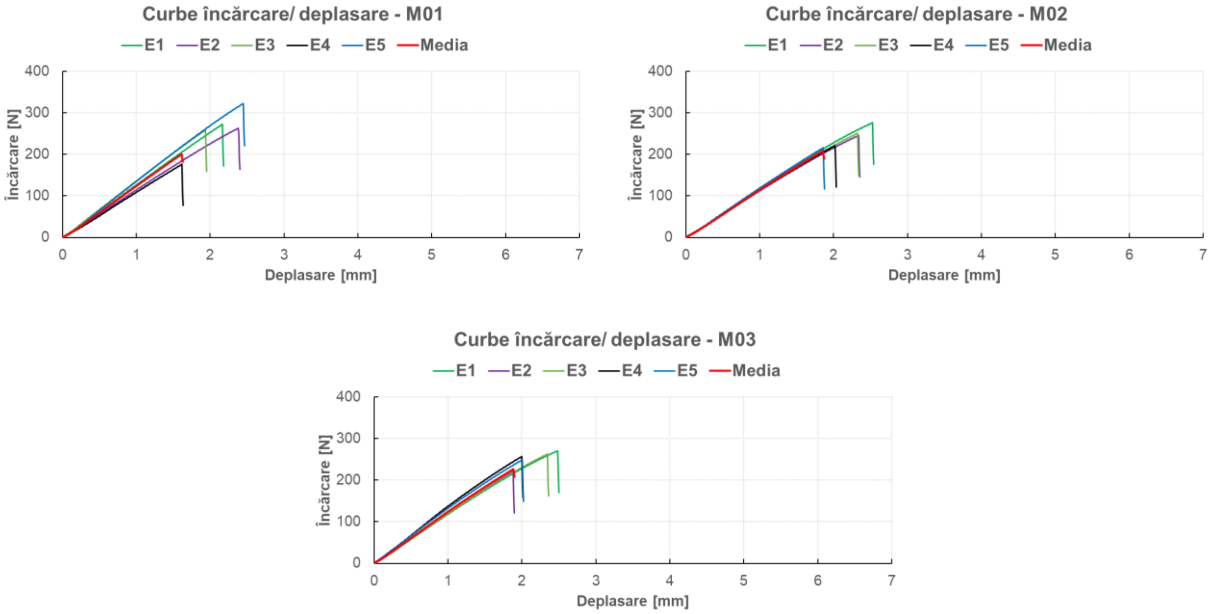

**Fig. 14.** Load/displacement curves-polymeric materials modified with black clay 5%,10%,15%

In Fig. 14. the individual curves (load/displacement) and the average curves of the specimens tested in three-point bending of the black clay-modified materials are presented. A first observation is related to the fact that (like epoxy resin), there is a greater dispersion of experimental data in the elastic domain.

Regarding materials modified with red clay (Fig. 15), the situation is different because the largest dispersion of the experimental data (for bending) is evident in the case of the 15% concentration, and the smallest dispersion of the data corresponds to the 10% concentration.

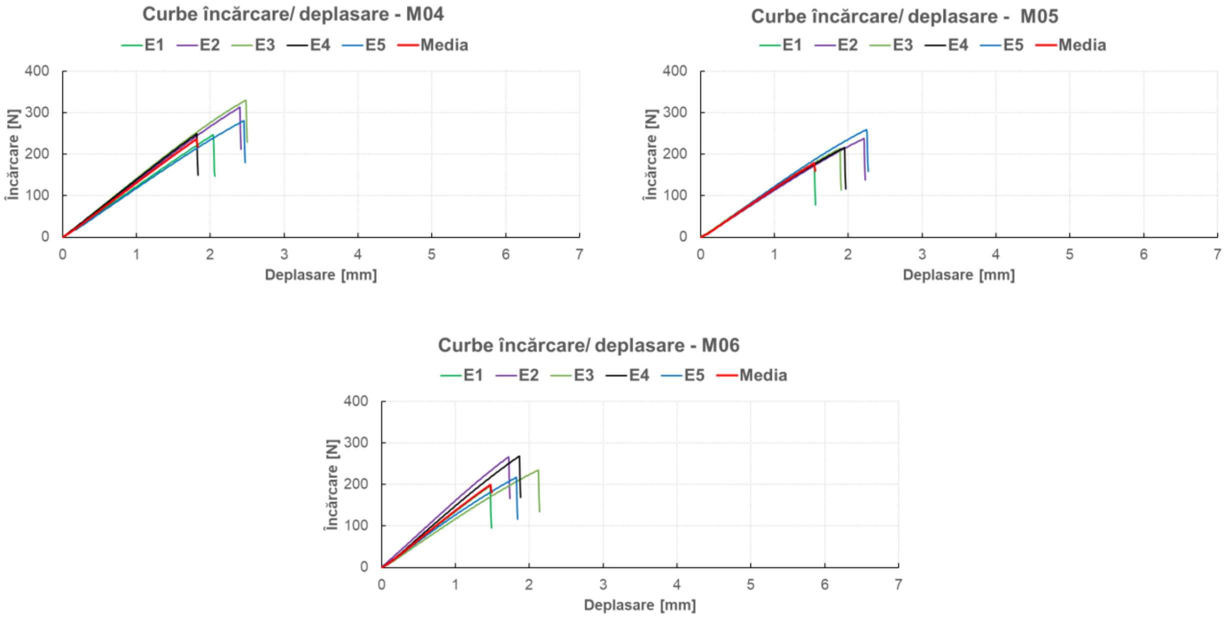

**Fig. 15.** Load/displacement curves-polymeric materials modified with red clay 5%,10%,15%

In the case of materials modified with white clay (Fig. 16), the dispersion of the data is smaller and decreases with an increase in the concentration of the modifying agent. A reduction in load may be observed at which the first rupture of a specimen occurs as the clay concentration increases. This observation is also valid for modified materials with red clay. In the case of modified materials with black clay, the load corresponding to the first rupture increases with the increase of the concentration of the modifying agent.

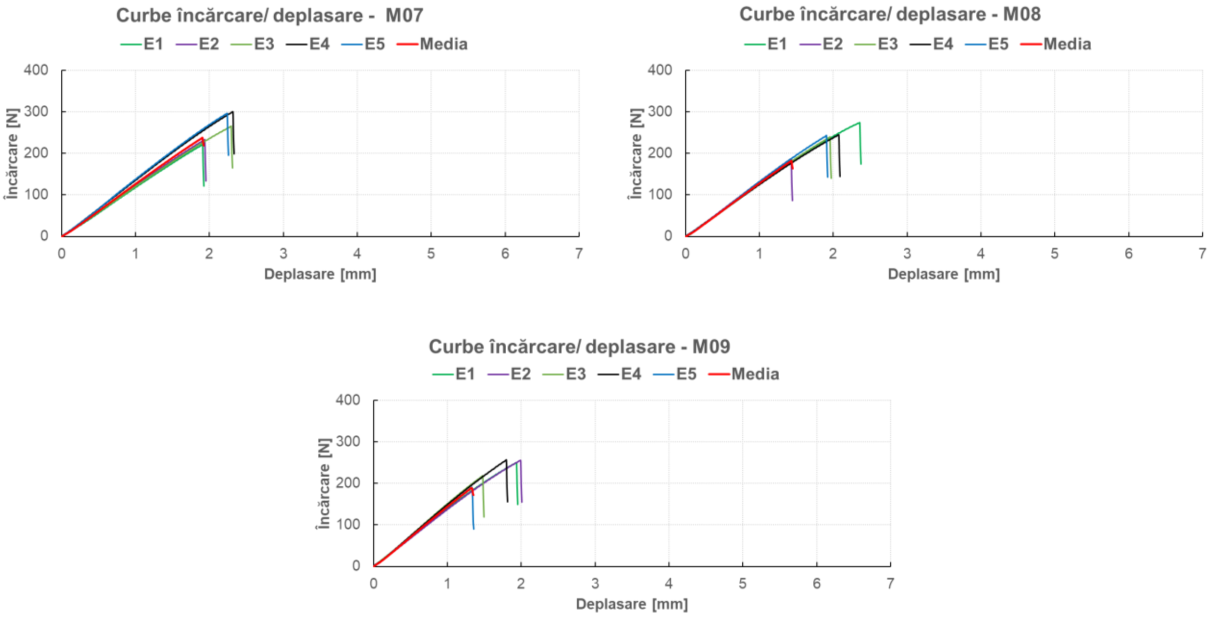

**Fig. 16.** Load/displacement curves-polymeric materials modified with white clay 5%,10%,15%

As with the tensile tests, to have an overview of the results of the three-point bending tests, an analysis of the average bending behavior for the studied materials is presented in Fig. 17. Such an analysis allows the identification of the effect of the concentration of the modifying agent in the polymer network.

A reduction in sample flexibility can be observed as the clay concentration increases, regardless of its nature, as measured by the displacement at which the first rupture occurs.

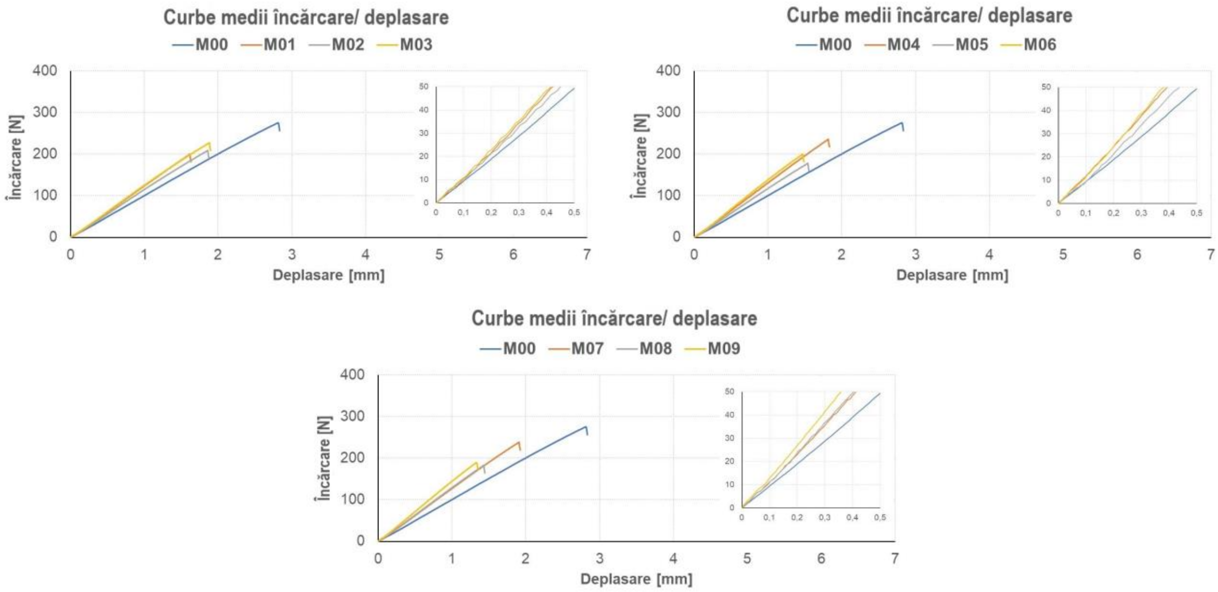

**Fig. 17.** Average load/displacement curves-polymer materials modified with clays

Table 2 shows the apparent flexural moduli of the clay-modified materials and, by comparison, the percentage increases of this parameter compared to its value for the epoxy resin.

**Table 2.** Flexural modulus of polymer materials modified with clays

| | M00 | M01 | M02 | M03 | M04 | M05 | M06 | M07 | M08 | M09 |
|---|---|---|---|---|---|---|---|---|---|---|
| **E[GPa]** | 2.77 | 3.49 | 3.22 | 3.53 | 3.63 | 3.28 | 3.30 | 3.56 | 3.58 | 4.02 |
| **E[%]** | 100 | 125.99 | 116.25 | 127.44 | 131.05 | 118.41 | 119.13 | 128.52 | 129.24 | 145.13 |

It can be seen that the highest increase in the flexural modulus is recorded for material M09 (modified with 15% white clay). A reduction in punch displacement (in effect, specimen deformation) with increasing modifier concentration signals stiffer materials.

In Fig. 18., a comparative analysis of the average behaviors of materials modified with clays is carried out. This time, the comparison criterion is the concentration of the modifying agent (clay). It can be seen that the materials modified with white clay have the best elastic responses.

Black clay-modified materials give the best average results for 10% and 15% concentrations, both in terms of load (at first break) and strain (at first break). In terms of elastic constant (mentioned above for analogy), white clay produces the best-responding materials regardless of concentration.

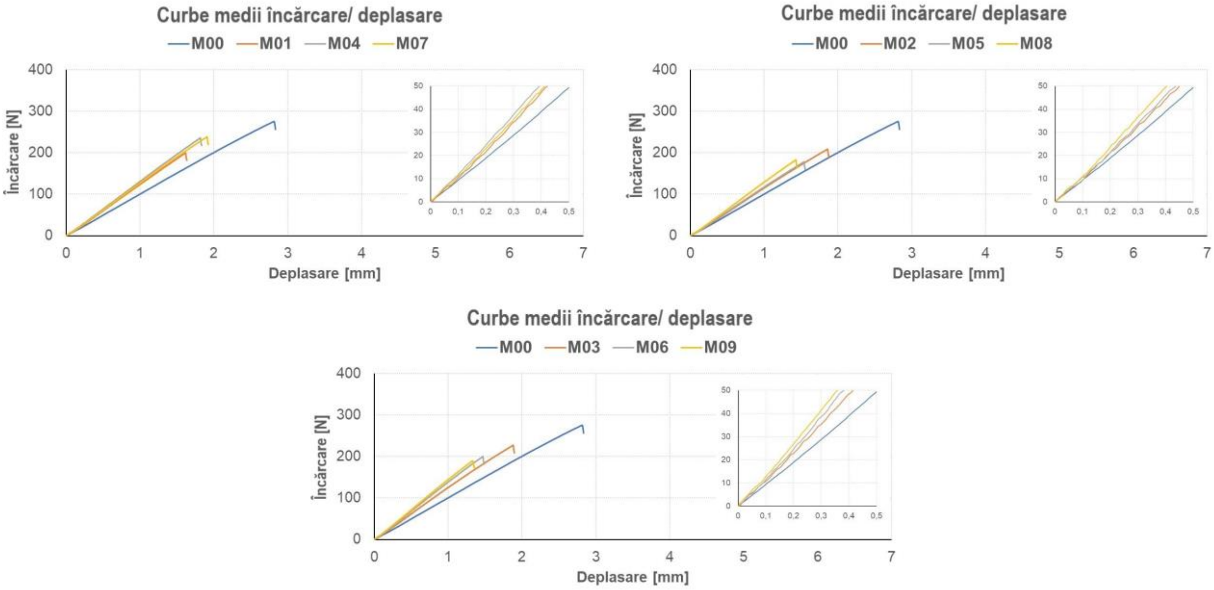

**Fig. 18.** Average load/displacement curves-polymer materials modified with clays

### 4.4.2.1. Partial conclusions – three-point bending

- as with the tensile tests, the three-point bending tests indicate an increase in the stiffness of the materials formed by modifying the epoxy resin with the three types of clays and the three clay concentrations;
- the materials are more fragile, but on the linear areas, the values of the apparent flexural modulus are higher than the value of the same modulus corresponding to the epoxy resin, as can be seen in Fig. 19.;
- in the case of bending tests, the highest values of the modulus of elasticity correspond to the highest values of the concentration of the modifying agent (clay);
- as in the case of the results obtained for the tensile tests, the values of the flexural modulus of elasticity determined automatically by the software application controlling the testing machine are higher than the values of the modulus of elasticity determined on the average curves corresponding to each tested material (with lighter blue in Fig. 19.);

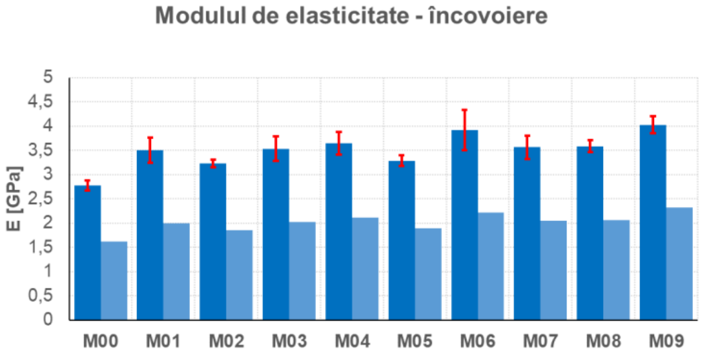

**Fig. 19.** Flexural modulus of polymer materials modified with clays

- the most important increase of this parameter (by more than 45% compared to epoxy resin) is obtained in the case of material M09 (15% mass fraction of white clay).

## 4.5. Conclusions – clay-modified materials

- the presence of clays in the polymer matrix produces morphological changes observable in the SEM micrographs made in the fracture sections of the specimens tested in three-point bending;
- these morphological changes have two main causes – the presence of inorganic phase granules of clay, which can cause oriented polymerization (semi-crystallization) with consequences of increasing material rigidity; and, on the other hand, any chemical interactions between the organic phase of any of the three clays and the prepolymeric mixture, which may lead to a better quality interface between the polymer and the modifying agent;
- mechanically – the polymer has an amorphous structure and, from this point of view, would be a homogeneous and isotropic material. The addition of modification agents is equivalent to placing a very large number of defects in that homogeneous and isotropic material, with obvious consequences for reducing its mechanical performance;
- the results obtained, both in terms of tensile and flexural tests, show that the best responses coincide with the use of the highest concentration of modifying agent (clay), i.e. 15% mass fraction, regardless of the type of clay used;
- the weakest results are obtained when using a concentration of 10% mass fraction (again, regardless of the type of clay used);
- the distribution of the modifying agent in the polymer matrix is random (even though we used the same preparation techniques of the prepolymer mixtures), which also depends on the atmospheric conditions in the laboratory (which were slightly different on the days when the castings of the materials took place), but also from the time when the pre-polymer mixture was poured into the mold (due to the fact that the viscosity of the mixture increases over time);
- these are some of the reasons why the values of the concentrations mentioned when making and testing the materials are only approximate or valid for the formed batch; moreover, we found that after each casting of a set of ten samples in the lower part of the vessel in which the pre-polymer mixture was made, significant amounts of modifying agent remained;
- a solution to this problem would have been the permanent mixing of the mixture (technically impossible), which, on the other hand, would have led to a permanent aeration of it.

## 5. Polymeric materials modified with vegetable powders

### 5.1. General observations

Lately, natural fiber-reinforced composites in the polymer matrix have found large-scale applications in civil engineering, the automotive industry, and the shipbuilding industry [58]. The use of natural fibers as reinforcement in polymer-based composites has gained increased attention due to the attractive characteristics of natural fibers, such as renewable nature, better mechanical properties, high specific surface area – compared to fibers traditionally used for polymer reinforcement, leading to a very large surface area of the interphase (polymer/fibers) and, implicitly, to increase the stiffness of the materials [59].

Fruits and vegetables are rich in micronutrients, including vitamins C and K, minerals, fiber, and phytochemicals. These products are considered perishable because they wither, gather, and decompose over time, reducing their commercial viability and consumer preference. Therefore, they have a limited shelf life, which leads to a large amount of food waste. Every year, about half of all manufactured products are discarded. Fruit and vegetable waste is abundant, consisting mainly of shells and other inedible parts of products, accounting for approximately 25 – 30% of total waste [60].

Fossil fillers are still more often replaced by natural fillers in the field of composite materials. Natural particles in the form of fruit residue powder serve to reduce costs and to optimize some mechanical characteristics in the field of composite materials [61]. Thus, systems appear that are able to compete or surpass the properties of conventionally used materials in many directions.

### 5.2. Structural analysis

The research presented below started with the idea of using vegetable powders (residues from the food industry) from some extremely popular fruits, especially due to their antioxidant properties. These fruits, with one exception, are recommended for consumption as such or for the consumption of juices produced from them (which leads to the appearance of residues) in the food industry.

As I presented in Chapter 3, I used sea buckthorn, kiwi, pomegranate, and red grapes from which the juice was cold-pressed. What remained - peel, seeds, pulp - that is, the residues were subjected to lyophilization. I want to thank, once again, Prof. Dr. Eng. Nicoleta Stănciuc for the support given at this stage of the research.

The way to nanostructure the polymers used at CCDCOMT was to disperse some powders in the pre-polymer mixture (the mixture between the resin and the hardener). The studies carried out over the years [62], [63], [64], have shown that, due to the viscosity of the pre-polymer mixture, most of the nanometric agents form large aggregates in the solid polymer network.

In Fig. 20., SEM micrographs (at the same magnifications) of epoxy resin and epoxy resin modified with sea buckthorn powder are shown. The morphological changes are obvious if we analyze the images on the left: the presence of gas intrusions (in smaller numbers than in the case of the samples modified with clays and presented in the previous Chapter) and the strong fragmentation of the polymer.

In Fig. 21., we performed a comparative SEM analysis between epoxy resin, buckthorn-modified epoxy resin, and starch-buckthorn-modified epoxy resin. Morphological differences are evident for M11 compared to the other two. A better uniformity of the matrix is found, although the number of gaseous intrusions is apparently higher.

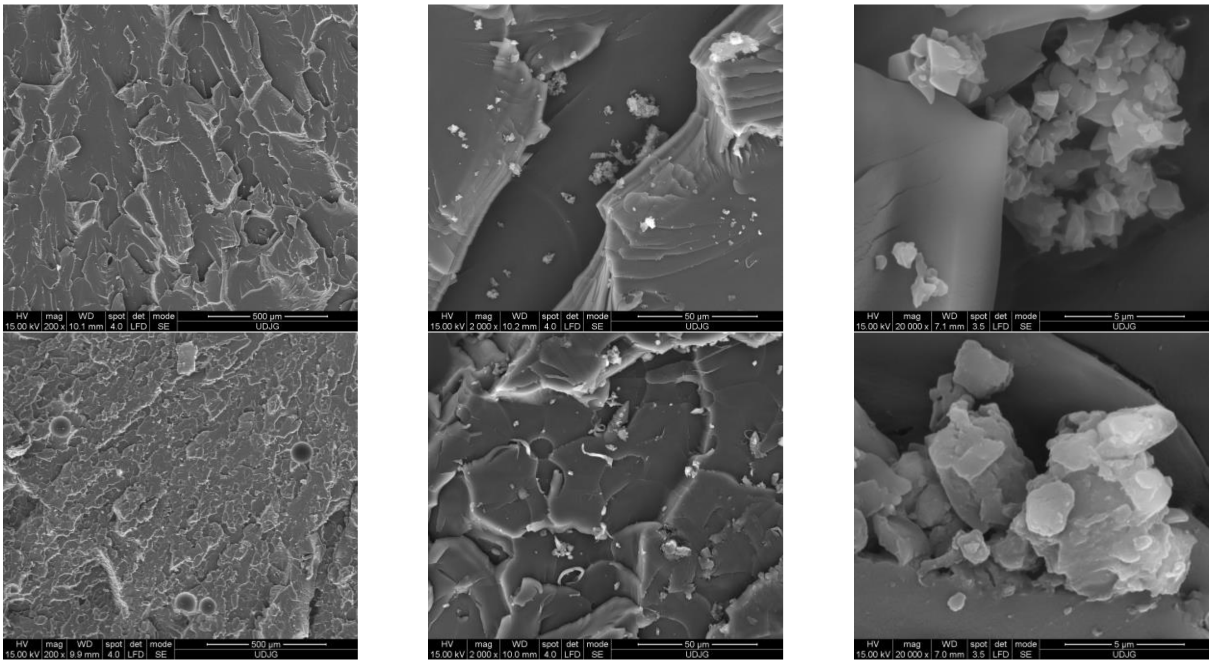

**Fig. 20.** Structural analysis of materials M00, M10

When forming the samples, I found that the precipitation of the plant powder aggregates was quite fast and, for this reason, I chose to increase the viscosity of the pre-polymer mixture using starch (a technique described by V. Bria in his PhD thesis) [330].

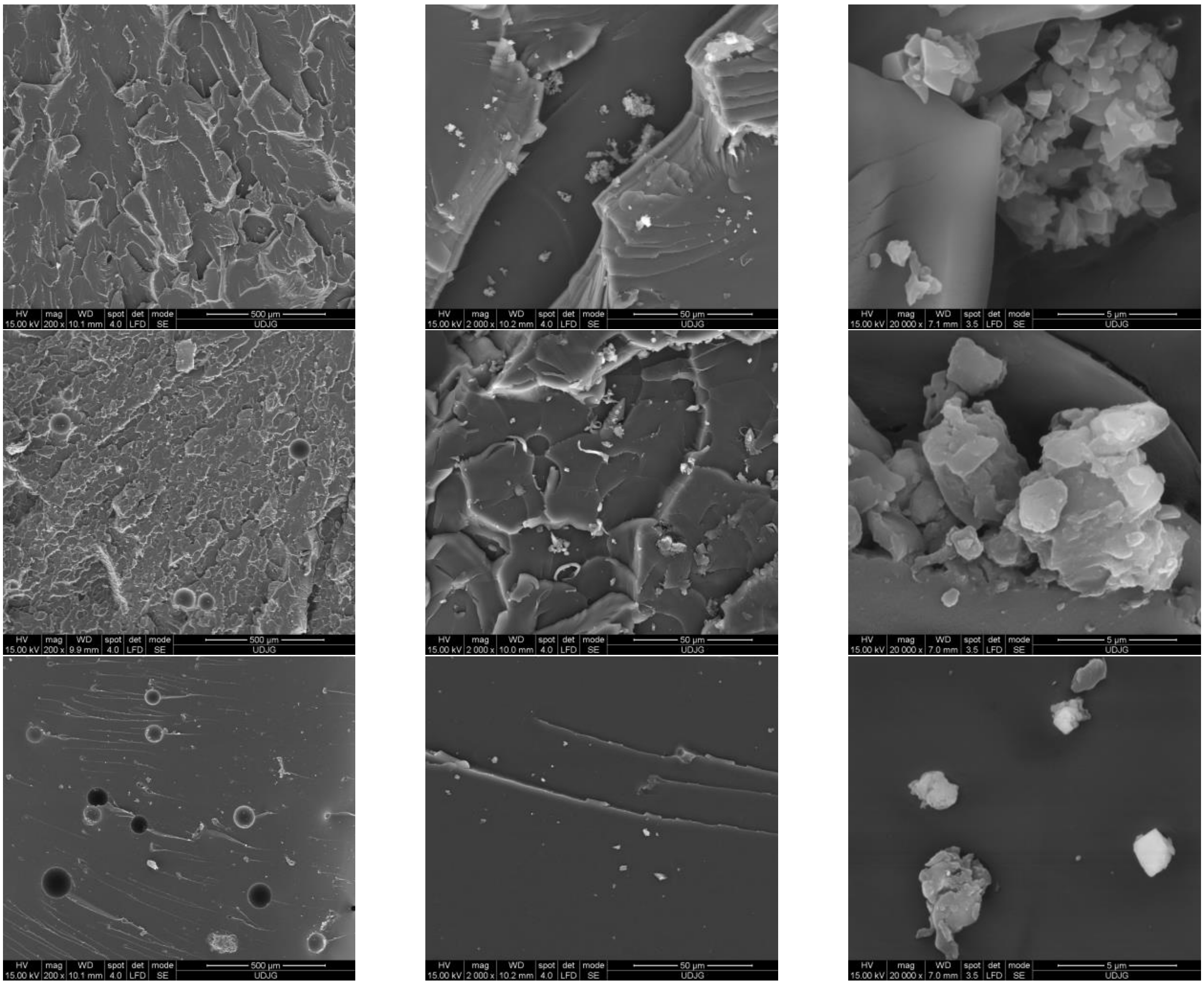

**Fig. 21.** Structural analysis of materials M00, M10, M11

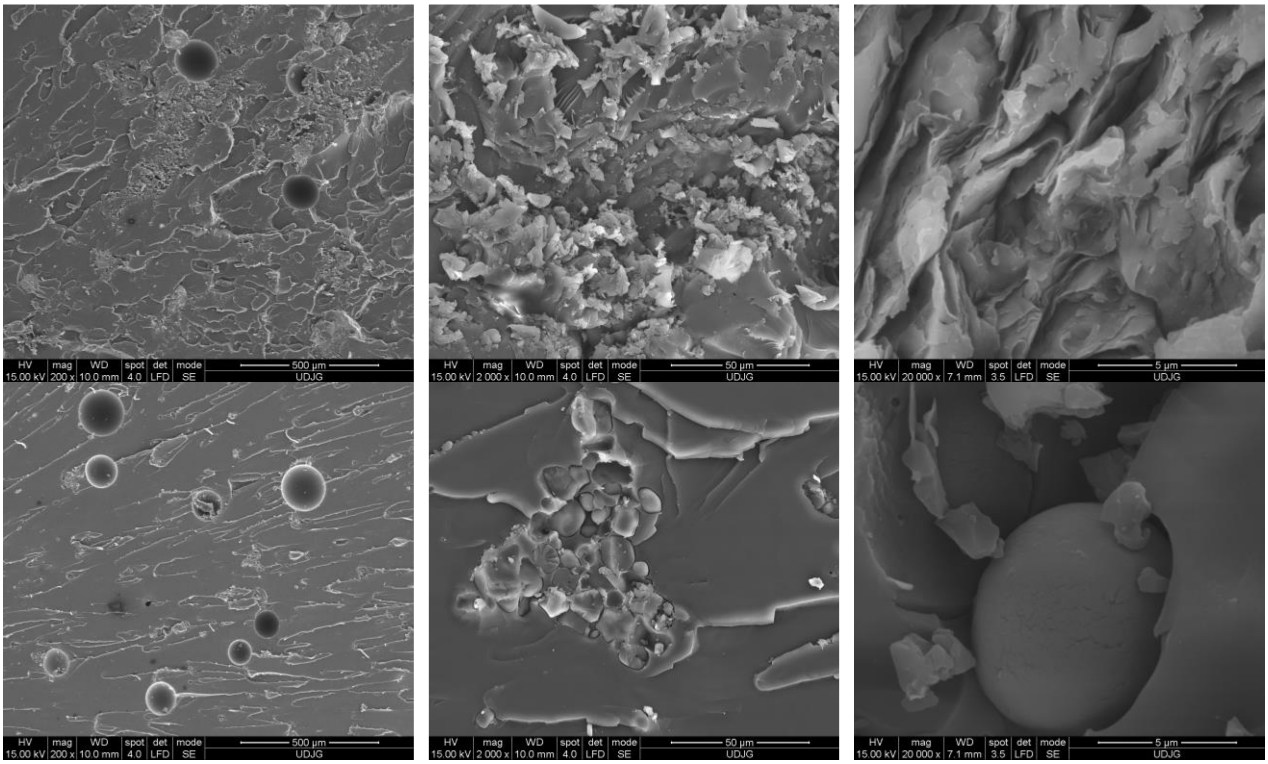

**Fig. 22**. Structural analysis of materials M01, M12

The next class of materials is that of materials modified with kiwi powder, and in Fig. 23., the comparative SEM analysis between epoxy resin and epoxy resin modified with kiwi powder is presented. We can talk, this time, of a reduction in the fragmentation of the epoxy resin but also of the presence of agglomerations of the components of the freeze-dried kiwi powder.

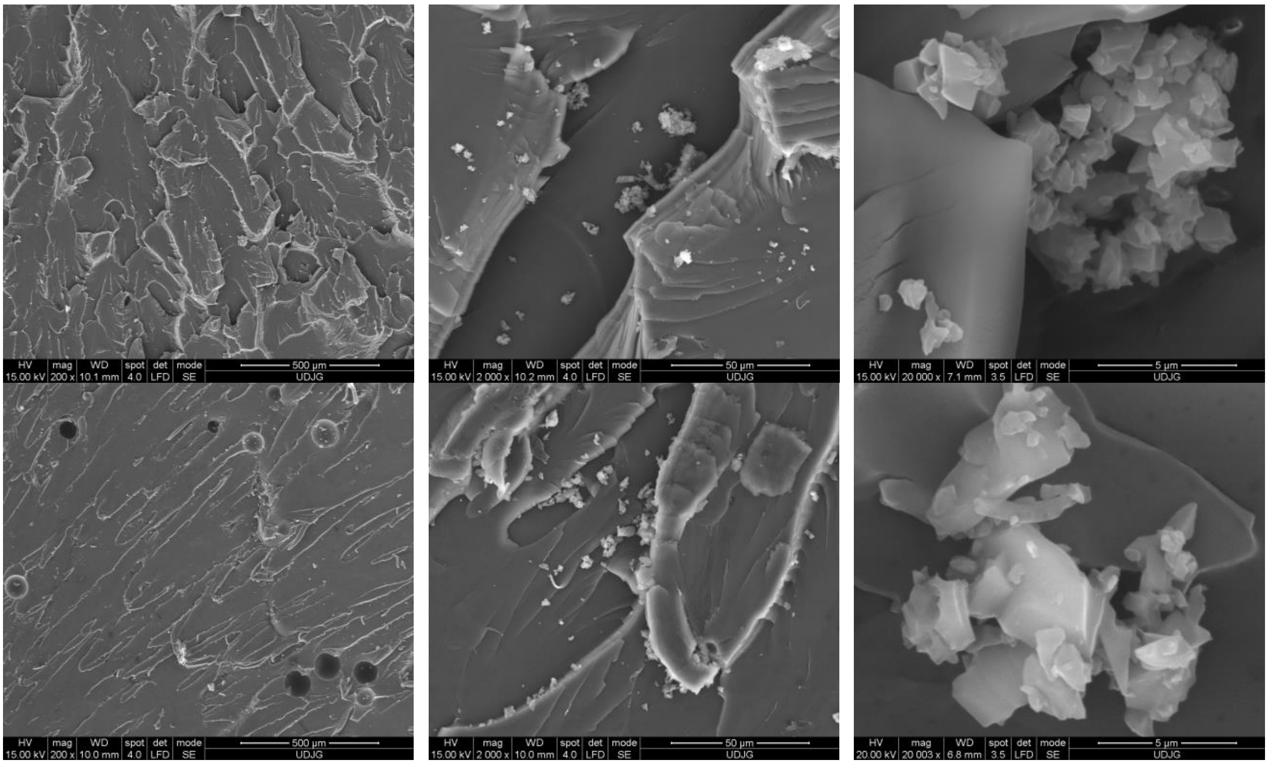

**Fig. 23.** Structural analysis of materials M00, M13

### *Polymeric materials modified with vegetable powders*

In the case of the material made with kiwi powder and starch (the decision to add starch was previously presented) – Fig. 24., it can be seen that the addition of starch reduces the size of the agglomerations of plant residues with an increase in the fragmentation of the epoxy resin structure compared to the M13 material (modified with kiwi powder).

As in the case of sea buckthorn, an analysis of the phytochemical agents content of the kiwi powder was carried out and the results are shown in Table 3., where DM stands for Dry Matter.

**Table 3.** Phytochemical agent content of freeze-dried kiwifruit powder

| | |
|---|---|
| Total flavonoids, mg catechin equivalents/g DM lyophilized powder | 0.64±0.02 |
| Total polyphenols, mg gallic acid equivalents/g DM lyophilized powder | 7.37±0.17 |
| Total chlorophylls, µg/g DM lyophilized powder | 186.31±6.16 |
| Total carotenoids, mg/g DM lyophilized powder | 510.59±21.20 |
| Antioxidant activity, mMol Trolox/g DM lyophilized powder | 2.67±0.01 |

As with the materials modified with lyophilized sea buckthorn powder, a third material was made by adding two grams of black clay to the M14 material recipe. The obtained material, M15, is compared (in Fig. 25.) with the material modified with 5% black clay (M01). It is possible to identify some morphological changes (in the analyzed images), especially at intermediate magnification (central column), from montmorillonite sheets (M01) to organic formations specific to kiwi powder (M15).

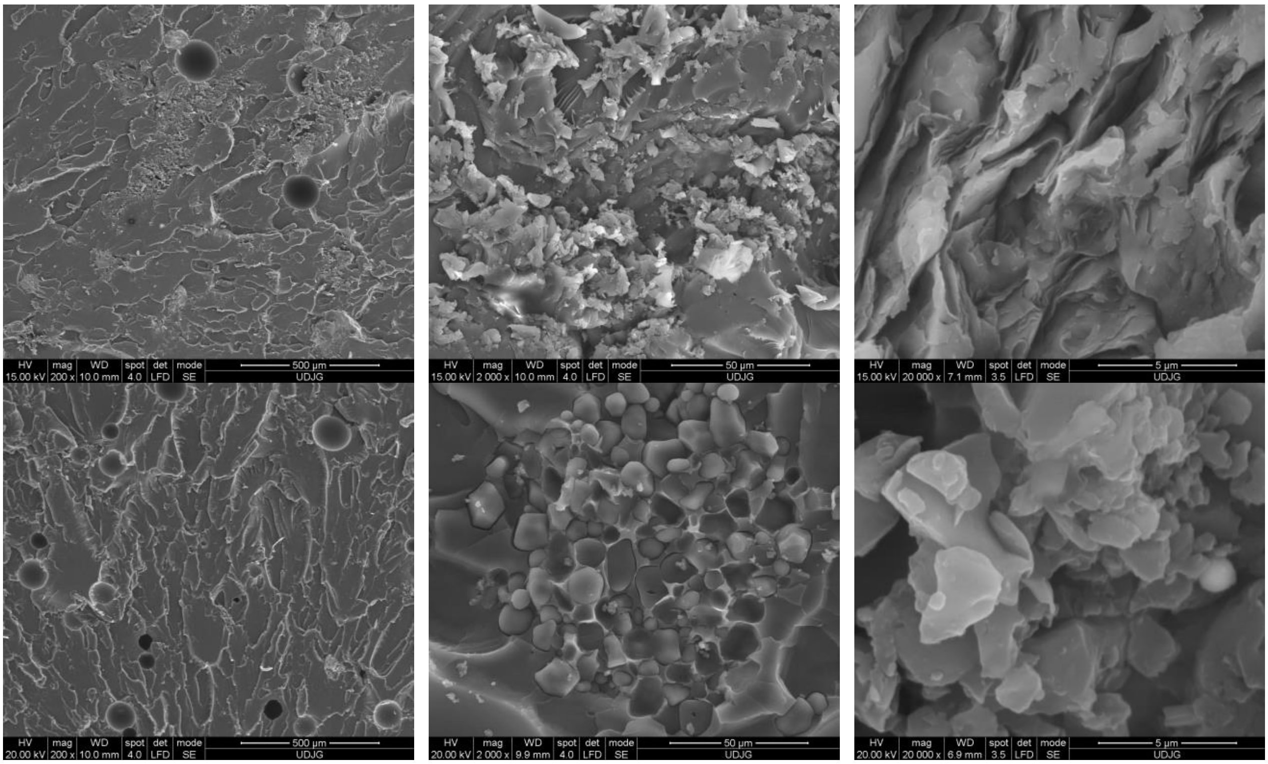

**Fig. 24.** Structural analysis of materials M01, M15

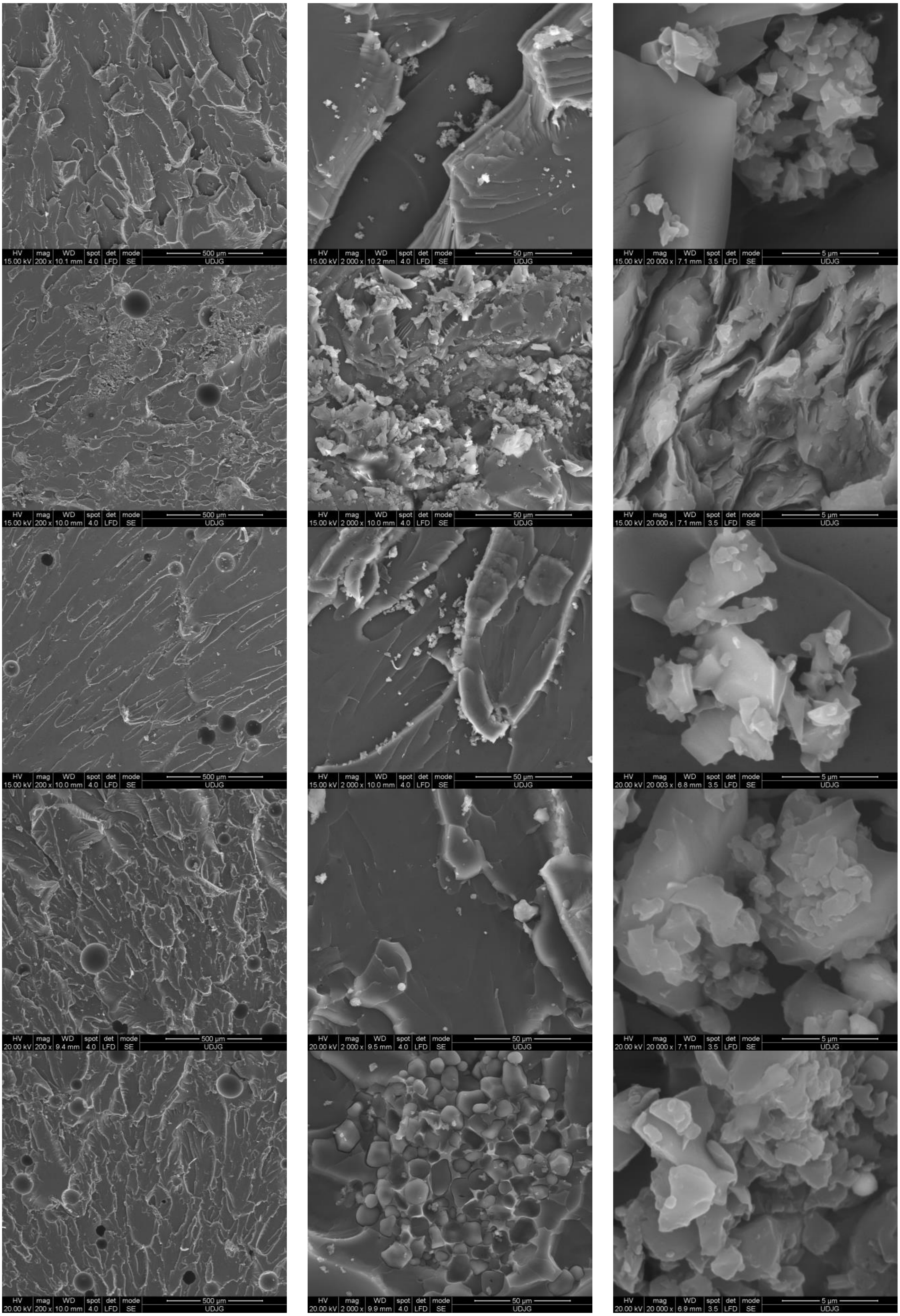

**Fig. 25.** Structural analysis of materials M00, M01, M13, M14, M15

In Fig. 26., the comparative structural analysis of material modified with lyophilized pomegranate powder in relation to epoxy resin is presented. Greater fragmentation of the matrix can be observed in the case of the M16 material, which means a reduction in the number of chemical bonds specific to the polymer.

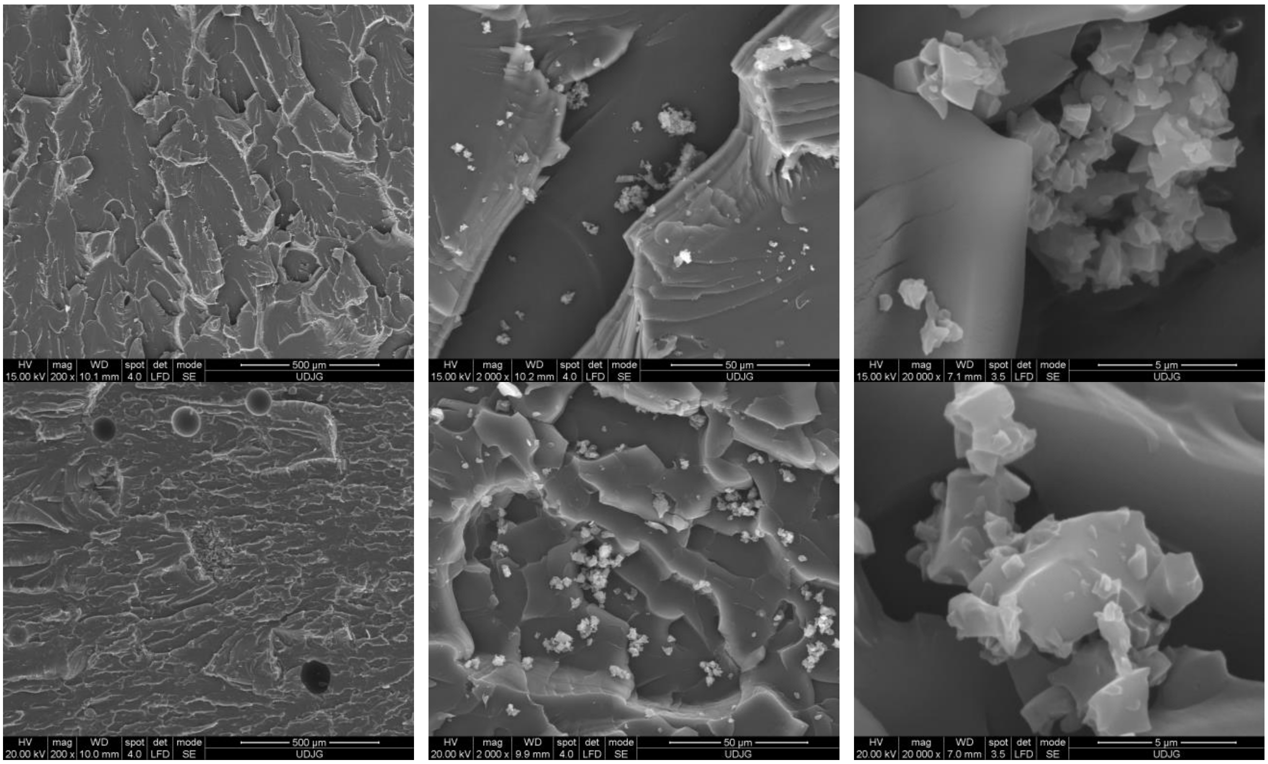

**Fig. 26.** Structural analysis of materials M00, M16

Table 4 shows the content of phytochemical agents in the lyophilized pomegranate powder. The fluidization of the pre-polymeric mixture must be a consequence of the existence of these agents (analyzed in the liquid extract with a solvent) or the presence of agents that cannot be separated and exist in the organic substance (remnants of cell walls, seed oils). When handling the powders, kiwi powder had the oiliest appearance, but no increases in the fluidity of the mixture were observed for the previously analyzed materials.

**Table 4.** Phytochemical agent content of freeze-dried pomegranate powder

| | |
|---|---|
| Total monomeric anthocyanins, mg cyanidin glucoside equivalents/g DM lyophilized powder | 0.07±0.008 |
| Total flavonoids, mg catechin equivalents/g DM lyophilized powder | 0.62±0.09 |
| Total polyphenols, mg gallic acid equivalents/g DM lyophilized powder | 41.61±1.92 |
| Antioxidant activity, mMol Trolox/g DM lyophilized powder | 24.30±0.12 |

In the material modified with pomegranate powder and starch (M17) – Fig. 27. – you can see the organic structures in the pomegranate powder, but you can also see that the matrix is more fragmented. During forming, we found that the addition of starch led to a reduction in fluidity and, therefore, a reduction in material loss. Unlike the freeze-dried kiwi powder, in this case, the amount of precipitate was less.

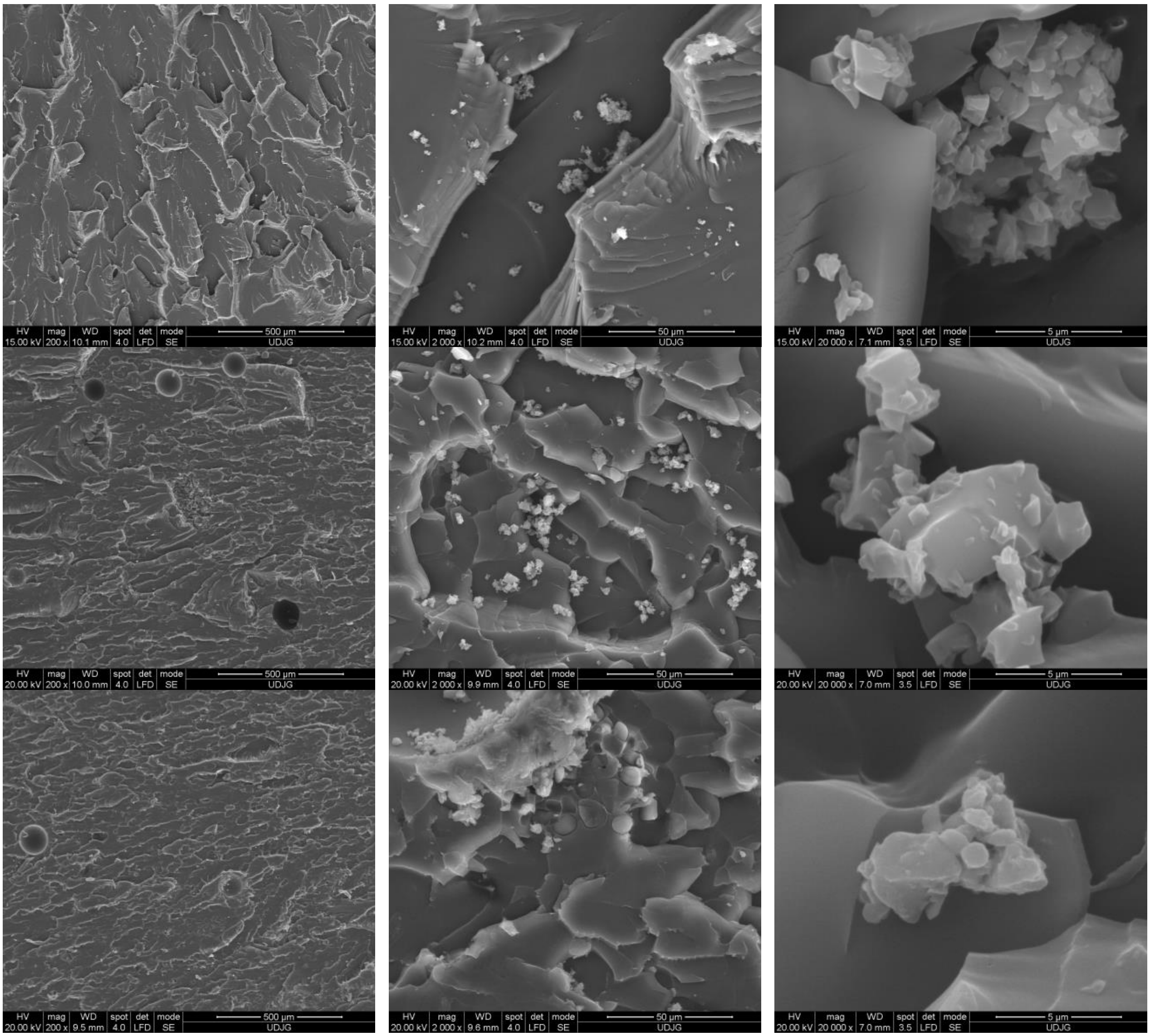

**Fig. 27.** Structural analysis of materials M00, M16, M17

For the M18 material, pomegranate powder, starch, and black clay were added to the pre-polymer mixture, and it would have been expected that the flowability of the mixture would be further reduced. During casting, however, we noticed that, in fact, the addition of clay led to an increase in fluidity compared to the M16 material (modified with freeze-dried pomegranate powder and starch), and, as a consequence, material losses increased, especially for samples in the form of plates.

In Fig. 28. the comparative structural analysis between material M01 (modified with 5% black clay) and material M18 (modified with lyophilized pomegranate powder, starch and black clay) is presented.

As the agglomerations of montmorillonite sheets are no longer observable in the M18 material, it could be said that in pomegranate powder there are components that produce their separation, as described in Chapter 3 (materials used). This separation can lead to a better dispersion of clay in the polymeric matrix, which has effects on the mechanical properties of the composite.

Unlike the M01 material, several gaseous intrusions (addition of three powders to the pre-polymeric mixture also means the addition of a larger amount of air). Earlier we talked about the high fluidity of the pre-polymeric mixture of the M16 material. It can be seen that in the case of M16 there are fewer gas intrusions, but their number is even lower in the case of M17.

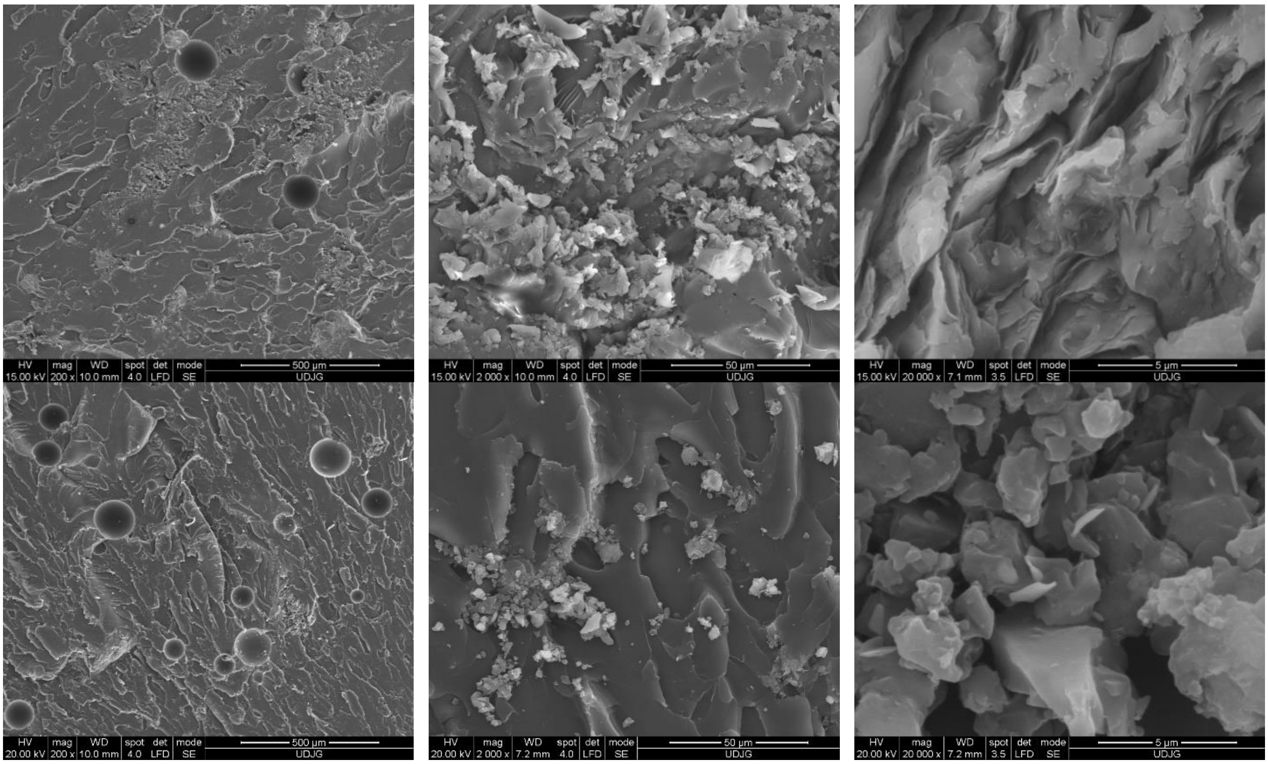

**Fig. 28.** Structural analysis of materials M01, M18

In the Fig. 29. a complete comparative analysis of modified materials with lyophilized pomegranate powder is presented, in order to facilitate the observation of the structural differences induced by each component added to the polymer.

Due to the fact that pomegranate powder is the material with the most uses, it is expected that the materials obtained with this type of modifying agent will be valuable materials. We talked about increasing the fluidity of the liquid mixture; if we put aside the disadvantage of material losses, we must see a possible advantage even further. High fluidity and fluid penetration into very small spaces can lead to a more intimate connection between the polymer matrix and the aggregates specific to each modifying agent used.

This means obtaining a good-quality interface that allows efficient transmission of efforts between the matrix and the constituents of the modifying agents and, consequently, materials with better mechanical properties.

However, the purpose of making and characterizing these materials is to observe the changes induced by them from the perspective of obtaining materials with nanometric phases.

By alphabetical criterion, the last agent to modify epoxy resin is lyophilized grape powder. Overcoming the biological benefits of the fermented product from black grape juice, it is known that oil extracted from grape seeds is increasingly entering gastronomy. Thus, the residues of the winemaking industry have become an important source of raw materials for other industries.

And grape extracts, as we showed in Chapter 2, have found various applications in obtaining nanostructures, so it seems interesting to try lyophilized grape powder to avoid agglomeration of nanostructures when nanostructuring of the polymer is done by dispersing some nanometric powders.

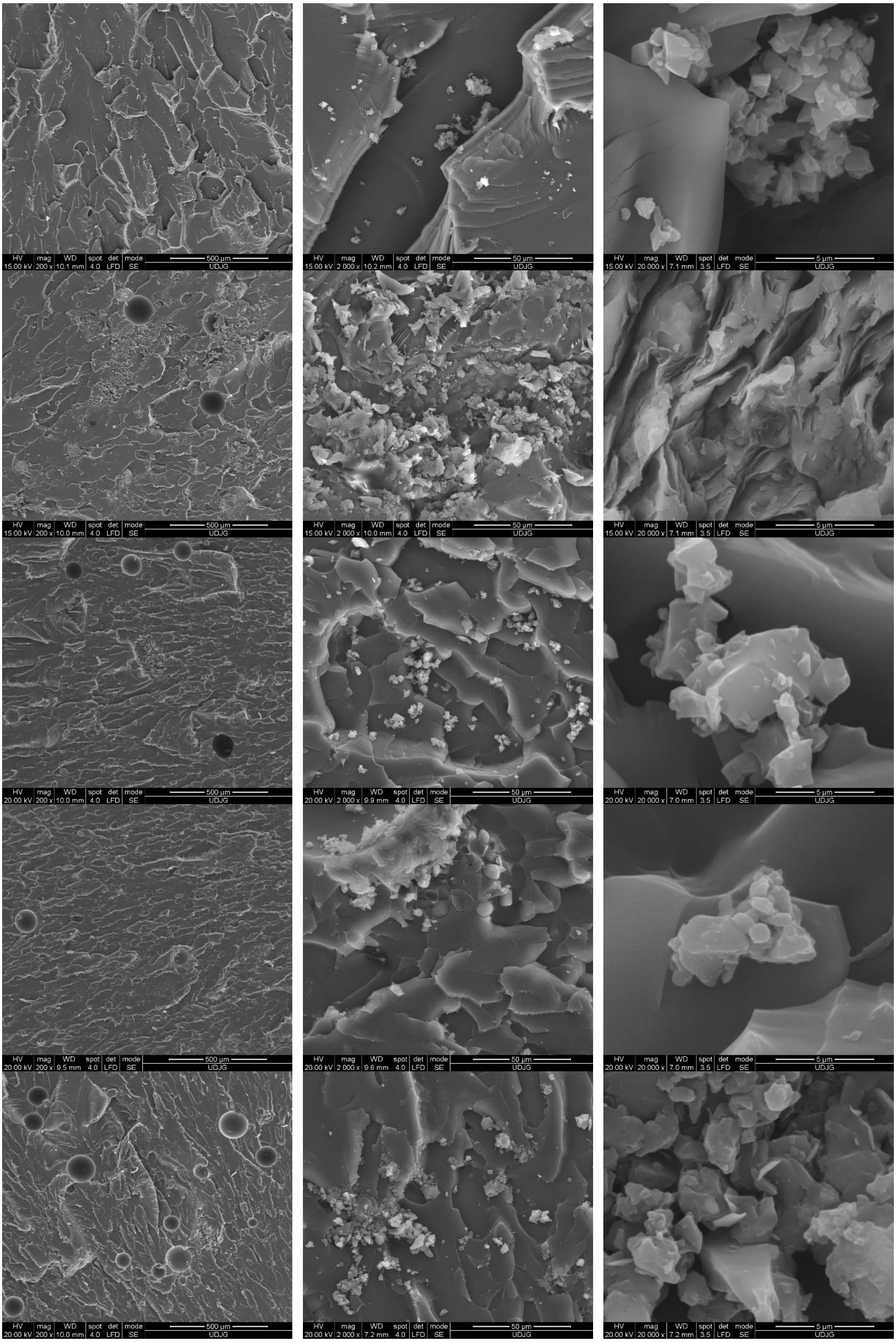

**Fig. 29.** Structural analysis of materials M00, M01, M16, M17, M18

**Table 5.** Phytochemical agent content of freeze-dried grape powder

| | |
|---|---|
| Total monomeric anthocyanins, mg cyanidin glucoside equivalent/g DM lyophilized powder | 327.85±3.50 |
| Total flavonoids, mg catechin equivalent/g DM lyophilized powder | 136.79±2.49 |
| Total polyphenols, mg gallic acid equivalent/g DM lyophilized powder | 345.45±11.29 |
| Antioxidant activity, mMol Trolox/g DM lyophilized powder | 58.95±4.12 |

An analysis of the data presented in Table 5. reveals that the grape powder contains the highest amounts (among the analyzed powders) of flavonoids and polyphenols, i.e., substances likely to chemically interact with the two liquid chemical formulations that constitute the epoxy system used in the study.

In Fig. 30. the comparative structural study of the above two materials and the material that is additionally modified with starch – M20 is carried out.

The addition of starch seems to lead to a return to the aspect of epoxy resin fragmentation, although in this case the islands have more complex edges than the edges of the islands in the case of M20 material. I have often used two terms in the description of the results: fragmentation and islands. The first term was adopted in opposition to the absolutely smooth image of a surface and is justified by the fact that this fragmentation occurs after the rupture of a specimen. For many of the images presented on the left columns, the direction of load can be identified, which coincides with the predominant direction of the dominant dimensions of the islands.

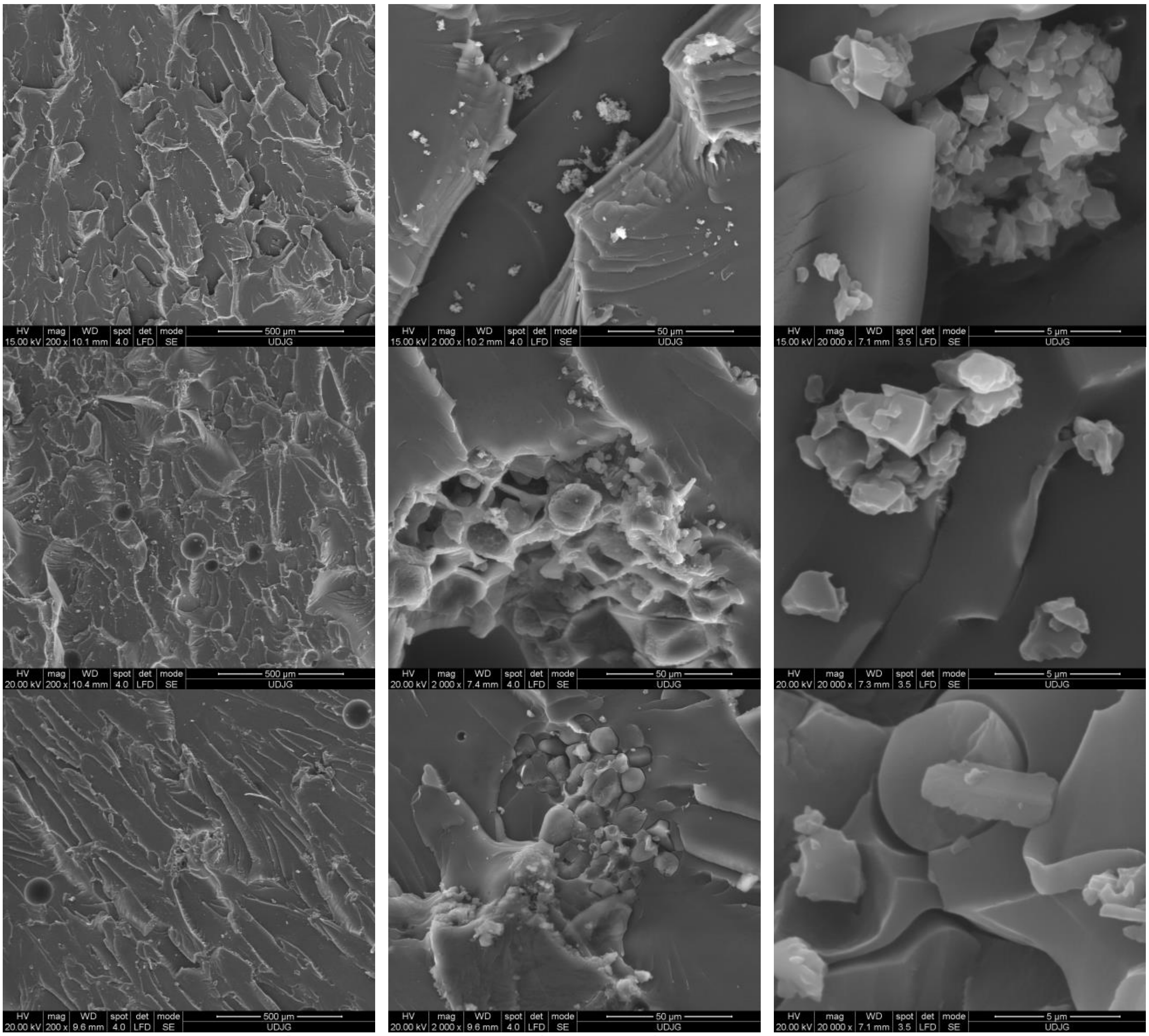

**Fig. 30.** Structural analysis of materials M00, M19, M20

In the Fig. 31. – as for the other materials analyzed, the complete picture of the structural analyses for the modified materials with lyophilized grape powder is presented to provide an overview of the changes induced by each component added to the polymer matrix.

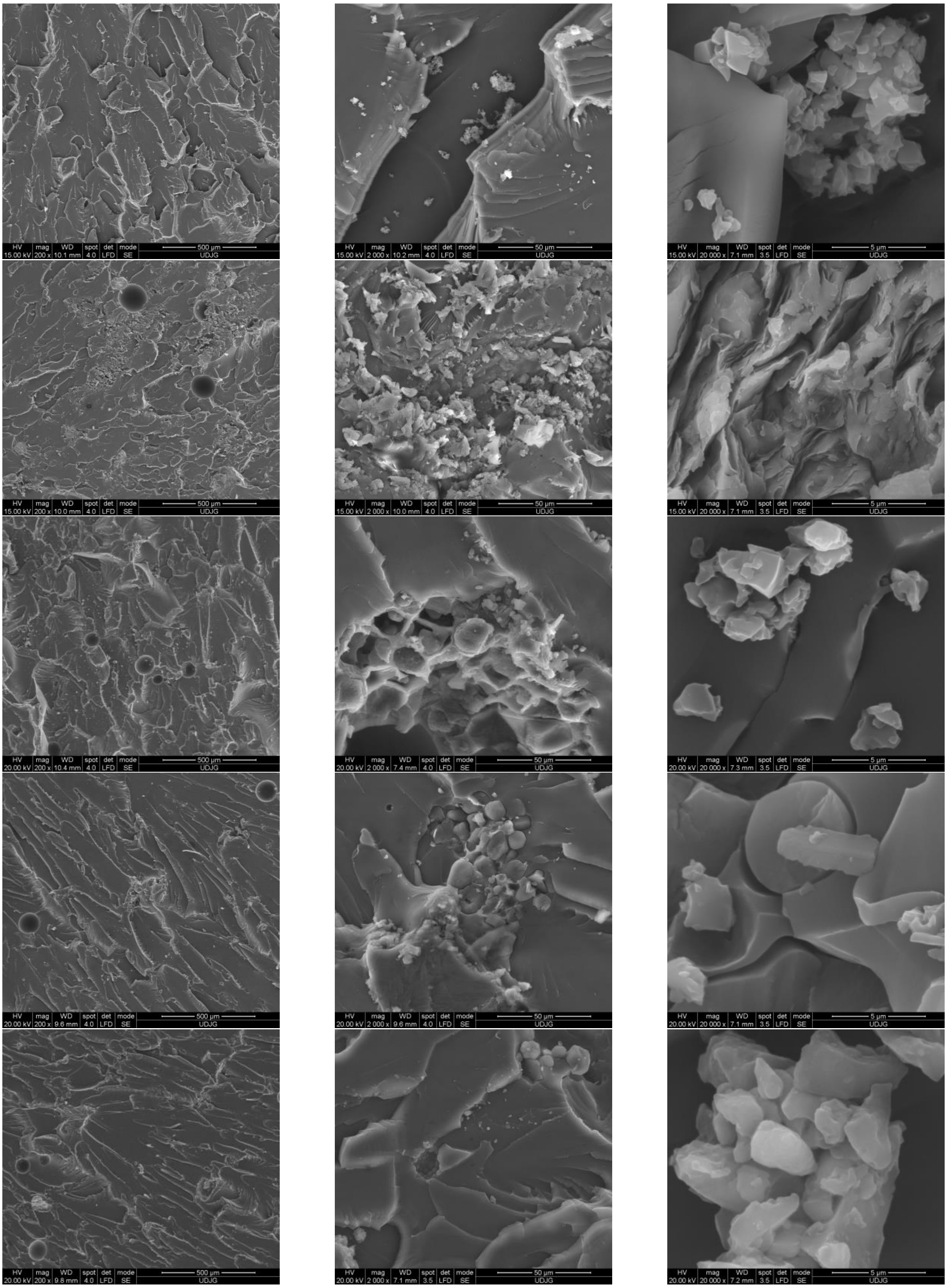

**Fig. 31.** Structural analysis of materials M00, M01, M19, M20, M21

### 5.2.1. Partial conclusions – morphological analysis of materials modified with vegetable powders

- the presence of phytochemical agents in lyophilized catina powders, kiwi, pomegranate, and grapes induces significant morphological changes of the polymeric matrix analyzed by means of electronic microscopy (SEM) on the surface resulting from the bending rupture of a sample of each material analyzed;
- although not sufficient for a complete analysis, this partial analysis provides some information on the induced changes (mostly resulting from interaction with the epoxy matrix and the inorganic clay phase);
- during my master's studies, also under the coordination of Mr. Adrian Cîrciumaru, we analyzed the properties of the same epoxy resin modified with gelatin and, respectively, gluten – the use of these agents did not lead to spectacular results and, therefore, I preferred to use the starch based on the research mentioned above [62];
- depending on the type of powder used, differences can be found between the morphologies of the surfaces resulting from fracturing, but as I have shown before, when choosing the surfaces for the microscopic analysis, the criterion was closeness to the flatness of the surface and, unfortunately, I cannot see the connection between the sample analyzed by SEM and the results obtained for the respective sample in the three-point bending test;
- freeze-dried plant powders were used because they have the ability (proven in other studies) to isolate nanostructures from other materials so that, when dispersed in the polymer, they no longer produce agglomerations.

## 5.3. Analysis of the mechanical properties of polymeric materials modified with vegetable powders

### 5.3.1. Tensile tests

For the materials described in subsection 5.2., the analysis of the mechanical properties is aimed at detecting the changes induced by the use of modifying agents by measuring the modulus of elasticity when stretched (tensile tests). Using the Instron testing machine from CCDCOMT on cylindrical specimens with a length of 200mm (engagement zone length of 100mm) and a diameter of 8mm, we obtained the stress/strain (or stress/strain σ/ε) curves, which were subsequently analyzed.

As we showed in Chapter 3, we followed a certain mixing regime, the same for each cast material. From this perspective, I tried to remove the variability of the mechanical properties of the samples due to the variability of the experimental conditions.

For all traction tests performed (ten specimens of each material), the ten specimens were chosen (for all materials) according to the data presented in Table 6. This sample management allows the identification of differences between the results obtained for specimens cast at different times. Of course, this system cannot take into account other existing defects – gaseous intrusions, small deviations from the cylindrical shape, etc.

**Table 6.** Numbering of the tensile tested specimens according to the moment of casting

| E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 4 | 5 | 7 | 9 | 11 | 12 | 14 | 15 |

In Fig. 32., individual stress/strain curves are shown for all materials modified with freeze-dried sea buckthorn powder (M10, M11, M12). As can be easily seen, there is a small dispersion of the experimental data on the elastic domains of the materials and a significant dispersion of the moments of failure.

Small deviations from the elastic range are given by the distribution of defects along the direction of employment (direction of cylinder height), while the dispersion of the moments of the rupture is given by the concentration of the defects in a transverse section of the cylinder (the one in which the rupture) takes place. The addition of starch to the material reduces the dispersion of the moments of rupture, while the addition of black clay increases the dispersion of the moments of tears (reported in the modified material with sea buckthorn powder and starch).

Table 7. presents some numerical data that shows that, in general, specimens formed towards the end of casting have better answers than those formed at the beginning of casting.

**Table 7.** Stresses [MPa] and strains [mm/mm] of the best response specimens (buckthorn)

| **material** | **M10** | | | **M11** | | | **M12** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E3 (4) | E5 (7) | E6 (9) | E2 (2) | E6 (9) | E7 (11) | E3 (4) | E9 (14) | E10 (15) |
| σ | 60 | 67 | 67 | 45 | 50 | 45 | 43 | 41 | 41 |
| ε | 0.045 | 0.057 | 0.07 | 0.034 | 0.035 | 0.033 | 0.029 | 0.031 | 0.029 |

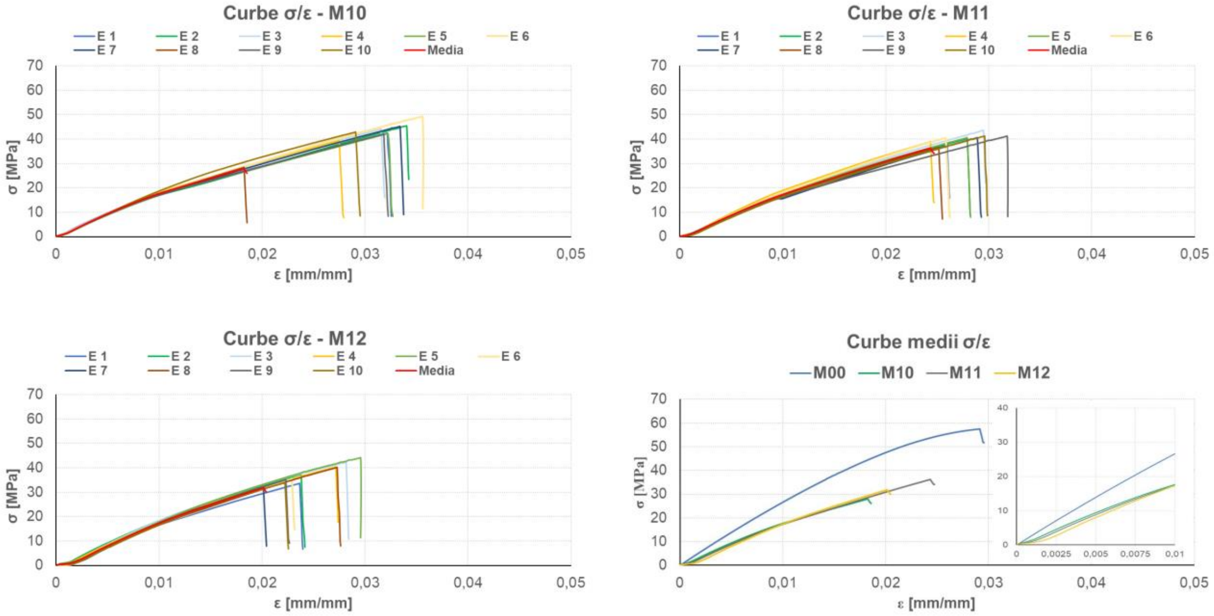

**Fig. 32.** σ/ε curves-polymeric materials modified with sea buckthorn powder

In the last graph in Fig. 32., the average curves of the modified materials with lyophilized sea buckthorn powder and the average curve of the epoxy resin are presented. It is obvious that all the materials mentioned have lower more elastic responses than epoxy resin. In the detail for small deformations, a certain deviation from the linearity of the analyzed materials can also be observed (the answer is not purely elastic), which means a weakening of the polymeric bonds.

In Table 8, the values of the maximum stresses and deformations of the samples with the best response for each analyzed material are shown. Contrary to the case of materials modified with sea buckthorn powder, in the case of materials modified with kiwi powder, the specimens formed in the first part of the casting seem to have better behaviors. In addition, the maximum voltages recorded for material modified with lyophilized catina powder are greater than their counterparts for modified material with lyophilized kiwi powder. With the addition of starch and black clay, respectively, the values of the maximum stresses are comparable.

**Table 8.** Stresses [MPa] and strains [mm/mm] of the best response specimens (kiwi)

| **material** | **M13** | | | **M14** | | | **M15** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E3 (4) | E5 (7) | E7 (11) | E3 (4) | E6 (9) | E7 (11) | E1 (1) | E2 (2) | E8 (12) |
| σ | 45 | 43 | 42 | 45 | 46 | 45 | 40 | 45 | 45 |
| ε | 0.03 | 0.03 | 0.033 | 0.032 | 0.033 | 0.031 | 0.03 | 0.034 | 0.035 |

In Fig. 33., the individual σ/ε curves of the tensile-tested specimens of materials M14, M15, and M16 (modified with freeze-dried kiwi powder, starch, and black clay) are exhibited. The different profiles (compared to materials modified with lyophilized sea buckthorn powder) of the curves and, consequently, the average curve profiles of the three materials can be observed.

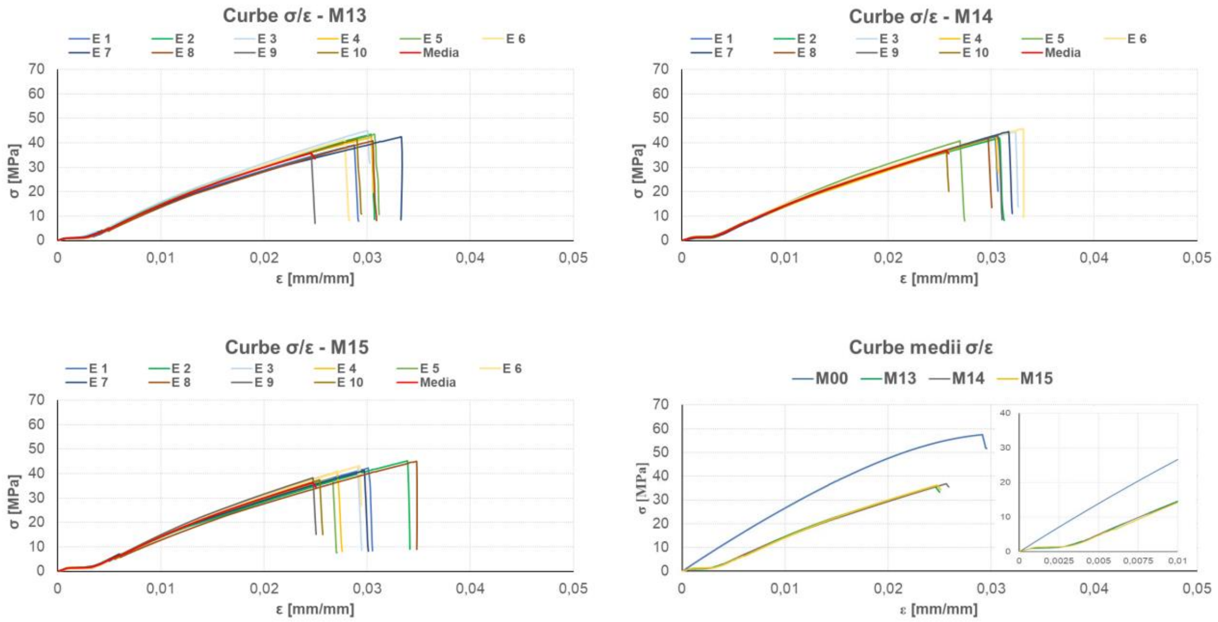

**Fig. 33.** σ/ε curves-polymeric materials modified with kiwi powder

In Table 9, the best responses of materials modified with lyophilized pomegranate powder are analyzed in the same way. The results, both in terms of maximum stresses and maximum strain, are comparable to those obtained for materials modified with kiwi powder. In this case, however, for clay-free materials, it appears that better results are obtained for specimens formed in the first part of the casting.

In the graphs presented in Fig. 34. – the individual σ/ε curves for the tensile-tested specimens of the materials modified with pomegranate powder (M16, M17, and M18) show the existence of response levels similar to those described for the materials modified with kiwi powder. For the material modified only with pomegranate powder it is easy to see that the dispersion of the data is the largest of those analyzed so far – both in terms of curve profiles and in terms of breaking moments.

Again, it is noteworthy that the addition of starch leads to materials whose behavior is more stable.

**Table 9.** Stresses [MPa] and strains [mm/mm] of the specimens with the best response (pomegranate)

| **material** | **M16** | | | **M17** | | | **M18** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E1 (1) | E2 (2) | E4 (5) | E3 (4) | E4 (5) | E10 (15) | E4 (5) | E7 (11) | E10 (15) |
| σ | 45 | 46 | 45 | 41 | 45 | 44 | 47 | 50 | 48 |
| ε | 0.033 | 0.033 | 0.031 | 0.03 | 0.033 | 0.03 | 0.035 | 0.036 | 0.033 |

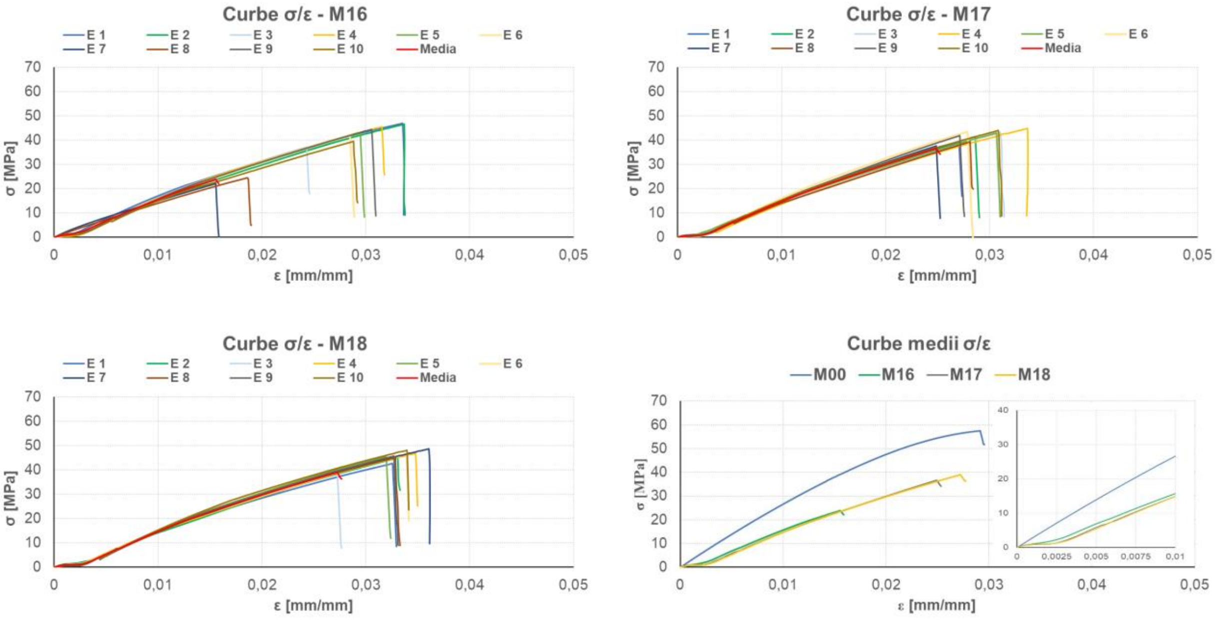

**Fig. 34.** σ/ε curves-polymeric materials modified with pomegranate powder

Table 10. shows the best tensile results for each of the modified materials with lyophilized grape powder. In this case, as can be easily seen, the specimens with good answers are those formed in the second part of the casting.

**Table 10.** Stresses [MPa] and strains [mm/mm] of the best response specimens (grape)

| **material** | **M19** | | | **M20** | | | **M21** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E8 (12) | E9 (14) | E10 (15) | E2 (2) | E9 (14) | E10 (15) | E6 (9) | E8 (12) | E10(15) |
| σ | 50 | 46 | 48 | 48 | 46 | 50 | 50 | 52 | 53 |
| ε | 0.034 | 0.032 | 0.034 | 0.034 | 0.033 | 0.035 | 0.035 | 0.036 | 0.037 |

Fig. 35., includes individual graphic representations of modified materials with grape powder, and, as in the case of modified materials with pomegranate powder, a dispersion of experimental data can be found.

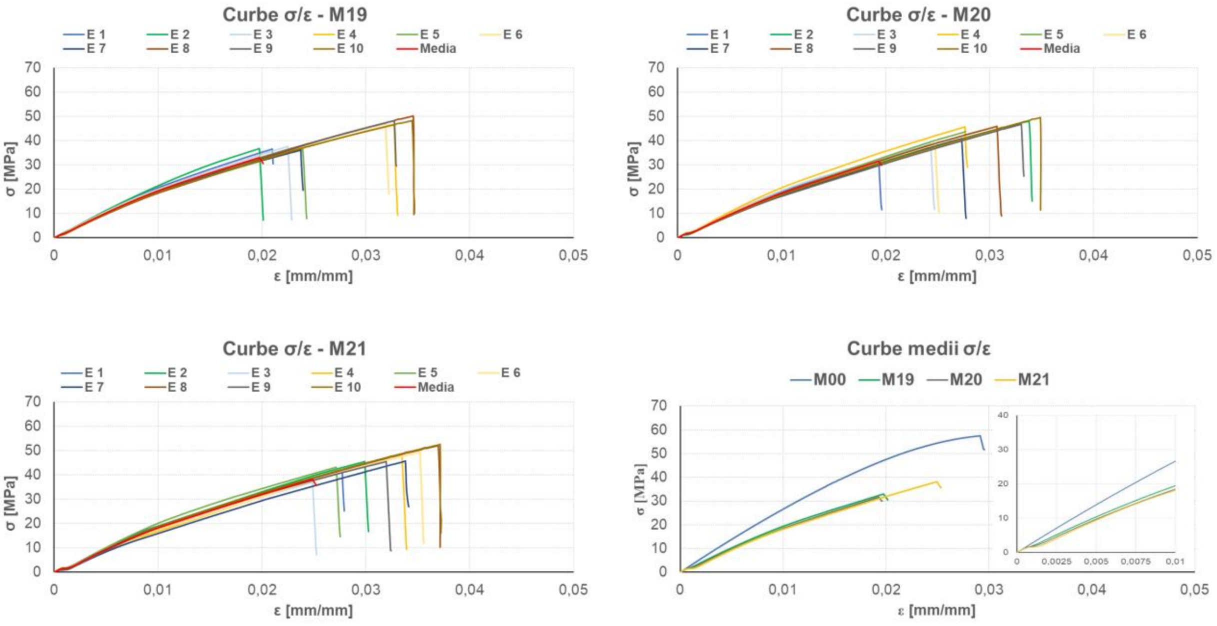

**Fig. 35.** σ/ε curves-polymeric materials modified with grape powder

In Fig. 36. a comparative study is made of the average σ/ε curves of the formed and tested materials, relative to the average curve of the epoxy resin, depending on the modification agent used. M10, M13, M16, M19 are materials obtained by adding lyophilized vegetable powder (sea buckthorn, kiwi, pomegranate, grape) to the pre-polymer mixture. All of these materials had an elastic (tensile) response lower than the elastic response of epoxy resin. This means that the addition of freeze-dried powders does not favor the strengthening of the bonds between the polymer constituents but, on the contrary, leads to their weakening. Materials are softer than epoxy, evidenced by the σ/ε curve profile, short linear bearing, horizontal passage, and quasi-linear growth (explained previously), and although they should break later, they break earlier than epoxy due to accumulated defects in the cross section where the fracture occurs.

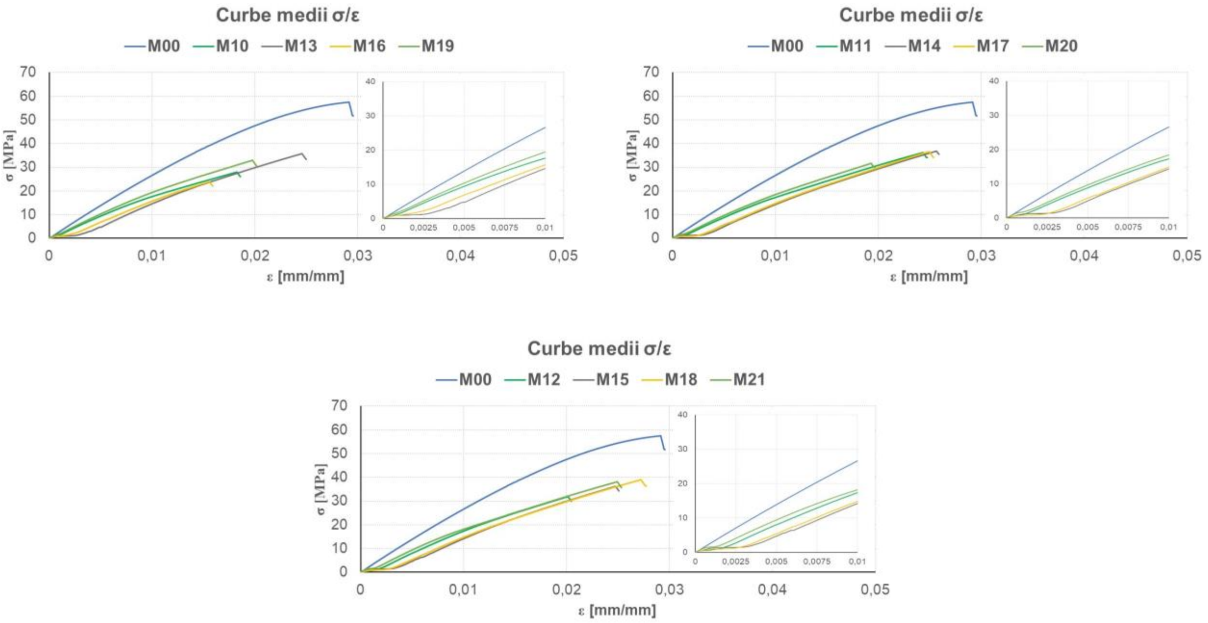

**Fig. 36.** Average σ/ε curves-polymeric materials modified with vegetable powders

Table 11., shows the values of the tensile modulus of the materials modified with lyophilized vegetable powders, starch, and black clay (as they were presented above).

**Table 11**. Tensile modulus of elasticity of polymeric materials modified with vegetable powders

| | **M00** | **M10** | **M11** | **M12** | **M13** | **M14** | **M15** | **M16** | **M17** | **M18** | **M19** | **M20** | **M21** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **E[GPa]** | 2.76 | 1.98 | 1.97 | 2.03 | 1.93 | 1.83 | 1.93 | 1.87 | 1.86 | 1.82 | 2.08 | 1.95 | 1.98 |
| **E[%]** | 100 | 71.74 | 71.38 | 73.55 | 69.93 | 66.30 | 69.93 | 67.75 | 67.39 | 65.94 | 75.36 | 70.65 | 71.74 |

#### 5.3.1.1. Conclusions – materials modified with vegetable powders – traction

- knowing from previous experience how epoxy resin behaves when different powders are added to the pre-polymeric mixture, I would have expected to obtain more resistant composite materials (with the higher elasticity mode of the epoxy resin);
- the materials formed with any of the four lyophilized powders studied have tensile modulus values lower than the corresponding value for the epoxy resin;
- in Fig. 37., the values of the traction elasticity modules for the materials analyzed in this Chapter are shown graphically. The two columns next to each material represent the value of the elaticity module automatically determined by the software application of the test machine (darker blue) and the values calculated strictly on the linear domains (within very small deformations). The first values are determined (automatically) as averages of the values

obtained for each specimen (in a material), while the others are determined on the average curve corresponding to each material;

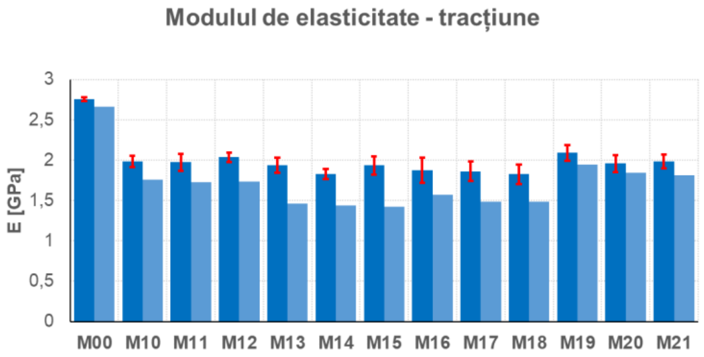

**Fig. 37.** Tensile modulus of elasticity of polymeric materials modified with vegetable powders

- reduction of mechanical tensile strength is a consequence of the chemical interaction between the substances that make up the chemical formulations of the two components of the epoxy system (resin and hardener) and the phytochemical agents present in the plant powders and lyophilisates used to modify the polymer;
- however, analyzing Tables 3-5 we find that kiwi powders, pomegranate and grapes contain the same types of phytochemical agents (in the case of grape powder, the highest concentrations), but the results obtained are different;
- this could mean that, in fact, there are other organic substances (that were not the target of investigations) which cause chemical reactions that we cannot suspect, or that the granulation of the powders is responsible for the various effects (we mentioned in Chapter 3 about the behavior of the powders after grinding);
- the addition of starch and starch with black clay, respectively, does not improve the situation created by the presence of freeze-dried powders.

### 5.3.2. Bending tests

The analysis of the bending response of polymeric materials modified with vegetable powders was carried out by three-point bending tests performed on ten specimens of each material (obviously, it is about materials analyzed in this Chapter). As I said in the course of Chapter 4, for these materials, we decided to have a more rigorous control of the test specimens (depending on the time of pouring the modified pre-polymeric mixture into the mold). In addition, to try to highlight the possible influence of the precipitation of the modifying agents on the responses to the bending, we organized the extraction of test specimens for these tests, taking into account which part of the cast material was at the bottom of the mold.

As we have shown, in Chapter 3, the cylindrical formed samples were kept upright during polymerisation. At the time of extraction of materials from polypropylene dies, apart from marking the number of the test specimen, we also marked its ends (s – up, j – down). In order to better cover the analysis of the possible influence of the moment of casting on the final properties of the materials, the samples chosen for the three-point bending tests were chosen according to Table 12.

**Table 12.** Numbering of specimens tested in three-point bending

| E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|
| 3s | 3j | 6s | 6j | 8s | 8j | 10s | 10j | 13s | 13j |

For modified materials with sea buckthorn lyophilized powder (M10, M11, M12) – in Fig. 38. The individual load/displacement curves corresponding to the test specimens for each of the mentioned materials are rendered, as is the comparison (in detail) between the average behavior of each material and the average behavior of the resin.

For the material modified only with lyophilized sea buckthorn powder, the linear behavior of the test specimens up to a 2mm movement of the punch can be observed; there is a reduced dispersion of data (up to the time of rupture of the first specimen). The analysis aimed at the dependence of the properties on the possible precipitation of the modifying agent reveals several aspects included in Table 13. in which the moments of the breaks are mentioned according to the displacement of the punch.

**Table 13.** Moments of rupture of the paired specimens according to the displacement of the punch – **M10**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 4.6 | 2.44 | 3.07 | 3.28 | 3.65 | 2.61 | 2.28 | 3.23 | 2.39 | 2.56 |

What can be seen is that the two halves of sample 3 (sections 1 and 2) break at a displacement difference of 2.16mm. This means that the top of the sample (E1-3s) and the bottom of it (E2-3j) have quite different properties. The pre-polymeric mixture, when cast, is fluid and favors the precipitation of larger aggregates of the modifying agent. For sample 6 (E3-6s and E4-6j), the material appears to have the same properties in both halves. The sample formed at mid-casting (E5-8s and E6-8j) has similar behavior to sample 3. From this point on, the specimens corresponding to samples 10 and 13 have, again, reversed behavior. For sample 10, the top is weaker than the bottom, while for sample 13, the responses of the two test specimens are comparable (high viscosity), which reduces the probability of precipitation.

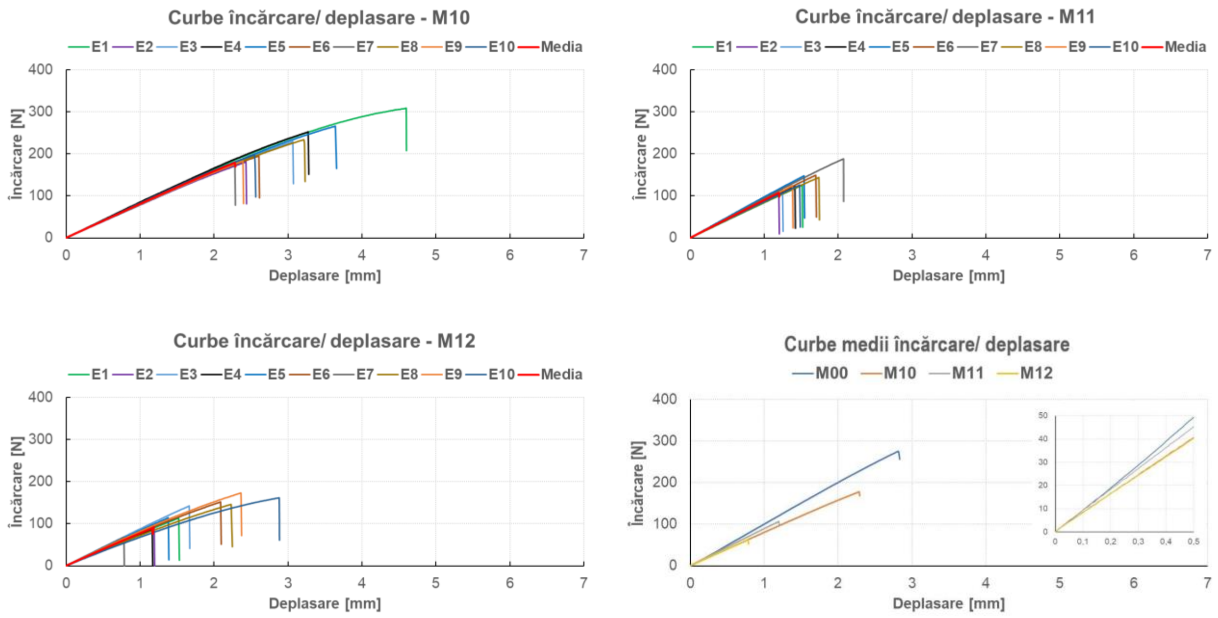

**Fig. 38.** Load/displacement curves-sea buckthorn modified polymeric materials

For material M11 – modified with sea buckthorn powder and starch it is easy to observe the effect of adding starch – the samples are more rigid (at bending) – all specimens have a linear elastic response and the dispersion of the rupture moments is much less than that corresponding to the specimens of the material M10, analyzed above – Table 14.

**Table 14.** Moments of rupture of the paired specimens according to the displacement of the punch – **M11**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.52 | 1.2 | 1.25 | 1.42 | 1.55 | 1.7 | 2.07 | 1.74 | 1.39 | 1.48 |

These (smaller) differences are due to the fact that from the beginning the presence of starch reduces the fluidity of the pre-polymeric mixture. In addition, we must also take into account the inherent errors – the deviation from the cylindricality of the test specimens (induced by the deformation of polypropylene tubes as a result of exoenergy chemical polymerization reactions) and possible local agglomerations of the amending agent aggregates – so that for samples 8 and 13, the small differences between movements at the time of rupture can be attributed to such errors. In the case of material M10, the samples in this situation are 6 and 13.

The results of the tests carried out on the material M12 – modified with sea buckthorn powder, starch, and black clay – indicate a significant dispersion of the experimental data both in terms of deviations from the average behavior and with regard to the moments of the ruptures of the specimens. The analysis of the effect of the possible precipitation of the aggregates of the modifying agents is shown in Table 15.

**Table 15.** Moments of rupture of the paired specimens according to the displacement of the punch– **M12**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.53 | 1.19 | 1.67 | 1.16 | 1.38 | 2.09 | 0.78 | 2.24 | 2.37 | 2.88 |

Analysis of the average behavior of materials modified with sea buckthorn lyophilized powder (bottom right graph of Fig. 39.) indicates that all three materials have lower bending behavior than the bending behavior of the epoxy resin. The addition of starch improves this response, while the addition - in addition - of black clay leads to a stiffer material (quick break), but basically with the same linear response as the material modified with only lyophilized sea buckthorn powder, as can be seen from the inserted detail.

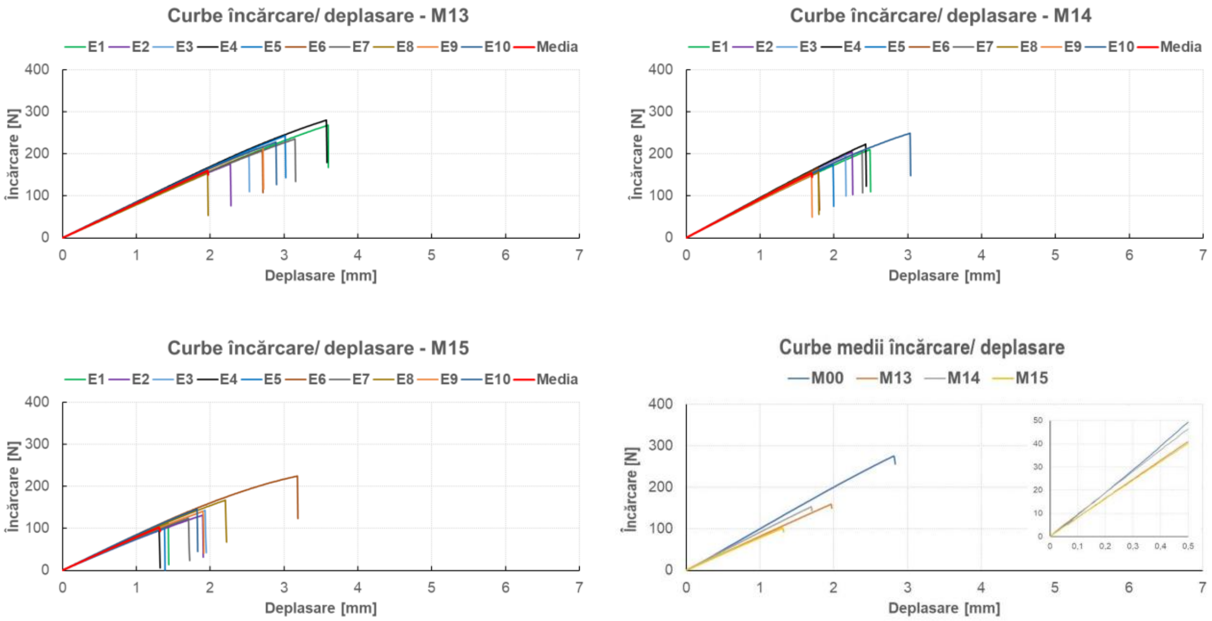

**Fig. 39.** Load/displacement curves-polymeric materials modified with kiwi powder

The analysis of the graph of the average behavior of these materials in relation to the average behavior of the epoxy resin again indicates that the elastic responses of the analyzed materials are inferior to the elastic responses of the epoxy resin. As with the buckthorn modified materials, at very small displacements of the punch (0.05mm), the average elastic responses coincide, with differences starting to appear after this displacement value. Material M14 (with kiwifruit and starch) has a response very close to that of the epoxy resin, while the other two materials (as in the case of the sea buckthorn material analysis) have an almost identical response, with a higher stiffness for material M15 (kiwifruit, starch, clay).

The analysis of the moments of rupture according to the displacement of the punch on pairs of specimens for each material again indicates significant differences. The reasons for these differences have already been explained.

**Table 16.** Moments of rupture of the paired specimens according to the displacement of the punch– **M13**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 3.6 | 2.28 | 2.53 | 3.58 | 3.02 | 2.71 | 3.15 | 1.97 | 2.72 | 2.89 |

For material M13 – Table 16., only in the case of sample 13 (E9 and E10) can we speak of a similar behavior (within the errors mentioned for materials M10-M12). In general, the top of the sample is more flexible (the exception is sample 6).

**Table 17.** Moments of rupture of the paired specimens according to the displacement of the punch– **M14**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.49 | 2.25 | 2.16 | 2.43 | 1.99 | 1.8 | 2.38 | 1.79 | 1.7 | 3.03 |

In the case of material M14 (modified with lyophilized kiwi powder) – Table 17. – samples 10 and 13 have inverted behaviors that are much different from the other three samples. The fact that the situation from sample 10 is reversed to sample 13 is related to the fact that the viscosity does not increase linearly over time.

**Table 18.** Moments of rupture of the paired specimens according to the displacement of the punch– **M15**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.43 | 1.9 | 1.94 | 1.32 | 1.38 | 3.18 | 1.72 | 2.22 | 1.91 | 1.83 |

For material M15 (freeze-dried kiwifruit and starch powder), the largest difference is observed for sample 8 and again, the behavior is reversed for samples 10 and 13.

For the materials formed with lyophilized pomegranate powder (Fig. 40.), we mentioned above that we observed a significant increase in the fluidity of the modified pre-polymer mixture.

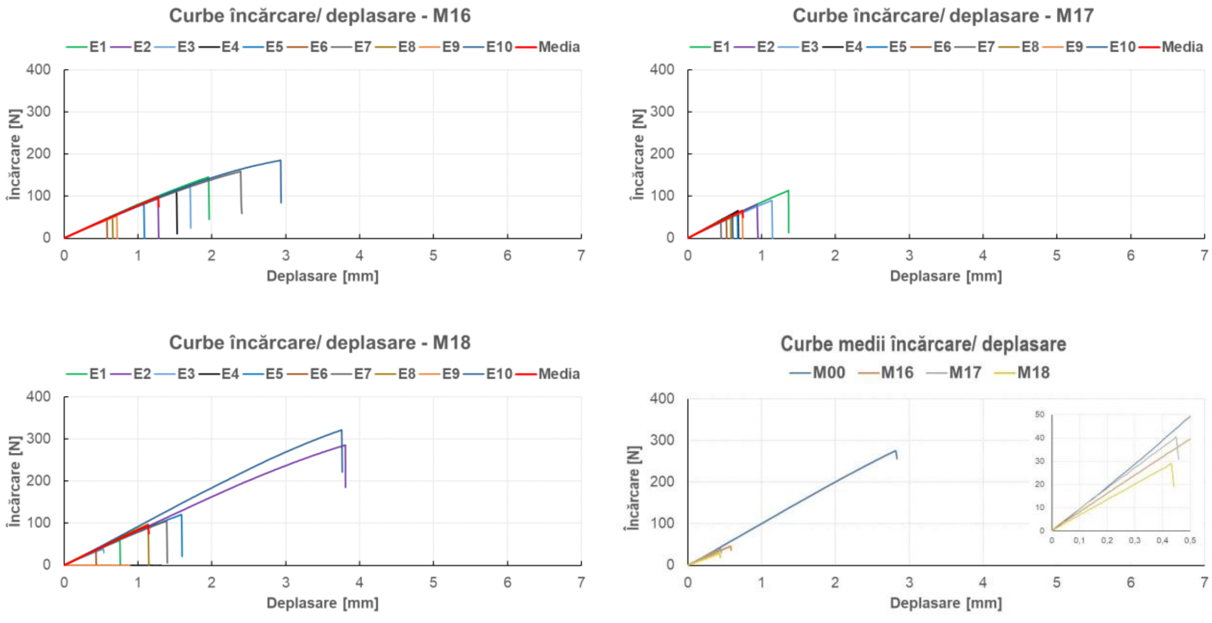

**Fig. 40.** Load/displacement curves-polymeric materials modified with pomegranate powder

Again, the addition of starch restores the elasticity of the material, but the presence of freeze-dried pomegranate powder has a much stronger influence than that of sea buckthorn powder or kiwi powder.

**Table 19.** Moments of rupture of the paired specimens according to the displacement of the punch– **M16**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.96 | 1.28 | 1.71 | 1.53 | 1.08 | 0.58 | 2.4 | 0.66 | 0.72 | 2.93 |

The range of displacements of the punch at which the breaks occur (Table 19.) highlights a very inhomogeneous material with elastic and flexural properties strongly dependent on the moment of casting.

The addition of starch (Table 20.) leads to obtaining a more homogeneous material, but the presence of starch no longer produces effects as important as in the case of sea buckthorn and kiwi powders, respectively.

**Table 20.** Moments of rupture of the paired specimens according to the displacement of the punch– **M17**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.36 | 0.95 | 1.14 | 0.69 | 0.68 | 0.53 | 0.45 | 0.59 | 0.74 | 0.61 |

In the case of material samples M17 (pomegranate and starch), the behavior of samples 3 and 6 is similar (high fluidity of the mixture) while, from sample 8, apparently (within the aforementioned errors) there are no more differences between the elastic responses induced by the time of casting the sample.

For material M18 (modified with pomegranate, starch and black clay) – Table 21. – we have already made the observation that two of the samples behave almost identically to epoxy resins.

**Table 21.** Moments of rupture of the paired specimens according to the displacement of the punch– **M18**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 0.76 | 3.8 | 0.53 | 1.31 | 1.59 | 0.43 | 1.39 | 1.14 | 0.88 | 3.76 |

The last part of the analysis refers to the materials modified with lyophilized grape powder – M19, M20 and M21 – for which the individual load/displacement curves as well as the comparative analysis of the average behaviors are shown in Fig. 41.

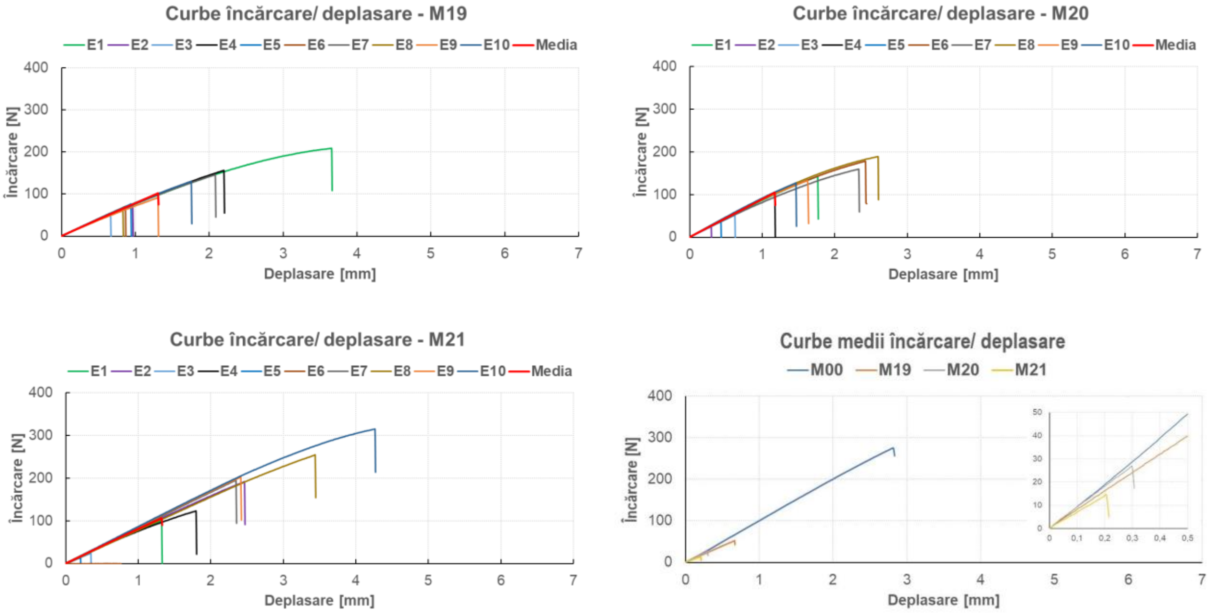

**Fig. 41.** Load/displacement curves-polymeric materials modified with grape powder

*Polymeric materials modified with vegetable powders*

As in previous cases, lyophilized vegetable powder produces a reduction in the elastic response of the material (at three-point bending) and the addition of starch relieves this situation. The addition of clay (in the mixture of modifying agents) produces the same effect for all freeze-dried powders. In the case of grape powder, the elastic response of the materials is the lowest of all the responses of the analyzed materials.

Regarding the homogeneity of the samples (samples), as in the previous cases, we performed the analysis of the moments of breakage of the samples according to the displacement of the punch. Table 22., shows this analysis for M19 (modified with lyophilized grape powder).

**Table 22.** Moments of rupture of the paired specimens according to the displacement of the punch– **M19**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 3.66 | 0.97 | 0.67 | 2.2 | 0.94 | 0.87 | 2.08 | 0.83 | 1.31 | 1.76 |

It can be seen that sample 8 (E5 and E6) can be considered homogeneous (in the range of errors already mentioned) and, perhaps, sample 13. For all other samples, the inhomogeneities are obvious and, as I said, are induced by chemical reactions.

**Table 23.** Moments of rupture of the paired specimens according to the displacement of the punch– **M20**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.77 | 0.3 | 0.63 | 1.18 | 0.43 | 2.43 | 2.33 | 2.6 | 1.63 | 1.47 |

Probably, as in the case of materials modified with pomegranate powder, a more complex hypothesis combining the results of chemical reactions, precipitation of aggregates of modifying agents, variation of viscosity should be considered. Another way could be to make, separately, materials modified only with phytochemical agents, which is practically impossible.

The addition of clay in the mixture of modifying agents produces – to material M21 – effects similar to those obtained on material M18 (modified with pomegranate, starch and clay) – Table 24.

**Table 24.** Moments of rupture of the paired specimens according to the displacement of the punch– **M21**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.33 | 2.47 | 0.35 | 1.8 | 0.21 | 0.76 | 2.35 | 3.44 | 2.42 | 4.27 |

None of the samples formed can be considered homogeneous. The differences between the two halves can only be explained by the precipitation of the aggregates, all the more so as, in the case of this material, it can be easily seen that the top is weaker than the bottom (for each sample individually).

Adding starch to the modification recipe (the same amount of starch added, respectively, to equal amounts of powder), at very small movements of the punch, the responses of the materials are similar, but the flexibilities are different – the least flexible material modified with grape powder and starch, the most flexible material modified with kiwi powder and starch. It should be noted that the kiwi powder (as we have already shown, could not be obtained at the same grain size as the other powders, under these conditions it is quite possible that most of its aggregates precipitated, contributing less to the modification of the polymer properties). At the same time kiwi powder contains the smallest amounts of flavonoids and polyphenols, so a lower probability of interaction with the pre-polymeric mixture.

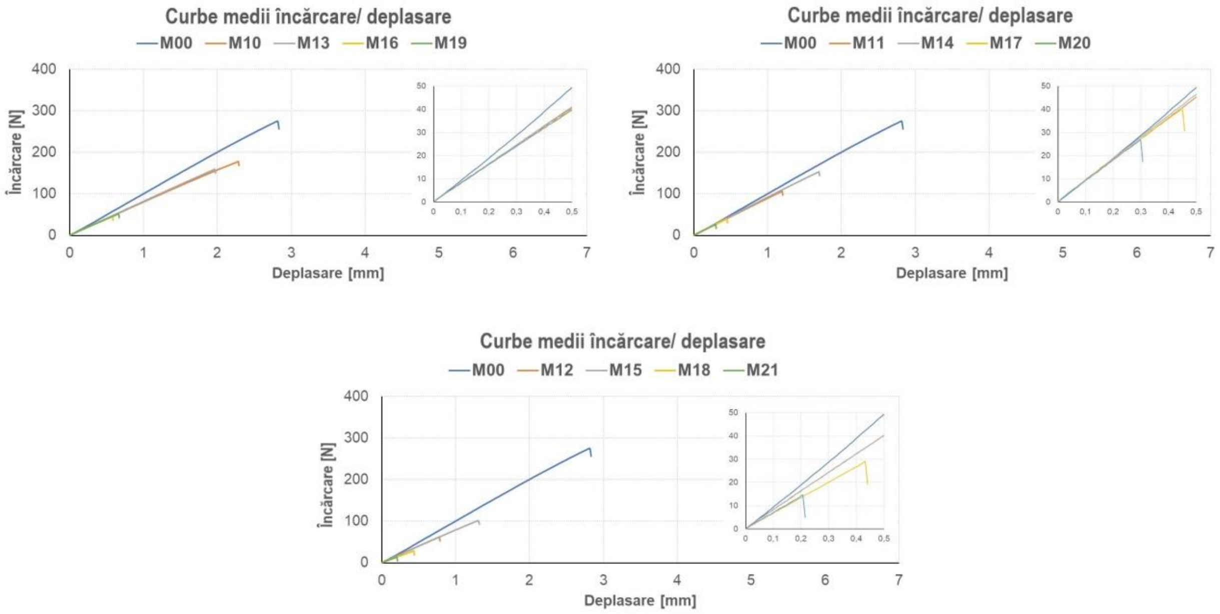

**Fig. 42.** Average load/displacement curves-polymeric materials modified with vegetable powders

The addition of clay (the same amount for all formed materials, in addition to the freeze-dried powders and starch) leads to the formation of materials with elastic flexural behavior more distant from the behavior of epoxy resin, the order of flexibility depending on the freeze-dried powder used remains that of the modification with vegetable powder and starch – kiwi, sea buckthorn, pomegranate, grape.

In Table 25., the values of the flexural modulus of elasticity of the materials analyzed in this Chapter are presented, and it can be easily observed that all the modified materials have values of the modulus lower than the value corresponding to the epoxy resin.

**Table 25.** Flexural modulus of polymeric materials modified with vegetable powders

| | **M00** | **M10** | **M11** | **M12** | **M13** | **M14** | **M15** | **M16** | **M17** | **M18** | **M19** | **M20** | **M21** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **E[GPa]** | 2.77 | 2.19 | 2.45 | 2.18 | 2.23 | 2.51 | 2.17 | 2.16 | 2.46 | 2.07 | 2.15 | 2.46 | 2.21 |

### 5.3.2.1. Partial conclusions – three-point bending tests

- all the materials analyzed in this Chapter show elastic responses to bending lower than the elastic response of epoxy resin;
- the values of the flexural modulus obtained from the three-point bending tests are lower than the value of the flexural modulus of the epoxy resin – Fig. 43.;

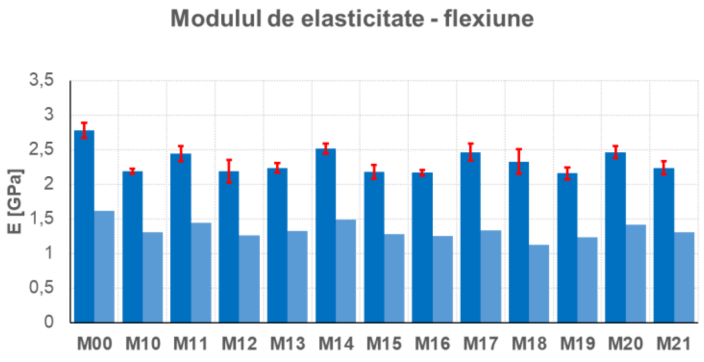

**Fig. 43.** Flexibility modulus of polymer materials modified with vegetable powders

- very large variations in test specimen behaviour (even from the same sample) indicate that material inhomogeneities exist;
- inhomogeneities may be generated by chemical reactions of phytochemical agents with substances in chemical formulations of the two components of epoxy resin – the hypothesis confirmed, somewhat by the reductions of the flexural modulus values for the modified materials with kiwi, pomegranate and grapes, reductions proportional to the content of the mentioned powders flavonoids, polyphenols and anthocyanins;
- another source of inhomogeneity may be associated with precipitation of the aggregates of the modifying agents (in particular the inorganic phase of the clay), and which would make the bottom parts of the samples stiffer than the top parts (the test and marked with even numbers);
- in the absence of finer tests – the modification of epoxy resin with the phytochemical agents of lyophilized powders in different concentrations – the two hypotheses outlined above are difficult to correlate based on the results presented.

## 5.4. Conclusions - modified materials with lyophilized powders

- regarding the morphological analysis – SEM – of the surfaces resulting from bending fracturing, one can notice differences generated by the presence of lyophilized powders. Equally, there are differences between the SEM aspect of these samples and that of the samples to which starch was added;
- given that for the pomegranate we found an increase in the fluidity of the casting mixture, it was expected that for the modified materials with this powder to favor the precipitation of the aggregates of the modifying agents, with consequences on the mechanical properties of the modified materials;
- except sea buckthorn powder, it appears that the effects of the presence of plant powders in the polymer matrix are proportional to the contents of – anthocyanins, flavonoids, – polyphenols of those powders;
- as regards the results obtained in the tensile and bending tests, there are differences between the results obtained in the sense that some materials are more tensile resistant and weaker at bending – for example, materials modified with lyophilized grape powder.

# 6. Polymeric materials modified with plant powders and nano blend

## 6.1. General observations

Epoxy nanocomposites (also called hybrid epoxy thermoset) are two-phase materials, a nanometer-sized inorganic domain, well dispersed in a cross-linked epoxy matrix [65]. These materials are one of the most useful hybrid materials, which usually contain silicate particles.

## 6.2. Structural analysis

For the production of composites, as we have shown in Chapter 3, we have prepared a mixture of equal masses of the four nanometer powders – graphite, silver, silver, strontium ferrite and tungsten carbide – mixture that was homogenized by grinding into a coffee grinder. The formed mixture has a uniform appearance, and from this were taken the quantities necessary for the formation of the materials studied in this Chapter, which are based on materials M12, M15, M18, and M21 presented in the previous Chapter, to which 1g, 3g and 5g of the mixture of nanoscale structures are added, respectively.

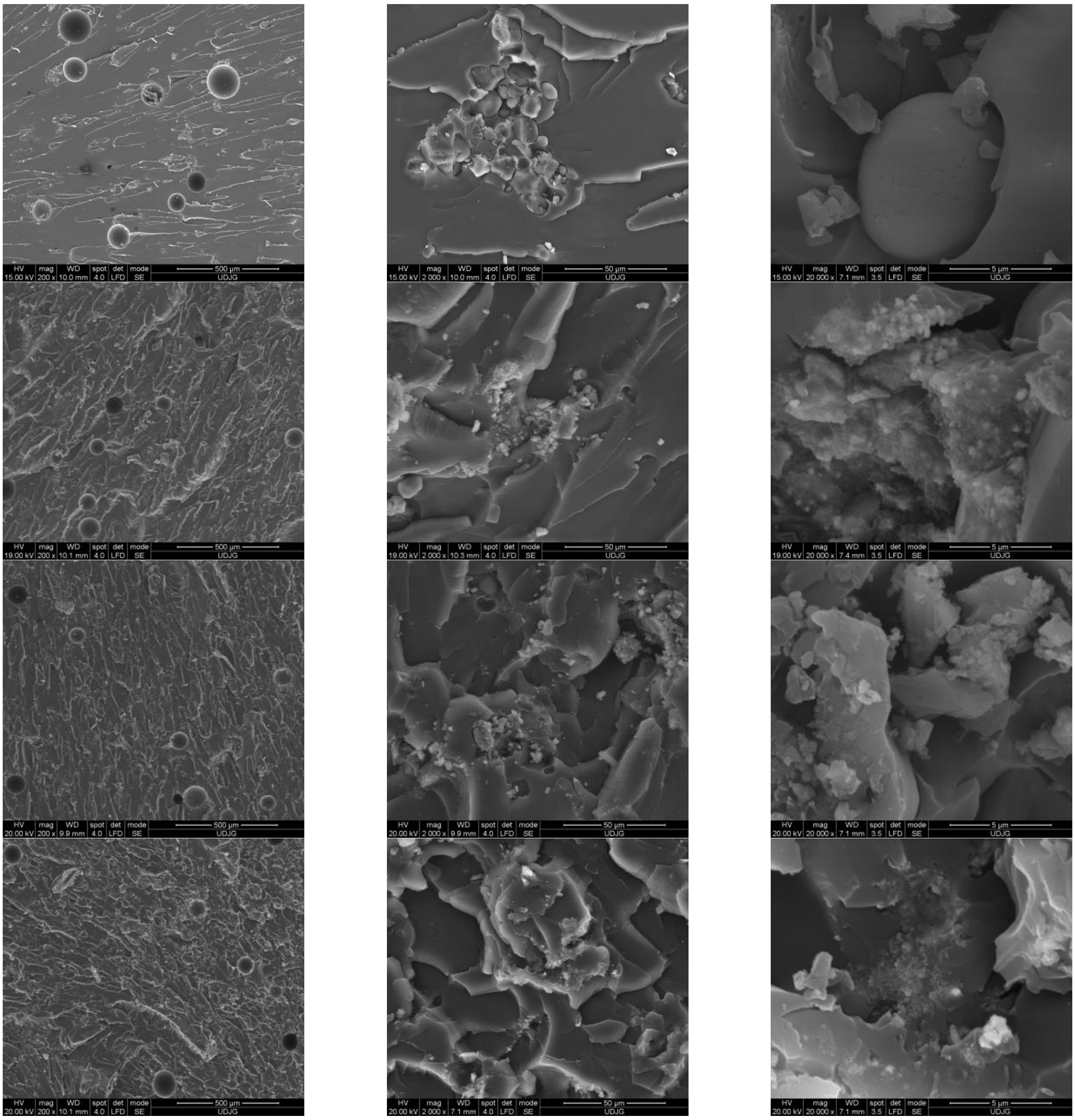

**Fig. 44.** Structural analysis of materials M12, M22, M23, M24

In Fig. 44., a morphological analysis of the materials formed on the basis of material M12 to which the said quantities of the mixture of nanopowders have been added shall be provided. Obviously, on the first line are the SEM micrographs of the base material and, on the following lines, the micrographs corresponding to the nanopowder materials, in the ascending order of the quantity of the mixture used.

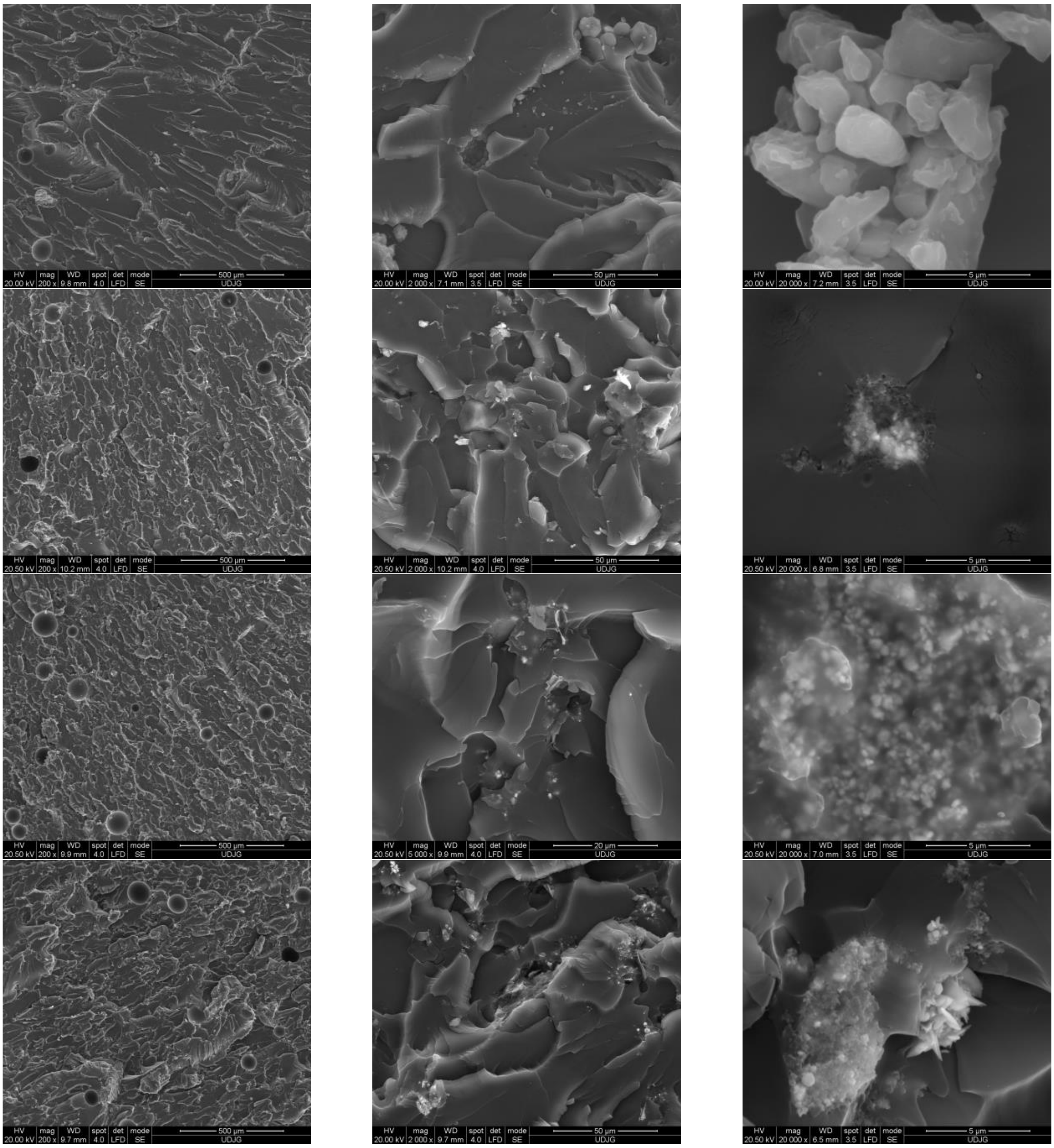

**Fig. 45.** Structural analysis of materials M21, M31, M32, M33

In Fig. 45., I presented the comparative analysis, based on SEM micrographs, for materials modified with a mixture of nanopowders and based on the M21 material (modified with grape lyophilized powder, starch, and black clay). And in this case, the fragmentation of the matrix is observed with the increase in the concentration of the nanopowder mixture in the modified base pre-polymer (which in turn – Chapter 5) had a greater fragmentation than epoxy resin. You can also see clumps of nano-constituents that seem to be embedded in organic structures (not necessarily modified polymer).

### 6.2.1. Partial conclusions – morphological analysis of materials modified with vegetable and nano powders

- apparently, the density and size of the gaseous intrusions appear to decrease with the increase in the amount of the mixture of nanopowders dispersed in the base materials;
- for all the materials analysed, the fragmentation of the matrix is observed to increase with the amount of nanopowder mixture used to modify the base material;
- when using lyophilized pomegranate powder, no significant changes in the fluidity of the mixture prepared for pouring are found when adding the nanopowder mixture, in this case, it would be interesting to study where lyophilized pomegranate powder is used together with starch to determine the optimal amount of starch to be added to counterbalance the effect pomegranate powder;
- the investigated areas are small in size and, as we mentioned, they present the details of very small areas in the area of rupture of a test specimen, tested at bending, so he could indicate why the specimen broke exactly there (the presence of defects);
- for an exhaustive study of the distribution of nano-structures in polymer, it would be necessary to slice a sample and analyze each surface resulting from the slicing (of course, that, in this situation, the optimal thickness of the slice should be established), moreover, as distributions of nano-constituents also differ by sample length (depending on the factors I mentioned in Chapter 5), each sample should be sliced and this is impossible;
- even under these conditions, the SEM analysis is interesting enough because it provides a picture of the distribution of nano-constituents that statistically can exist in any section of the sample.

## 6.3. Analysis of mechanical properties of polymeric materials modified with plant powders and nano blend

### 6.3.1. Tensile tests

As in the cases presented in Chapter 4, test specimens tested at traction (stretching) were obtained by cutting the ends of the samples formed in polypropylene tubes, so these specimens have a length of 200mm (length of the test area is 100mm) and an average diameter of 8mm. Specifying, that the value of the diameter is an average one is related to the fact that due to the fact that the polymerization reaction is exoenergetic, the, some of the polypropylene tubes have deformed (not so much that they cannot be considered cylindrical as a whole).

The numbering of test specimens tested at traction is the same as for the materials presented in Chapter 5 (Table 6), to preserve the possibility of correlations between the moment of rupture of the specimen and the moment when it was cast.

In Fig. 46., the individual stress/strain (σ/ε) curves are shown for the materials resulting from the modification of the M12 material with 1g, 3g and 5g nanopowder mixture. The last graph (bottom right) represents the average behavior of each material.

In the case of the materials analyzed in Chapter 5 (modified with lyophilized powders, lyophilized powders, and starch, respectively, lyophilized powders, starch, and black clay), we specify that, unlike the materials modified only with clays (Chapter 4), the appearance of the profile of the σ/ε curves is modified by the appearance of a step parallel to the horizontal axis (the samples lengthen without the force increasing significantly). The same observation is valid for materials M22-M25 without being able to specify any relationship between the length of the horizontal bearing and the amount of nanopowder mixture added in the recipe of the base material (M12).

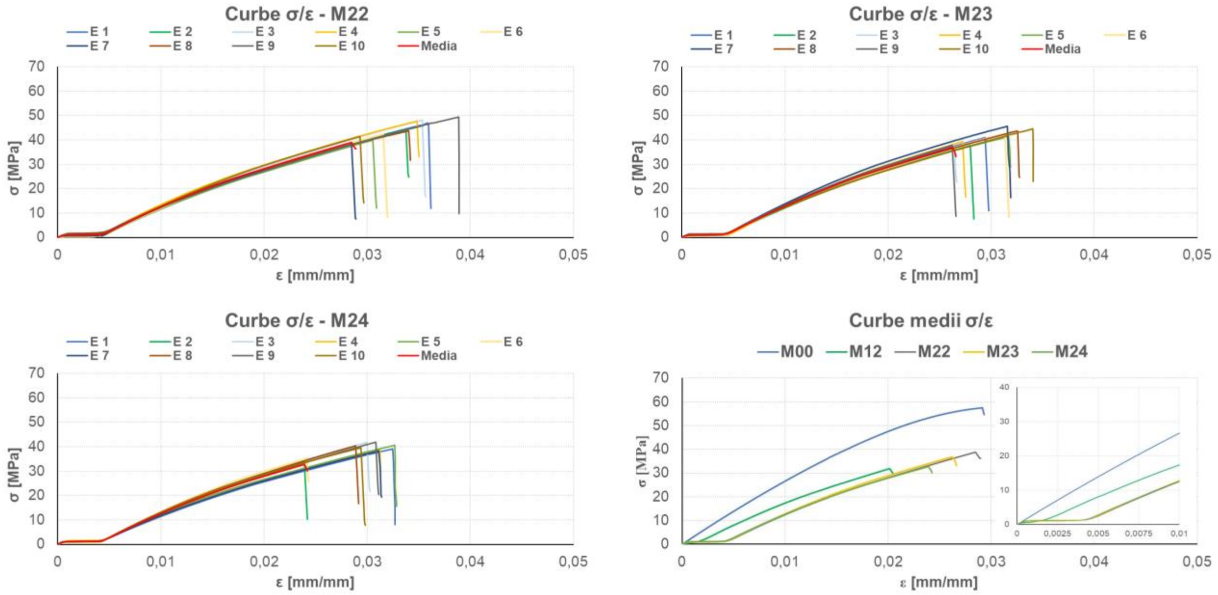

**Fig. 46.** σ/ε curves-polymeric materials modified with sea buckthorn powder and nanoparticles

**Table 26.** Stresses [MPa] and strains [mm/mm] of the best response specimens (M12+nano)

| material | M22 | | | M23 | | | M24 | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E1 (1) | E3 (4) | E9 (14) | E7 (11) | E8 (12) | E10 (15) | E5 (7) | E9 (14) | E10 (15) |
| σ | 46 | 47 | 50 | 46 | 43 | 45 | 40 | 42 | 40 |
| ε | 0.036 | 0.035 | 0.038 | 0.031 | 0.032 | 0.034 | 0.032 | 0.03 | 0.029 |

As regards the responses of the test specimens according to the time of pouring (Table 27.), it can be found that only for M23 material all specimens with good answers are poured into the second part of the casting (beyond sample 8). In Table 27., an analysis of the averages of the best answers is made, in which the average of the best responses of the base material is also introduced.

**Table 27.** Averages of the three best responses of the M12 and M12+nano material specimens

| material | M12 | M22 | M23 | M24 |
|---|---|---|---|---|
| σ(medium)[MPa] | 41.67 | 47.67 | 44.67 | 40.67 |
| ε(medium)[mm/mm] | 0.023 | 0.036 | 0.032 | 0.030 |

Regarding the dispersion of the data presented graphically in Fig. 52. it can be seen that this is less than the dispersion of the M12 base material data, including the dispersion of the moments of rupture. In the same figure, in the lower right corner, the average behaviors of the epoxy resin (M00), the base material (M12) and the three materials made with the three amounts of nanopowder mixture are shown for comparison.

All analyzed materials have the same elastic response, the difference being made by the average breaking moment. The specific strain at average break decreases with an increasing amount of nanopowder mixture added to the base material recipe.

The second class of materials modified with a mixture of nanopowders is that of materials based on M15 (modified with freeze-dried kiwi powder, starch and black clay). In Fig. 47., the individual responses of the tested samples and the average curves characteristic of each material are presented in graphic form. The scattering of experimental data is once again lower than in the case of the basic material (as in the case previously analyzed). The observation also applies to the scattering of the moments of the breakers. These, together, can lead to the hypothesis of obtaining more homogeneous materials than the base material.

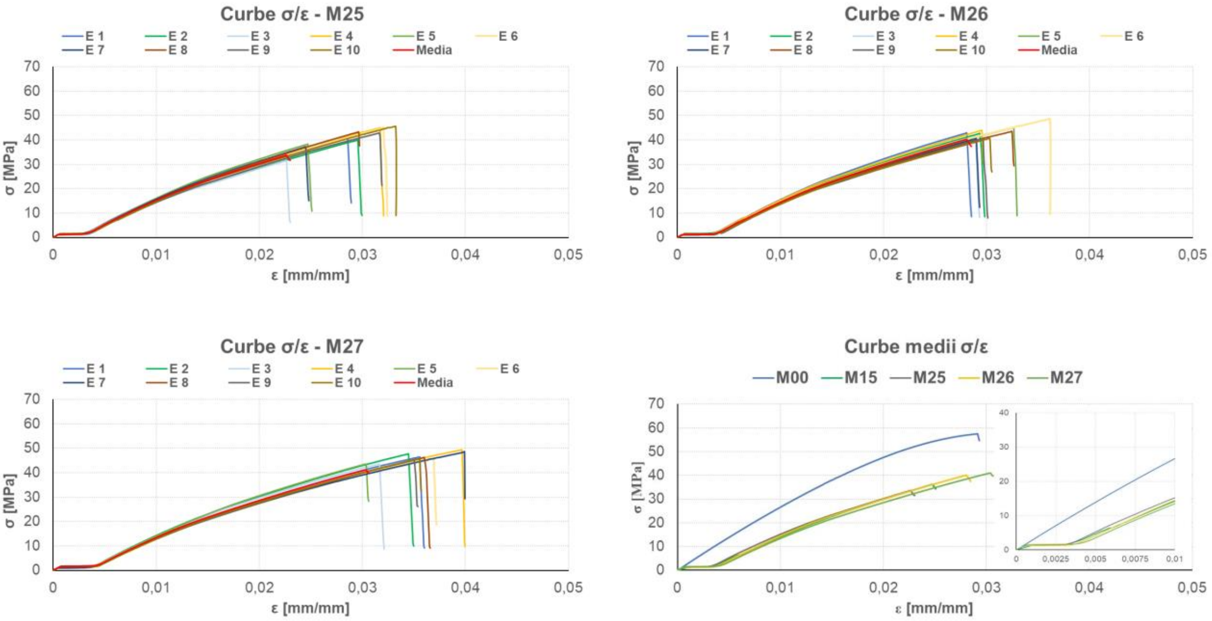

**Fig. 47.** σ/ε curves-polymeric materials modified with kiwi powder and nanoparticles

The analysis of the dependence of the elastic response on the timing of the sample pouring is given in Table 28 and, as in other cases, in, it can be seen that the samples with maximum answers are those in the vicinity of the moment from the middle of the casting (it reminds me here that the 8th samples, 10 And 13 were used for bending tests).

**Table 28.** Stresses [MPa] and strains [mm/mm] of the best response specimens (M15+nano)

| **material** | **M25** | | | **M26** | | | **M27** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E6 (9) | E9(14) | E10(15) | E5 (7) | E6 (9) | E8 (12) | E4 (5) | E6 (9) | E7 (11) |
| σ | 43 | 41 | 45 | 44 | 50 | 43 | 50 | 46 | 49 |
| ε | 0.031 | 0.031 | 0.033 | 0.032 | 0.036 | 0.032 | 0.039 | 0.036 | 0.04 |

As regards the averages of the best responses, they are presented in Table 29 and it can be seen that both the maximum voltage level and the maximum specific deformation, only in the case of material with 1g nanopowder mixture the values are comparable to those of the base material. For the other two materials, the values of the two parameters increase with the increase in the amount of nanopowder mixture. This is an opposite result to that obtained for materials modified with lyophilized sea buckthorn powder, which means, in a first analysis, that kiwi powder is effective in dispersing used nanostructures.

**Table 29.** Averages of the three best responses of the M15 and M15+nano material specimens

| **material** | **M15** | **M25** | **M26** | **M27** |
|---|---|---|---|---|
| σ(medium)[MPa] | 43.3 | 43 | 45.6 | 48.3 |
| ε(medium)[mm/mm] | 0.033 | 0.031 | 0.033 | 0.038 |

In Fig. 47., the situation of the average responses (reported to the epoxy resin – M00 and the base material M15) can be seen, as in the case of modified sea buckthorn materials, the fact that the average responses of the materials modified with nanopowders have the same profile, they differ only by the time of tearing (average) and are all superior to the response of the base material, but inferior to the response of the epoxy resin.

In Fig. 48. the response of each sample from the three materials made on the basis of the M18 material (modified with lyophilized pomegranate powder, starch and black clay) is shown graphically. For each material, the graph also includes the average response of that material (average of specific stresses/average of specific strains automatically performed by the software application controlling the testing machine).

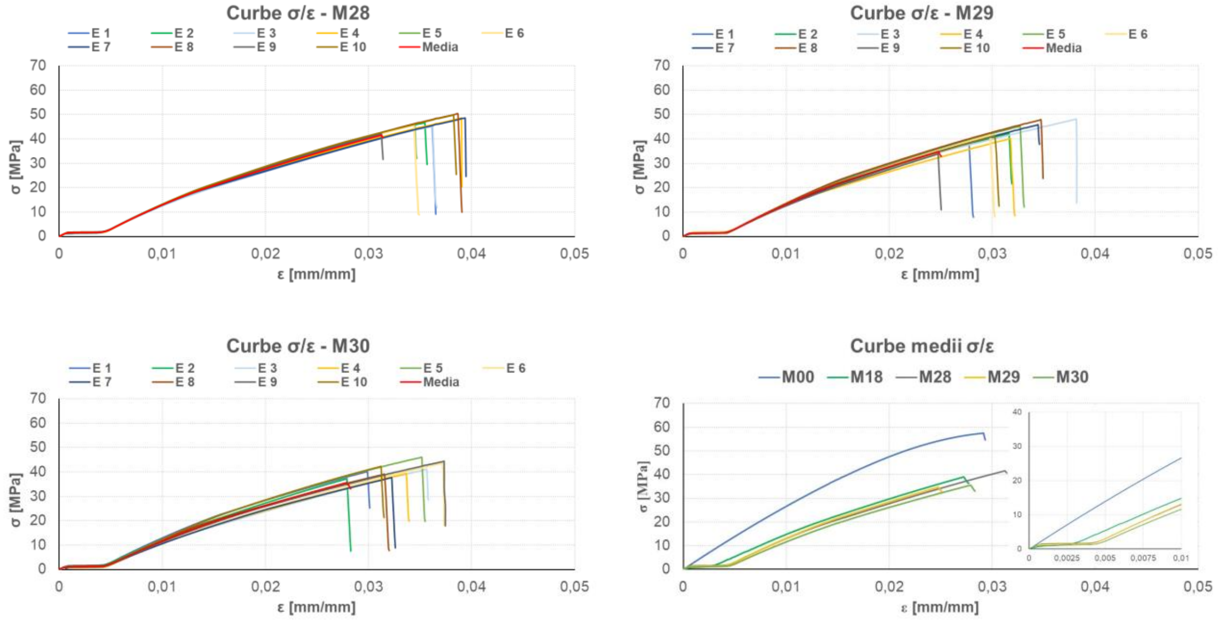

**Fig. 48.** σ/ε curves-polymeric materials modified with pomegranate powder and nanoparticles

Compared to material M18, all materials analyzed here have a longer horizontal palier length, but the lengths of these appear to not depend on the amount of nanopowder mixture. The average responses of these materials are inferior to the average responses of the base material (and obviously to the response of the epoxy resin). In this case, however, unlike the previously analyzed cases, the material responses with 1g and, respectively, a 3g mixture of nanopowders are almost overlapping (the material with 1g – M28, shows greater elasticity than M29).

**Table 30.** Stresses [MPa] and strains [mm/mm] of the specimens with the best response (M18+nano)

| **material** | **M28** | | | **M29** | | | **M30** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E4 (5) | E7(11) | E8 (12) | E3 (4) | E7 (11) | E8 (12) | E5 (7) | E6 (9) | E9 (14) |
| σ | 44 | 48 | 50 | 48 | 46 | 48 | 46 | 44 | 45 |
| ε | 0.038 | 0.04 | 0.038 | 0.038 | 0.034 | 0.034 | 0.035 | 0.036 | 0.037 |

As in the previous cases, in table 31, the averages of the three best responses for each material, including the base material, are rendered. It can be seen that the average strength of the base material is higher than the tensile strength of any of the materials to which the nanopowder mixture has been added.

**Table 31.** Averages of the three best responses of the M18 and M18+nano material specimens

| **material** | **M18** | **M28** | **M29** | **M30** |
|---|---|---|---|---|
| σ(medium)[MPa] | 48.3 | 47.3 | 47.3 | 45 |
| ε(medium)[mm/mm] | 0.034 | 0.038 | 0.035 | 0.036 |

In Fig. 49. specific stress/strain curves shall be provided for all test specimens of modified materials with grape lyophilized powder and a nanopowder mixture. It can be found that the dispersion of experimental data decreases with an increase in the amount of nanopowder mixture used to modify the base material. The behavior of the material M21 (the basic material, in this case) is copied by the material M31 (modified by 1g nanopowders); this means that this quantity does not counterbalance the effects of the modification with lyophilized powder of grapes, starch, and clay (M21).

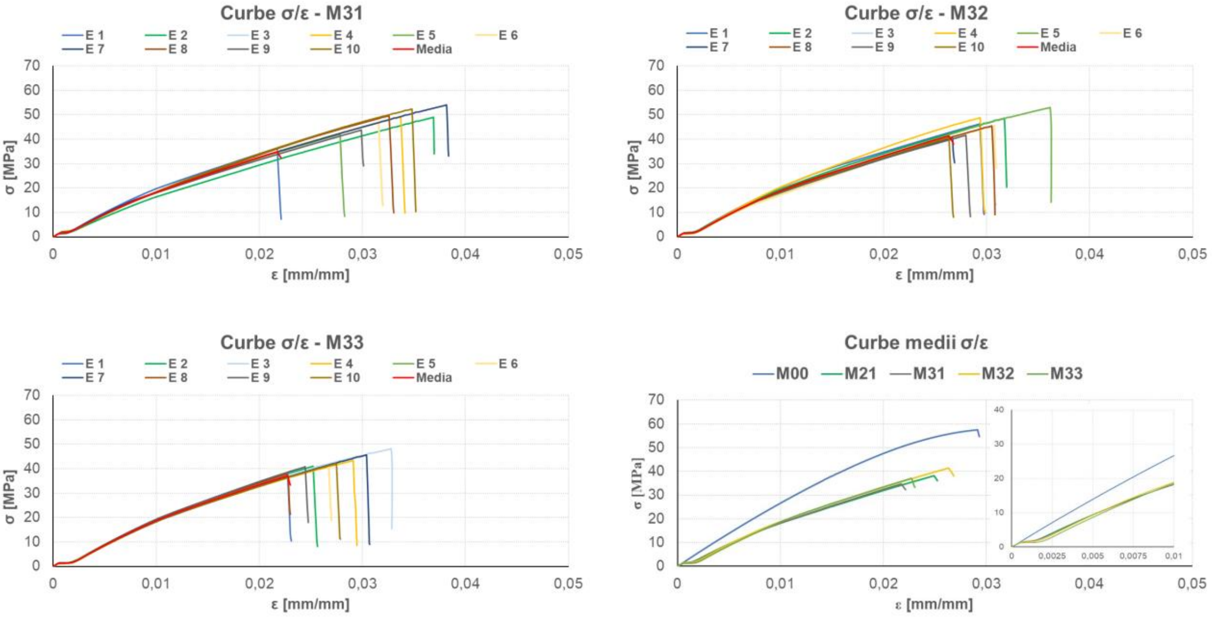

**Fig. 49.** σ/ε curves-polymeric materials modified with grape powder and nanoparticles

The increase in the amount of nanopowder mixture used for modification leads, as can be seen, to the reduction of the dispersion of experimental data that is, to more homogeneous materials.

Regarding average responses (bottom right graphical representation – Fig. 49.), it can be noted that there are no large differences between the base material (M21) and the three modified materials with the nanopowder mixture (M31, M32, etc, M33) and all their responses are inferior to the epoxy resin response.

Table 32., contains the analysis data on possible non-homogeneities generated by the moment of casting. In the case of M31, the best responses correspond to samples poured at the end of the process, for M32 and M33 the best responses correspond to the first part of the casting process.

**Table 32.** Stresses [MPa] and strains [mm/mm] of the specimens with the best response (M21+nano)

| **material** | **M31** | | | **M32** | | | **M33** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E7(11) | E8(12) | E10(15) | E2 (2) | E4 (5) | E5 (7) | E3 (4) | E4 (5) | E7 (11) |
| σ | 55 | 50 | 53 | 48 | 48 | 53 | 48 | 44 | 45 |
| ε | 0.038 | 0.033 | 0.035 | 0.031 | 0.029 | 0.036 | 0.033 | 0.028 | 0.03 |

Table 33., contains relevant data regarding the reduced amplitude of the changes induced by the presence of the nanopowder mixture in the base material (M21) – a slight reduction in the average value of the specific strain at break for the three best responses can be observed by increasing the amount of nanopowder mixture used. The same trend is observable for breaking stress.

**Table 33.** Averages of the three best responses of the M21 and M21+nano material samples

| **material** | **M21** | **M31** | **M32** | **M33** |
|---|---|---|---|---|
| σ(medium)[MPa] | 51.6 | 52.6 | 49.6 | 45.6 |
| ε(medium)[mm/mm] | 0.036 | 0.035 | 0.032 | 0.03 |

The diversity of responses, generated by the differences between plant powders, cannot be explained – in the case of modified materials with nanopowder mixture – only on the basis of differences between plant powders. And in this case, as in the case of the materials analyzed in Chapter 5, as well, the results obtained appear to indicate quality changes in the interphase generated by the mixture of nanopowders (in Chapter 5 it was starch and clay).

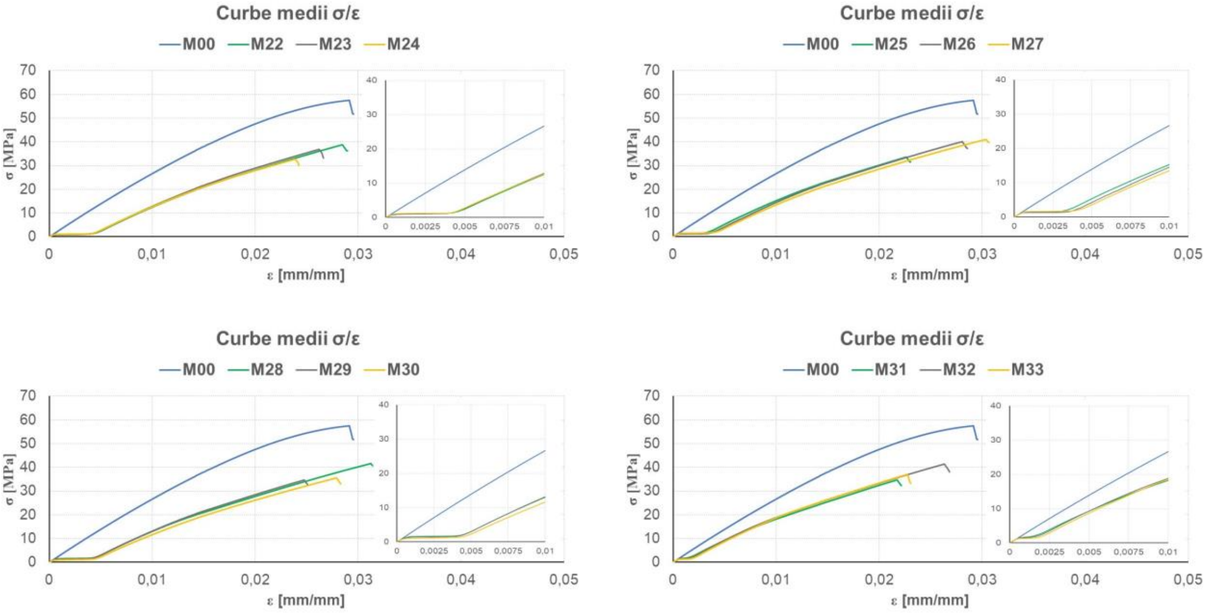

**Fig. 50.** Average σ/ε curves-polymeric materials modified with vegetable powders and nanoparticles

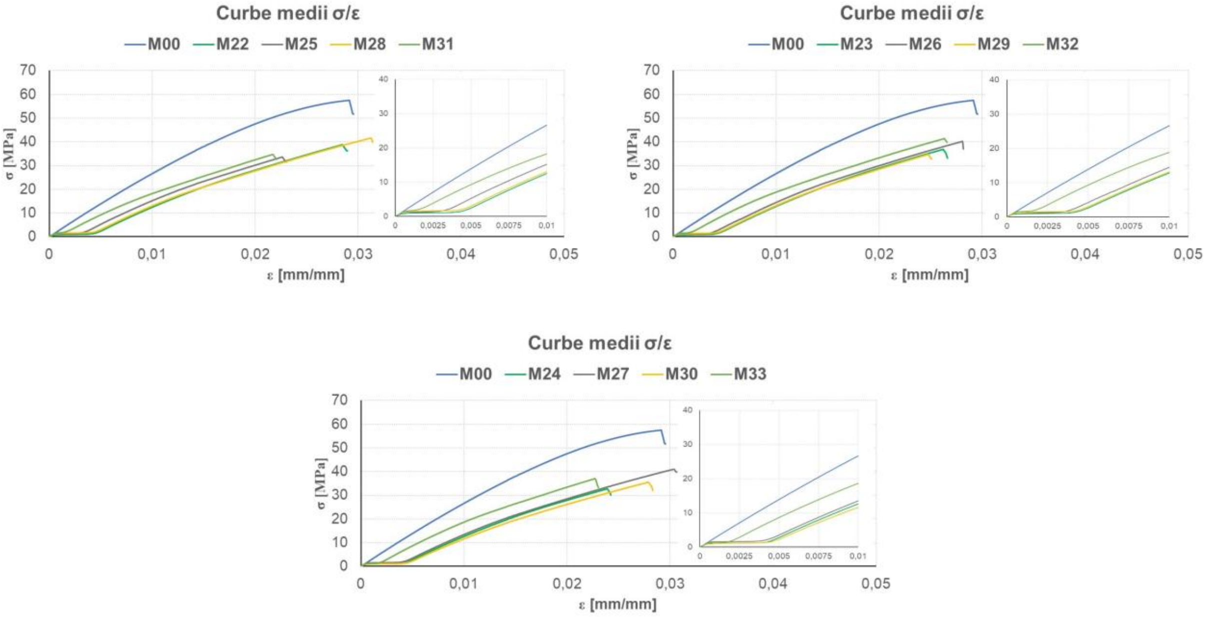

**Fig. 51.** Average σ/ε curves-polymeric materials modified with vegetable powders and nanoparticles

In Fig. 51., a comparative analysis of the materials covered by this Chapter is carried out from the perspective of the lyophilized powder used, at the same amount of the mixture of nanopowders added. The best results are recorded by materials modified with lyophilized kiwi powder (regardless of the amount of nanopowder mixture). The length of the horizontal palaces in the profiles of the average curves depends on the type of lyophilized vegetable powder (as already mentioned).

**Table 34.** Tensile modulus of polymer materials modified with vegetable powders and nano blend

| | M00 | M22 | M23 | M24 | M25 | M26 | M27 | M28 | M29 | M30 | M31 | M32 | M33 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **E[GPa]** | 2.76 | 1.97 | 2 | 1.95 | 2 | 1.88 | 2.03 | 1.86 | 1.99 | 1.78 | 1.94 | 1.98 | 2.03 |
| **E[%]** | 100 | 71.38 | 72.46 | 70.65 | 72.46 | 68.12 | 73.55 | 67.39 | 72.1 | 64.49 | 70.29 | 71.74 | 73.55 |

As regards the elastic modulus of the materials analyzed in this Chapter, in relation to the modulus of elasticity of epoxy resin, it can be seen that the lowest reduction in the value of this parameter is about 25.45%, while the highest is 35.51%.

### 6.3.1.1. Partial conclusions – materials modified with vegetable powders and mixture of nanopowders – tensile

- the results from the test results of tensile tests on samples of modified materials with a nanopowder mixture indicate that the elastic properties of these materials are comparable to those obtained for the corresponding base materials (M12, M12, M15, M18, M21) analysed in Chapter 5;
- this would mean that adding the mixture of nanopowders does not increase the number of defects in the matrix network (which obviously cannot be true);
- in these circumstances, it is necessary to formulate the hypothesis that the addition of the nanopowder mixture to the base materials is the premise of obtaining materials with better interphase quality, following a complex chemical interaction;
- modulus of elasticity when stretched - Fig. 52. – indicates a decrease in the value of this parameter for the materials analyzed in this Chapter, but this reduction is comparable to that obtained for the basic materials (Chapter 5);

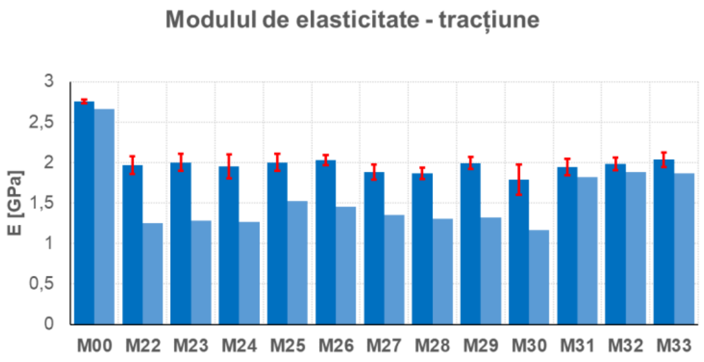

**Fig. 52.** Tensile modulus of elasticity of materials modified with vegetable powders and nano blend

- regarding the dependence of the elastic responses on the moment of casting, as in the case of the materials analyzed in Chapter 5, it is difficult to identify a constant behavior of the materials (probably also due to the variability of the casting conditions);
- however, for some materials, it appears that better responses are obtained on specimens cast early in the process (high pourability of the casting mix), for others on specimens cast late in the process (increased viscosity of the casting mix).

### 6.3.2. Bending tests

Regarding the flexural tests (three-point bending), we followed the analysis protocol used in Chapter 5 – we used the same samples (from the batch) to obtain the necessary specimens and controlled the area in the sample (top or bottom) where they came from, in an attempt to identify possible effects of precipitation of the constituents of the used modifying agents. As in Chapter 5, also in an attempt to compare the responses of the materials, I chose to use three specimens with the maximum responses.

In Fig. 53. the individual responses of all tested specimens for materials modified with a mixture of nanopowders and based on material M12 (modified with lyophilized sea buckthorn powder, starch and black clay) are shown. One can observe the very large scattering of experimental data, indicating material inhomogeneities. Once again, as in the case of the materials analyzed in Chapters 3 and 4, such behavior was expected from the perspective of the fact that the presence of defects (neomogeneities) has a stronger influence on the application of load in the transverse direction than in the case of longitudinal loading (stretching).

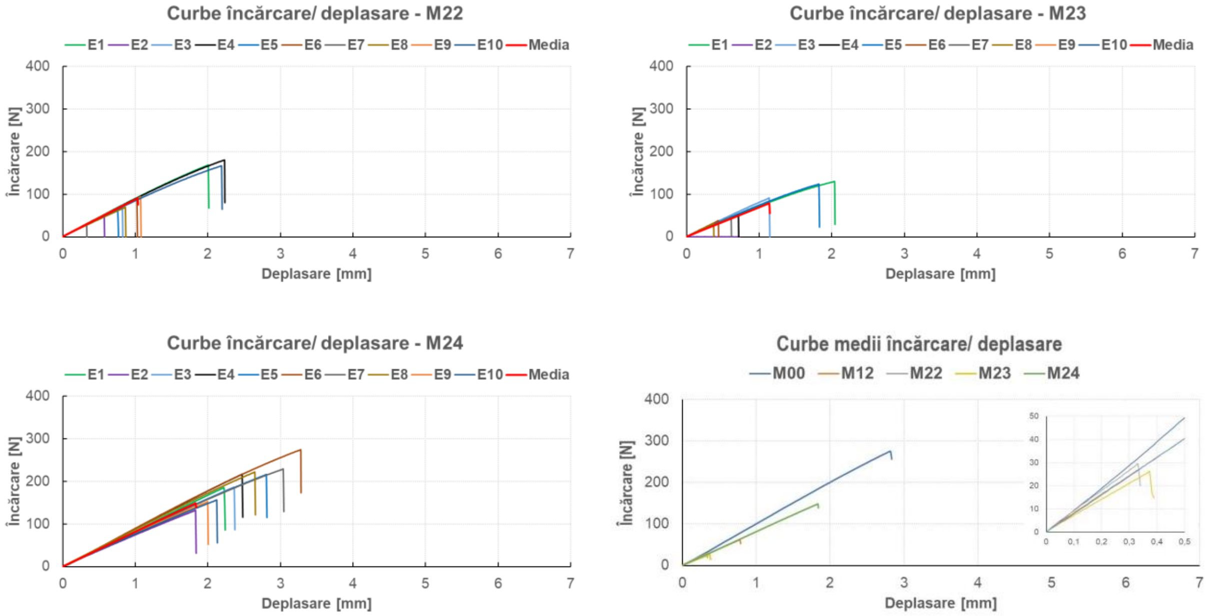

**Fig. 53.** Load/displacement curves-modified polymer materials with nano blend and M12 base

The analysis of the results obtained for the best-responding test specimens (Table 35.) does not provide sufficient details to allow the detection of conclusions.

**Table 35.** Loads [N] and displacements [mm] of the best response specimens (M12+nano)

| **material** | **M22** | | | **M23** | | | **M24** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E1(3s) | E4(6j) | E10(13j) | E1(3s) | E5(8s) | - | E6(8j) | E7(10s) | E8 (10j) |
| Load[N] | 155 | 180 | 165 | 130 | 120 | | 275 | 225 | 220 |
| Displacement[mm] | 2 | 2.4 | 2.3 | 2.1 | 1.8 | | 3.3 | 3.1 | 2.7 |

The averages of the three best responses (Table 36.) compared to the average of the three best responses of the base material confirm the statement made in the analysis of the graphical representations (the best response of the M24 material).

**Table 36.** Averages of the three best responses of the M12 and M12+nano material specimens

| **material** | **M12** | **M22** | **M23** | **M24** |
|---|---|---|---|---|
| Load(medium)[N] | 165 | 166.6 | 125 | 240 |
| Displacement(medium)[mm] | 2.7 | 2.23 | 1.95 | 3.04 |

Regarding the analysis of the possible effects of the precipitation of the constituents of the agents used to modify the properties of the polymer, in table 37. the moments of the paired samples' breaks are presented. It can be observed that only in the case of the first pair, sample E1 (sample 3s) responds better than sample E2 (3j).

For all other samples, the bottom responds better than the top. This could be a consequence of precipitation followed by stiffening of the material at the bottom. It should be noted, however, that E2 is cast first in the series of specimens used for flexural testing.

**Table 37.** Moments of rupture of the paired specimens according to the displacement of the punch–**M22**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.01 | 0.58 | 0.83 | 2.23 | 0.77 | 1.03 | 0.33 | 0.87 | 1.08 | 2.19 |

The same analysis, however, carried out on the test specimens of the material obtained by adding 3g of nanopowder mixture to the M12 material, reveals that almost without exception, the top of the sample responds better than the bottom. In this case, the viscosity of the casting mixture is higher than in the previous case, and precipitation is less likely.

**Table 38.** Moments of rupture of the paired specimens according to the displacement of the punch– **M23**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.04 | 0.73 | 1.14 | 0.72 | 1.83 | 0.44 | 0.62 | 0.38 | 0.38 | 0.38 |

In the case of the last material (modified with 5g of nanopowder mixture) the results are alternating, but the differences between the movements of the punch at breaking are not very large. This signals that the casting mixture is more stable than those corresponding to materials of the same class previously analyzed where differences of the order of 1mm and higher can also be observed.

**Table 39.** Moments of rupture of the paired specimens according to the displacement of the punch– **M24**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.23 | 1.83 | 2.37 | 2.48 | 2.81 | 3.28 | 3.04 | 2.65 | 2.00 | 2.13 |

The next class of materials – modified materials with nanopowder mixture based on material M15 (modified with lyophilized kiwi powder, starch and black clay) individual test results and average behaviors of the materials are shown in Fig. 54.

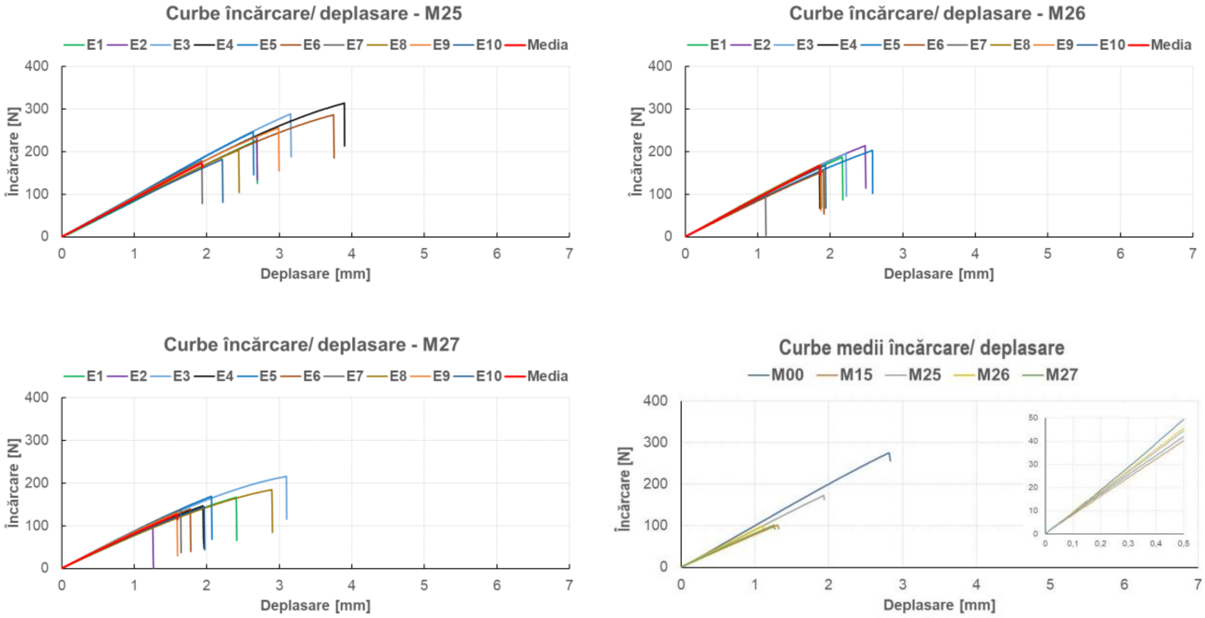

**Fig. 54.** Load/displacement curves-polymer materials modified with kiwi powder and nano blend

Table 40. includes the moments of failure of the specimens with the best responses, and a much smaller variation of the experimental data can be observed than that obtained in the case of analogous materials, but modified with sea buckthorn.

Only for the first two materials it could be concluded, that the specimens from the samples cast in the first part of the process respond better than those cast in the second part.

**Table 40.** Loads [N] and displacements [mm] of the best response specimens (M15+nano)

| **material** | **M25** | | | **M26** | | | **M27** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E4(6j) | E6(8j) | E3(6s) | E5(8s) | E2(3j) | E3(6s) | E3(6s) | E5(8s) | E8(10j) |
| Load[N] | 312 | 280 | 290 | 200 | 210 | 195 | 215 | 170 | 185 |
| Displacement[mm] | 3.9 | 3.7 | 3.1 | 2.6 | 2.5 | 2.2 | 3.1 | 2.1 | 2.9 |

As regards the averages of the three best responses relative to the average of the three best basic material responses (M15) – Table 41. – it can be verified the observation made when analyzing the graphical representations (better responses of materials with nanopowders than that of the base material). The exception is material M27 whose values are, however, close to the values of the base material.

**Table 41.** The averages of the three best responses of the M15 and M15+nano material specimens

| **material** | **M15** | **M25** | **M26** | **M27** |
|---|---|---|---|---|
| Load(mediu)[N] | 197.5 | 294 | 201.6 | 190 |
| Displacement(mediu)[mm] | 2.7 | 3.5 | 2.4 | 2.7 |

The analysis of sample pairs responses for material M25 is shown in Table 42. The first two test specimens yield at the same movement of the punch – homogeneous sample (this is the third sample), after which for the mid-process samples (6, 8, 10) The bottom has greater elasticity than the top. Only for the last sample the situation is reversed.

**Table 42.** Moments of rupture of the paired specimens according to the displacement of the punch– **M25**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.69 | 2.69 | 3.16 | 3.89 | 2.64 | 3.75 | 1.93 | 2.44 | 2.99 | 2.22 |

For material M26, the same analysis is shown in Table 43. It can be noted that, unlike the material M25 (1g of nanopowder mixture), in this case the sample 3 (high fluidity) the response of the lower part is better than that of the upper part, it can be observed, but the first cast in the mold is the lower part.

**Table 43.** Moments of rupture of the paired specimens according to the displacement of the punch– **M26**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.17 | 2.49 | 2.22 | 1.85 | 2.58 | 1.91 | 1.11 | 1.88 | 1.87 | 1.93 |

For material M27 – table 44. – the upper part responds better than the lower part (for the first three samples) and the situation is opposite for the last two. In this case, the mixture amount of nanopowders is 5g and the total amount of mixture of modifying agents is the largest.

**Table 44.** Moments of rupture of the paired specimens according to the displacement of the punch– **M27**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.41 | 1.27 | 3.1 | 1.96 | 2.07 | 1.78 | 1.64 | 2.9 | 1.59 | 1.97 |

In the case of materials modified with a mixture of nanopowders and based on material M18 (lyophilized pomegranate powder, starch, black clay), the situation of the individual responses of the samples and the average responses are shown graphically in Fig. 55.

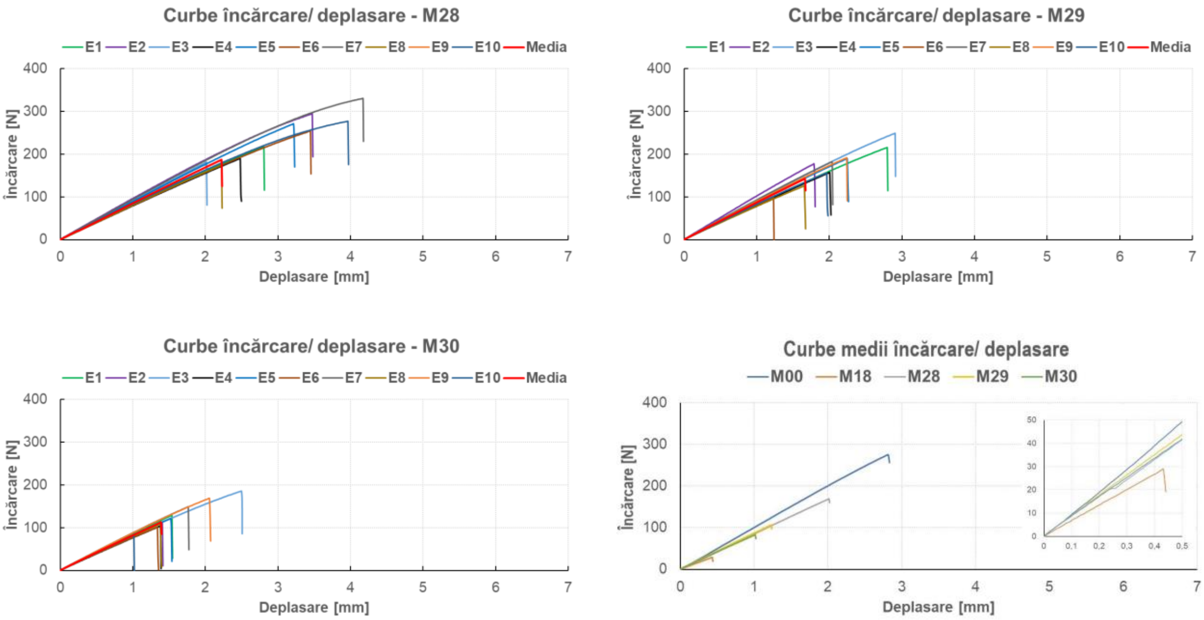

**Fig. 55.** Load/displacement curves-polymeric materials modified with pomegranate and nano blend

The analysis of the best three (two) answers - table 45. - indicates once again that the formed materials are not homogeneous - there are practically no two specimens broken at the same time for any of the analyzed materials, in addition, for this class of materials and the moments are very dispersed.

**Table 45.** Loads [N] and displacements [mm] of the specimens with the best response (M18+nano)

| material | M28 | | | M29 | | | M30 | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E7(10s) | E10(13j) | - | E1(3s) | E3(6s) | E9(13s) | E3(6s) | E9(13s) | - |
| Load[N] | 330 | 275 | | 215 | 250 | 190 | 185 | 167 | |
| Displacement[mm] | 4.12 | 3.9 | | 2.8 | 2.9 | 2.2 | 2.5 | 2.1 | |

For the average values of the best three (two) responses the data presented in table 46. confirm that M28 responds better than M18.

**Table 46.** Averages of the three best responses of the M18 and M18+nano material specimens

| material | M18 | M28 | M29 | M30 |
|---|---|---|---|---|
| Load(mediu)[N] | 302.5 | 302.5 | 218.3 | 176 |
| Displacement(mediu)[mm] | 3.76 | 4.01 | 2.63 | 2.3 |

For material M28 (1g of nanopowder mixture), it can be noted that for all samples, the response of the lower part is more elastic than that of the upper part, except for sample 10 (E7 and E8) as shown in Table 47. Perhaps the only homogeneous sample could be considered sample 8 (E5 and E6) for which the dimensional errors of specimens (the explanation was given in chapter 4) could explain the small difference between the responses the two sides.

**Table 47.** Moments of rupture of the paired specimens according to the displacement of the punch– **M28**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.81 | 3.48 | 2.02 | 2.49 | 3.23 | 3.45 | 4.17 | 2.23 | 2.23 | 3.97 |

For material M29 – Table 48. – without any exception, the upper parts of the samples are more elastic than the lower ones – probably a precipitation effect in conditions where the fluidity of the casting mixture remains high (because of the presence of lyophilized pomegranate powder). Due to the increase in viscosity, only the last sample analyzed – of the 13th – seems to be more homogeneous.

**Table 48.** Moments of rupture of the paired specimens according to the displacement of the punch– **M29**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.8 | 1.8 | 2.9 | 2.02 | 2.26 | 1.23 | 2.04 | 1.67 | 2.24 | 1.98 |

For the M30 material derived from M18 by adding 5g of nanopowder mixture – table 49., as in the case of the M29 material, the upper parts of the samples respond better than the lower ones. One cannot speak of homogeneity and, in contrast to M29, the last sample shows the greatest difference in the displacement of the punch at the moment of breaking the sample.

**Table 49.** Moments of rupture of the paired specimens according to the displacement of the punch– **M30**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.54 | 1.41 | 2.5 | 1.38 | 1.53 | 1.35 | 1.77 | 1.39 | 2.07 | 1.02 |

The last class of materials analyzed is the class based on the M21 material (modified with lyophilized grape powder, starch and black clay) to which a mixture of nanopowders is added. The load/displacement curves for each tested specimen and the corresponding mean curve are shown in Fig. 56., alongside the average curves corresponding to the epoxy resin and the base material, respectively.

It can be seen that the smallest dispersion of the experimental data corresponds to the material M32 and the fact that all class materials are less rigid than the base material. It is interesting that the most rigid material of the class is the one that shows the slightest dispersion of the data recorded experimentally.

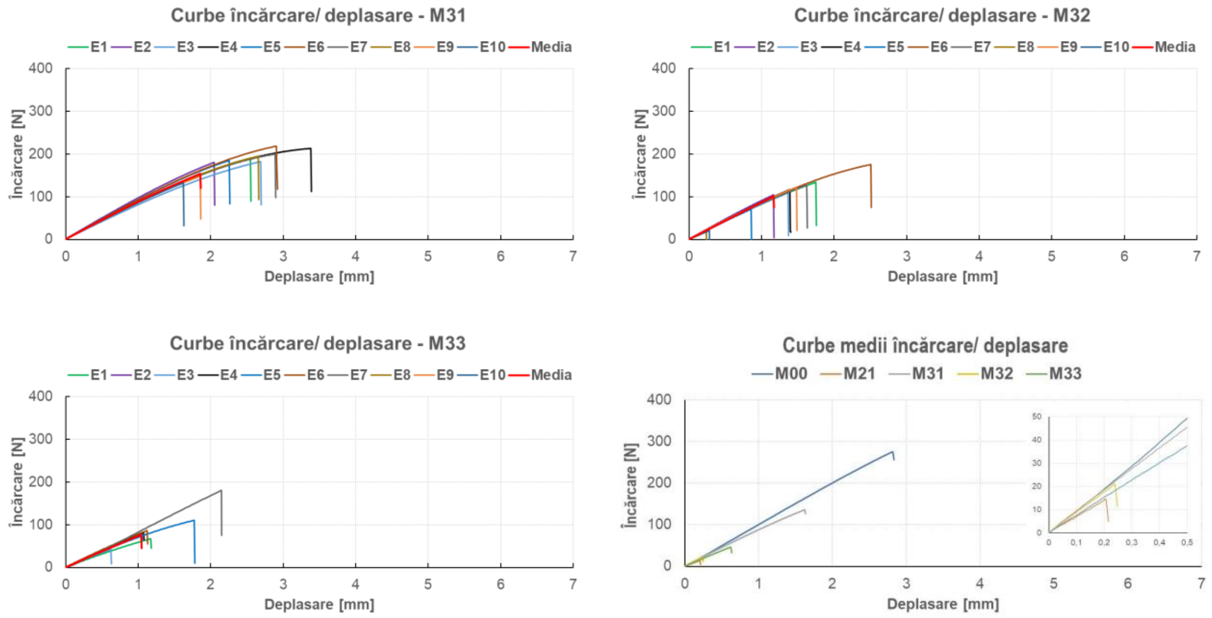

**Fig. 56.** Load/displacement curves-materials modified with grape powder and nano blend

The situation of the three best (two) answers for each material is shown in Table 50. where it can be seen that only for M31 material we were able to choose three samples with close answers.

**Table 50.** Loads [N] and displacements [mm] of the best responding specimens (M21+nano)

| **material** | **M31** | | | **M32** | | | **M33** | | |
|---|---|---|---|---|---|---|---|---|---|
| specimen | E4(6j) | E6(8j) | E7(10s) | E1(3s) | E6(8j) | - | E5(8s) | E7(10s) | - |
| Load[N] | 215 | 220 | 200 | 135 | 175 | | 110 | 180 | |
| Displacement[mm] | 3.4 | 2.9 | 2.88 | 1.7 | 2.5 | | 1.8 | 1.8 | |

The averages of the three best (two) responses to the three-point bending test are shown in Table 51., for comparison with the average of the three best answers of the core material inbending test specimens (M21). It can be seen that in terms of the best responses, the averages are decreasing (both for loading and driving), with the increase in the amount of nanopowder mixture added to the base material recipe.

**Table 51.** Averages of the three best responses of the M21 and M21+nano material samples

| **material** | **M21** | **M31** | **M32** | **M33** |
|---|---|---|---|---|
| Load(mediu)[N] | 285 | 211.6 | 155 | 145 |
| Displacement(mediu)[mm] | 3.84 | 3.06 | 2.1 | 1.8 |

The fracture analysis of the paired samples (from the same sample) is presented, for the M21 material, in Table 52. For the samples cast at the beginning of the process, the difference in displacement is relatively large, while for the last samples the differences are smaller.

**Table 52.** Moments of rupture of the paired specimens according to the displacement of the punch– **M31**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 2.55 | 2.05 | 2.69 | 3.38 | 2.26 | 2.92 | 2.89 | 2.66 | 1.86 | 1.63 |

For the last two materials: M22 (table 53.) and M33 (table 54.) it can be seen that the materials are fragile (small or very small displacements) and one could speak of material homogeneity only for the pair E3, E4 (the sample 6 – M32) and for the pair E1, E2 (sample 3 – M33).

**Table 53.** Moments of rupture of the paired specimens according to the displacement of the punch– **M32**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.75 | 1.17 | 1.37 | 1.4 | 0.86 | 2.5 | 1.63 | 0.24 | 1.48 | 0.29 |

**Table 54.** Moments of rupture of the paired specimens according to the displacement of the punch– **M33**

| Specimen | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Displacement | 1.18 | 1.05 | 0.63 | 1.08 | 1.78 | 1.13 | 2.15 | 0.6 | 0.6 | 0.6 |

The fact that in the case of the use of pomegranate and grape powders, respectively, precise conclusions cannot be drawn is probably also related to the high content of anthocyanins, polyphenols and flavonoids that interact with metals and can lead to complex structures whose behavior in liquid environment is difficult to know.

Like the materials analyzed in the previous chapter, these materials also have elastic flexural responses lower than the elastic response of epoxy resin. The slopes of the average curves, especially in the area of small deformations, are however not very different, as can be seen in Fig. 63. This observation could be explained by the fact that, at first, the response of the material is that of the polymer, after which the effect of the presence of modifying agents (defects) starts to become predominant.

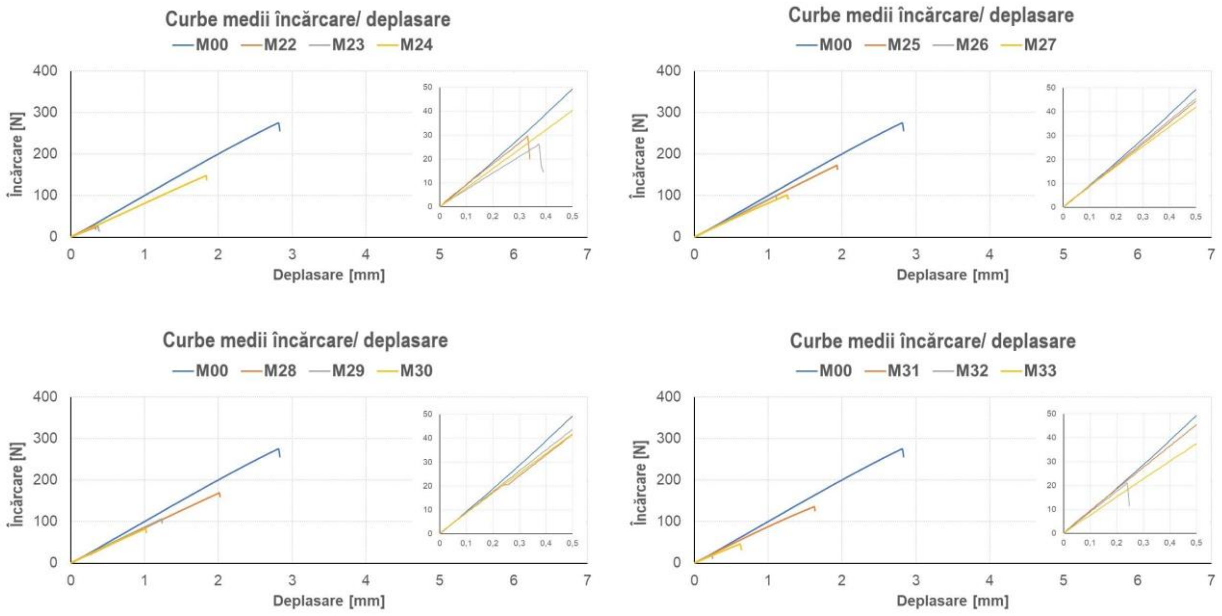

**Fig. 57.** Average load/displacement curves-polymeric materials modified with vegetable powders and nano mixture

In Fig. 57., the analysis of the materials in this chapter is carried out in terms of the response to the bending and according to the type of lyophilised powder to the same amount of nanopowder mixture added to the basic recipe. It's about the average curves, it can be noted that at each value of the amount of the mixture of nanopowders added the best answers are given by the modified materials with lyophilized kiwi powder (the closest slope to the slope of the resin epoxy). It can also be noted that the response of modified materials with sea buckthorn lyophilized powder improves with the increase in the amount of nanopowder mixture added.

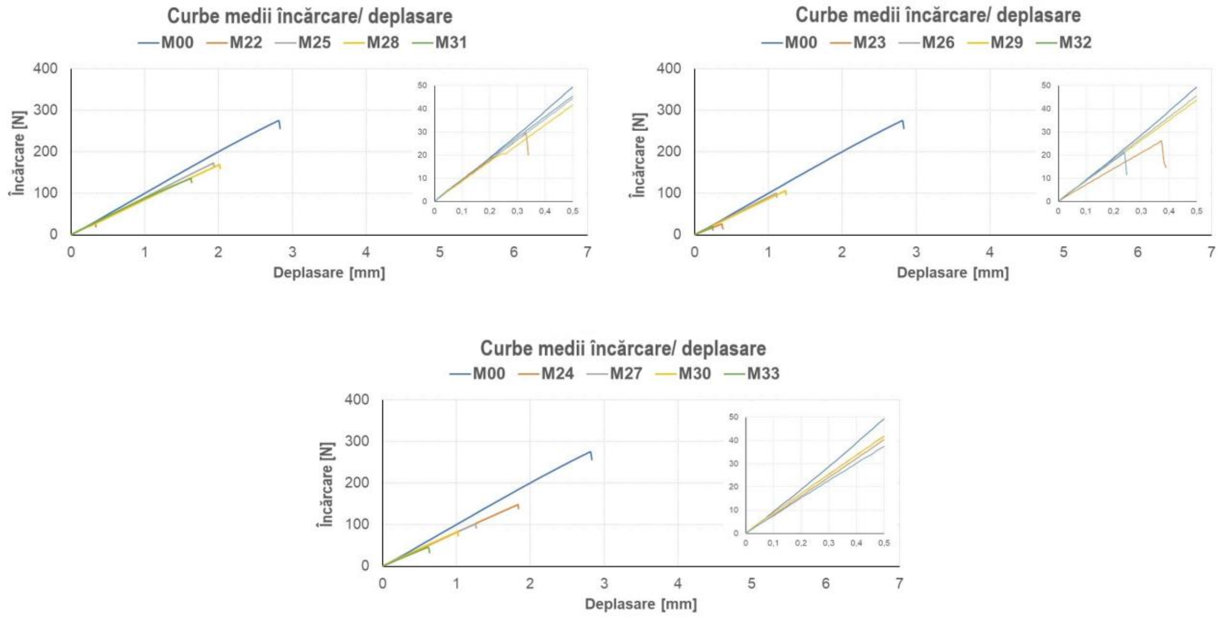

**Fig. 58.** Average load/displacement curves-materials modified with plant powders and nano blend

In table 58. the apparent flexural modulus values for the materials analyzed in the current chapter and their percentage values with reference to the value of the apparent flexural modulus of the epoxy resin are included. It is very clear that the value of the modulus of elasticity decreases, but there is no rule after which this decrease occurs.

The smallest variations (between the three values corresponding to the three amounts of the nanopowder mixture) are found when using lyophilised pomegranate powder.

**Table 55.** Flexural modulus of materials modified with plant powders and nanopowder mixture

| | M00 | M22 | M23 | M24 | M25 | M26 | M27 | M28 | M29 | M30 | M31 | M32 | M33 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **E[GPa]** | 2.77 | 2.39 | 1.97 | 2.25 | 2.49 | 2.5 | 2.26 | 2.35 | 2.37 | 2.26 | 2.45 | 2.41 | 2.18 |
| **E[%]** | 100 | 86.28 | 71.12 | 81.23 | 89.89 | 90 | 81.59 | 84.84 | 85.56 | 81.59 | 88.45 | 87.00 | 78.70 |

### 6.3.2.1. Partial conclusions – materials modified with vegetable powders and mixture of nanopowders – bending

- the bending tests (three-point bending) led to very different results and depended on the lyophilized powder used in the base material (lyophilized powder, starch, black clay), as well as the quantity of the nanopowder mixture, without a relationship of proportionality depending on this variable, for all the materials analysed;
- the best responses correspond to materials modified with lyophilized kiwi powder and these improve with the increase in the amount of nanopowder mixture added to the basic recipe (M15 – Chapter 5);
- in the case of materials modified with sea buckthorn powder, the answers are all the better as the amount of nanopowder mixture is smaller;
- for the other two classes of material it is very difficult to find a link between the response to the bending and the parameters analyzed previously;

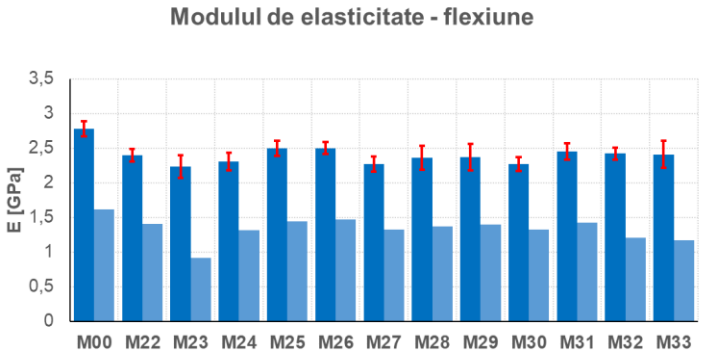

**Fig. 59.** Flexural modulus of polymeric materials modified with plant powders and nanopowder mixture

- as for the apparent flexural modules – calculated directly by the soft-ware application that controls the test machine – they are shown in Fig. 59.;
- analyzed from this perspective, the changes do not seem very important, but the problems are related to the stability of the responses of the specimens and the fact that, in the case of flexural tests, the specimens from the same sample have different responses;
- if the magnetic and electrical properties of these materials prove valuable, then a more extensive study looking at the amount of starch to add to recover the modulus value.

### 6.4. Conclusions – materials modified with lyophilized and nano powders

- SEM analysis of complexly modified materials, by adding to the basic recipe (epoxy resin modified with lyophilized powder, starch and black clay) the quantities, set at the design of the research, the, the mixture of nanopowders (1g, 3g, 5g) does not reveal agglomerations of modification agents, which would mean that the proposed recipes are effective;

- the appearance of the surfaces investigated by electron microscopy (resulting from the bending fracture of a specimen of each material) depends on the type of lyophilised powder used (as in the case of the materials analyzed in Chapter 5);
- no massive clumps of nanometric granules are found, which means that the mixture of modifying agents (lyophilized powder, starch, black clay, nano-graphite, nano-silver, nano-ferrite, nano-ferite, nano-ferrite, tungsten nano-carbide) made in an electric coffee grinder, it was a mixture well enough mixed so that all its components were equally present in all volume (despite the different densities of the powders used);
- the tensile tests led to obtaining scatters of the experimental data – dependent on the properties of the vegetable powders, but also on the amount of nanopowder mixture added to the base material;
- this type of analysis would lead to the conclusion that the formed materials have no mechanical properties worthy of attention, but the analysis of the tensile modulus of elasticity shows that the largest reductions in the value of this parameter, relative to the value of the tensile modulus of the epoxy resin, are about 35%;
- if the formed materials have remarkable electrical or magnetic properties, then the value of the stretch elastic modulus can be adjusted by increasing the amount of starch (according to the studies conducted by Vasile Bria, according to the, also at CCDCOMT) or by using any of these materials as a matrix for a fabric-reinforced composite;
- the analysis of the dependence of the properties (modulus of elasticity) depending on the moment of casting of the sample reveals small differences between the responses of the different samples, but no conclusions can be drawn regarding the causes of these differences, since the powders used change in various ways the fluidity of the pre-polymer mixture and, in following the interaction between them and the chemical constituents of the epoxy resin, changes appear that are difficult to explain;
- the bending tests, like the tensile ones, led to scattered results, in the material analysis these scatters appear to be significant, but – as in the case of the tensile tests – the maximum percentage reduction in the value of the flexural modulus of elasticity, compared to the value the same parameter for the epoxy resin, is 29% and represents an isolated case among the twelve materials analyzed (M23);
- analyzing the data presented in Fig. 52. and Fig. 59., it can be seen that the standard deviations of the calculated values (automatic calculation) are not very large, but reflect the dispersions of the recorded experimental data.

## 7. Personal contributions, conclusions and future research directions

We formed hybrid organic-inorganic polymeric materials to analyze several factors. The modifiers added in different concentrations primarily have the role of preventing agglomerations in the material of some nanopowders that could be used to regulate the behavior of the composite from the perspective of physical properties.

The formation of hybrid polymer materials was carried out according to the pre-established objectives. The use of polypropylene tubes as a mold, facilitated the removal of the material without damaging it. This method is constantly being used at the CCDCOMT research excellence centre (Research and Development Centre for Composites with Thermo-Matrix).

The processes of obtaining metal nanostructures, as well as their stabilization after forming, involve complex apparatus, and generally the quantities of nanostructures obtained are very small. Then once obtained and stabilized, they must be extracted from the colloids in which were formed – other complex equipment.

From previous studies conducted at CCDCOMT we knew that clays can be used to modify the properties of an epoxy resin, so, I decided to carry out a comparative analysis regarding the use of three types of clays (all cosmetic use) in three different concentrations to modify the properties of the Epiphene RE4020-DE4020 epoxy system (most used in studies conducted at CCDCOMT).

- we have established the strategy of casting the samples, so that the required number of samples for the tensile tests and the flexural tests is ensured;
- we formed and consolidated (through heat treatment) the formed samples and subsequently prepared the samples for the respective tests;
- although, as we pointed out in Chapter 3, we took great care to separate large aggregates from the three clays before dispersing them into the pre-polymer mixture, we found that during pouring in the mixing bowl, with the passage of time not only the viscosity of the mixture changes, but also a precipitation of some clays aggregates occurs;
- to avoid this problem, for the next stage of the study, I decided to also use starch to increase the viscosity of the pre-polymer mixture;
- flexural tests (three-point bending) - also performed on five samples of each material - indicated an increase in the value of the flexural modulus of elasticity (for all materials modified with clays) in relation to the value of the same parameter for the resin epoxy - Fig. 66.;

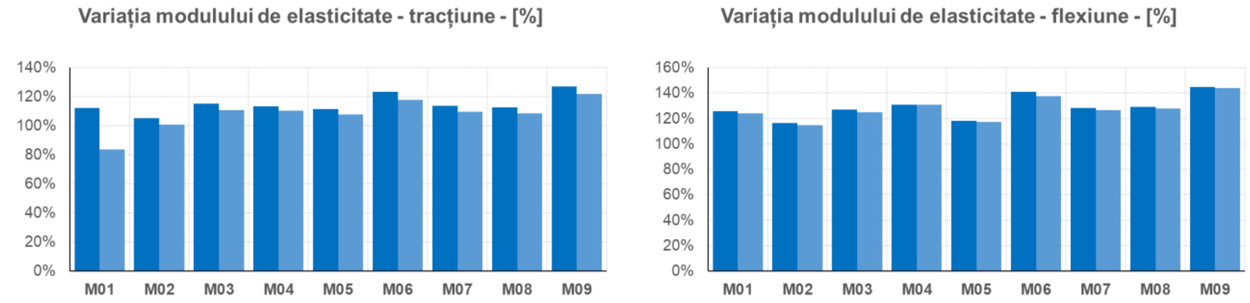

**Fig. 60.** Percentage variations of elastic moduli compared to epoxy resin

* a very interesting study that could provide additional data would be the one in which to use only the mineral phase of clay – that is to say, it should be used as a modifying agent only after a heat treatment to ensure the destruction of the organic phase, thus correlations could be found between the results obtained for the materials formed and tested in this study;

- for these materials we also did a complex tribological study in which three samples from each material (out of 10) were tested, in pin-on-disk geometry, to determine the sliding friction coefficient and the wear rate on three types of discs – brass, aluminum and steel and in three different tribological regimes, the results of these tests are published in the article mentioned in the text;

- the following materials were those modified with lyophilized powders of sea buckthorn, kiwi, pomegranate and grape, respectively, and when they were formed we found the different effect they have on the viscosity of the pre-polymer mixture;
- to ensure some control over the viscosity I decided to use starch (based on a study by Vasiel Bria) – this is how the materials modified with lyophilized powder (each of them) and starch appeared;
- tensile and flexural tests (despite the large variations in individual behaviors) indicate that, for the materials modified with lyophilized plant powders, the recorded results lead to lower values of the respective elastic moduli, compared to the epoxy resin, for which we recorded a value of 2.76GPa in tension and 2.77GPa in bending – Fig. 67.

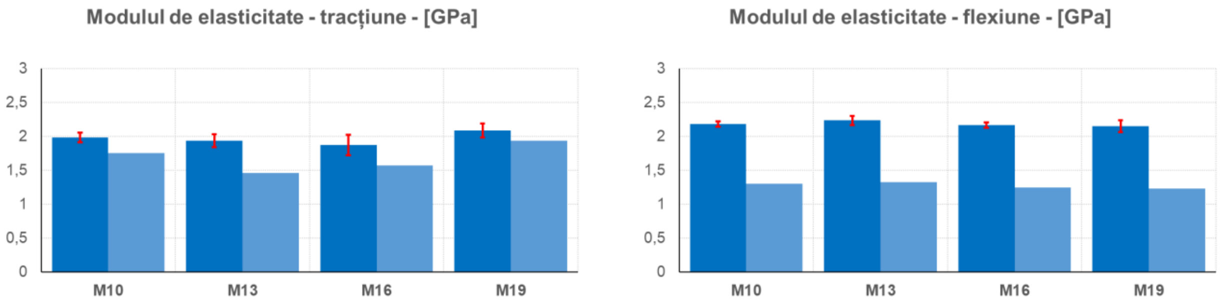

**Fig. 61.** Tensile and flexural modulus of elasticity-materials modified with vegetable powders

- the reductions seem to be unrelated to the type of lyophilized vegetable powder – in the case of bending, while in the case of stretching the differences seem to be determined by the nature of the powder;
- after adding starch to the modification recipe, the values of the elasticity modules are modified - Fig. 68., as expected, although, in the case of stretching, the changes are not spectacular;

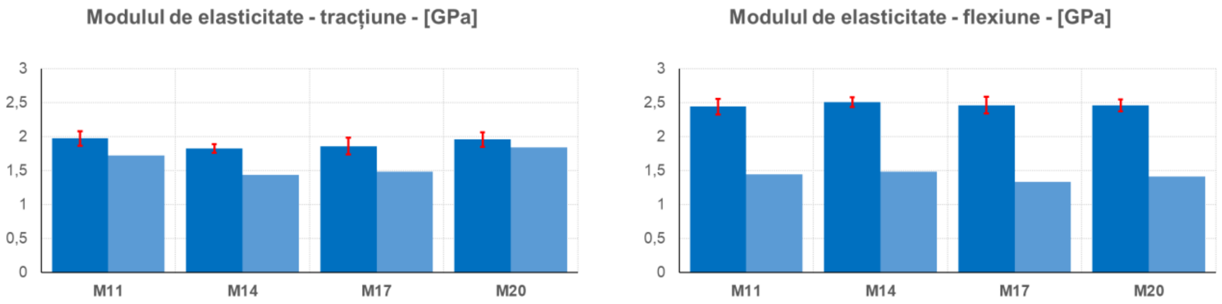

**Fig. 62.** Values of modulus of elasticity-materials modified with vegetable powders and starch

- in the case of bending, the presence of starch produces a considerable increase in the value of the modulus of elasticity, the responses of the materials remaining, however, similar;
- a first conclusion would be related to the fact that the addition of lyophilized plant powders produces a reduction in the values of the elasticity modules of the materials (compared to epoxy resin) regardless of the nature of the powder used (the variations being very small);
- before being dispersed in the epoxy resin - the freeze-dried powder and the starch were homogenized in the grinder, this homogenization, it is possible, produced reactions to generate some organic structures (water from the vegetable powders and starch) to be dispersed with high efficiency in the polymer matrix and leading to the effect on the flexural modulus;

- the results of the stretching and bending tests - Fig. 69. – indicates reductions in the flexural modulus of elasticity, but it does not seem that the presence of clay would have a major effect on the values of the tensile modulus of elasticity;

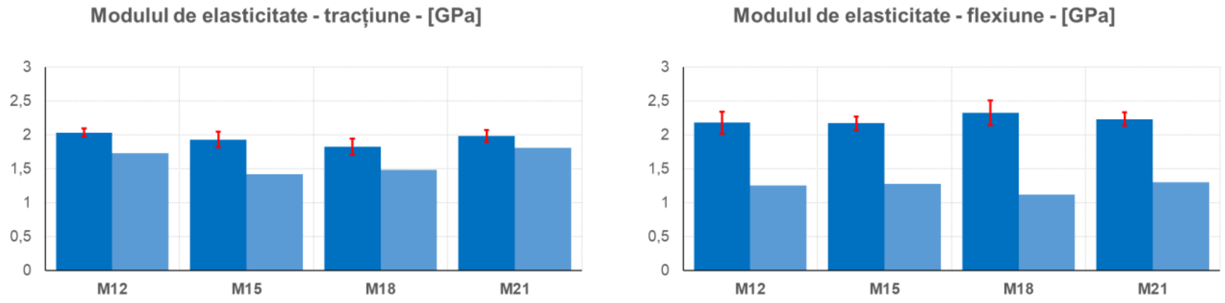

**Fig. 63.** Modulus of elasticity values-materials modified with vegetable powders, starch and clay

* the choice of nanopowders was made for their special properties and an investigation of the electrical and magnetic properties of the formed materials is required;
* the presence of so many modification agents (even if, in total, the quantities used are small in relation to the polymer mass) certainly also produces changes in the thermal behavior of materials, including, thus, a study on the specific heat of materials and their linear thermal expansion coefficient is absolutely necessary for validation;
* here another problem arises - what happens to the material if, with the increase in temperature, the degradation of the organic components of the modifying agents occurs? Do the mechanical, electrical, magnetic and thermal parameters change?
- for the materials with the smallest mass of nanopowder mixture added, the situation is shown in Fig. 70. and indicate slight increases in the values of the two modulus of elasticity, compared to the corresponding values of the base materials (Fig. 69.);

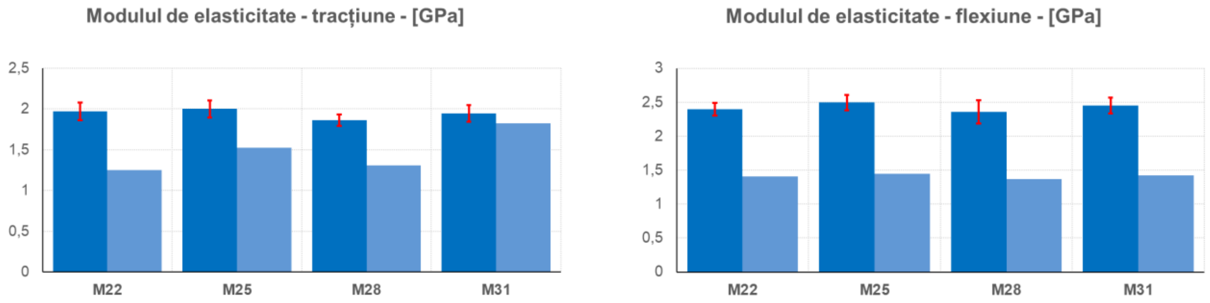

**Fig. 64.** Moduli of elasticity of materials modified with 1g mixture of nanopowders

- and in this case the explanation could come from the presence of nanographite, but the hypothesis of chemical interaction between the phytochemical agents present in the plant powders and the constituents of the nanopowders should not be ruled out;
- all materials have these ratios, the differences between their mechanical responses are given by the different properties of the freeze-dried powders that interact in different ways or in different proportions with the constituents of the nanopowder mixture;
- under the conditions shown above, the mass rate of each component of the nanopowder mixture in the final material is 0.00092 (0.092%) for materials with 1g of mixture, 0.0028 (0.28%) for materials with 3g of mixture and 0 .0048 (0.485) for materials modified with 5g nano mixture;
- analyzing the data from Fig. 71. it can be observed that with regard to the tensile modulus of elasticity, there are increases in the values and the responses of the materials are almost uniform, while for the values of the flexural modulus of elasticity, the situation is oscillating –

decrease for materials with pomegranate, increase for materials with kiwi, practically the same value for the pomegranate materials and a slight decrease for the grape modified materials, all with reference to the values recorded for the corresponding materials modified with only 1g of nanopowder mixture;

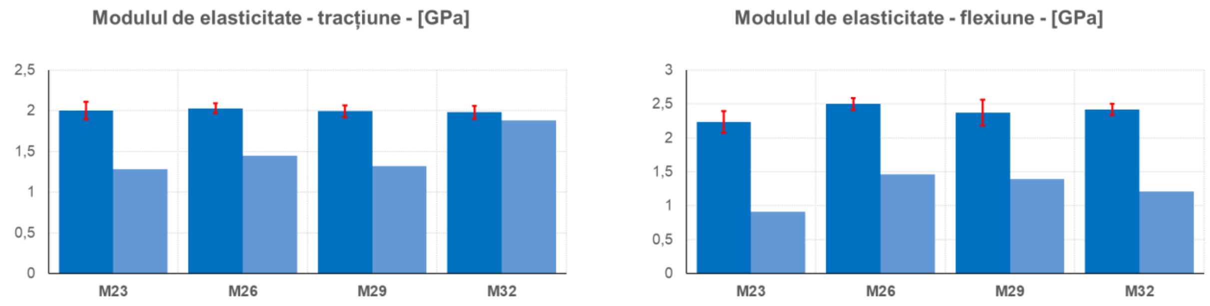

**Fig. 65.** Moduli of elasticity of materials modified with 3g mixture of nanopowders

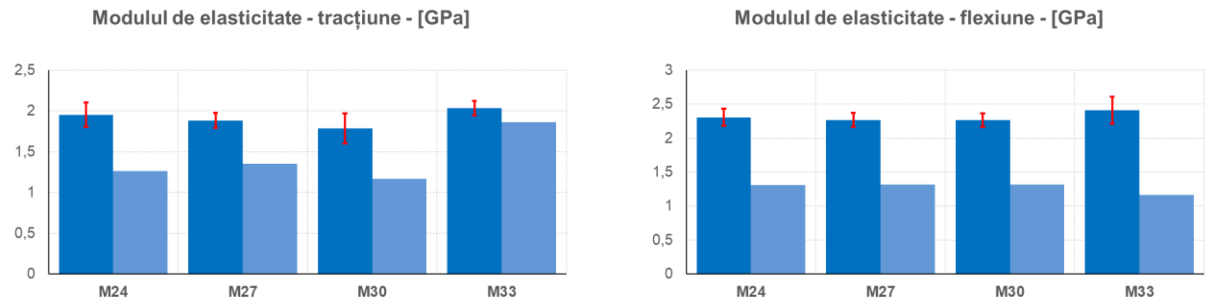

**Fig. 66.** Moduli of elasticity of materials modified with 5g mixture of nanopowders

- all these judgments are made by comparison within the class, when comparing with epoxy resin the changes, as I stated above, are important;
- if we were to compare the modulus values of these materials with the modulus values obtained for materials modified with clays, we would find even more important reductions;
- the addition of starch and clay aimed to control the viscosity of the pre-polymer mixture in order to disperse the nanopowder mixture;

* a study in which only the lyophilized powders and the mixture of nanopowders with variations of their mass presence in the final material would be interesting;

* another study that definitely needs to be done is the one aimed at the uniformity of dispersions using vegetable powders, clay (or its mineral component) and the mixture of nanometric powders;

* surely an analysis of the compressive properties could generate results that can be explained by the interactions between the components of the modification mixtures or between them and the chemicals that make up the formulations of the two components of the epoxy system;

- I believe that the idea of increasing the uniformity of nanopowder dispersions in epoxy resin using lyophilized plant powders has been confirmed and this is a success;
- I think this study is a success if not from the perspective of the materials formed, from the perspective of the experimental data obtained, but I am not the one who has to decide.

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