IOSUD – UNIVERSITATEA „DUNĂREA DE JOS” DIN GALAȚI

Școala doctorală de Inginerie Mecanică și Industrială

ABSTRACT

A study regarding mechanical properties of fabric reinforced composites with thermoset matrix

Doctoral student,
Tamara APARECI (GÎRNEȚ)

Scientific coordinator:
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Seria I6 Inginerie Mecanică Nr 67
GALAȚI
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Scientific references,	Prof univ. dr. ing. Anton HADĂR
	Prof univ. dr. ing. Dan-Mihai CONSTANTINESCU
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nr. 20 / 6.01.2023

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

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

având în vedere referatul conducătorului științific Prof. univ. dr. fiz. Adrian CÎRCIUMARU cu numărul C93/05.01.2023, privind propunerea comisiei de susținere publică a tezei de doctorat;

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2. Conducător de doctorat	**Prof. univ. dr. fiz. Adrian CÎRCIUMARU** Universitatea „Dunărea de Jos" din Galați
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Art. 2. Şcoala doctorală de Inginerie mecanică şi industrială, Secretariatul doctorat, Biroul salarizare şi Serviciul financiar vor duce la îndeplinire prevederile prezentei decizii.

RECTOR,
Prof. dr. ing. Puiu-Lucian GEORGESCU

Content

Introduction

The need to create and produce new materials even through non-conventional technologies is determined not only by economic and social causes but also by the fact that, in the conditions of the continuous development of traditional production, a deep crisis of raw material and energy resources has appeared, with the increase in aggression towards the environment.

The rapid spread of polymer composite materials in today's markets requires not only innovations in technological processes but also the modernization of existing polymer processing technologies to allow them to expand into more branches of social life.

When designing composite materials, a fundamental aspect is related to knowing the level at which the materials used are chemically compatible so that a quality interphase is established between the components. This is due to the fact that the possibilities of changing the composite phases and the phase joining and forming techniques are practically infinite. It is obvious that in certain circumstances, the combination of two or more different materials can have better results than in the case of using individual materials. If the materials do not interact it is easy to assume that there will be no interface. For example, the fibers or reinforcing elements will be surrounded by matrices having at most contact points but without creating a continuous surface to ensure the transfer of loads between phases [1].

The evolution of knowledge in the field of engineering was and is possible simultaneously with the emergence of new materials and technologies, with the promotion of superior structural systems and with the ability to use complex analysis and analytical calculation procedures. Composite materials incorporate all these qualities and represent the future of engineering.

The technology of forming composite materials has been developed during several years of research in this field of activity. Considerable efforts have been made in recent years to improve the quality and reliability of thermoset polymer composite materials.

Composite materials are studied by scientists because of their unique properties. The researches are thorough given the fact that the main goal is to replace traditional materials (most often metals) with composite materials, because they have a lower density, are more resistant to various chemical agents, have a longer service life, are easy to replaced and have lower costs.

Generally speaking, polymer composite materials are nothing but a giant step in the effort to achieve high performance materials. This natural way of increasing demand led to the birth of a concept, that of combining different materials into an integral composite material, to meet the demands of the user. Due to the complexity of modern mechanical structures, the replacement of classic materials with unconventional ones has become a necessity. Most of these non-conventional materials are represented by composite materials. Their mechanical, electromagnetic and thermal properties can be designed and obtained according to the objectives pursued. Their properties depend on the types of reinforcement, the nature of the matrix, the quality of the matrix-reinforcement interphases, the orientation of the fibers, and last but not least, the forming technique.

Currently, it is known that technological development depends on the progress achieved in the field of composite materials. The worldwide development of new materials research is today especially encouraged by the recent and impressive evolution in the field of micro and nanotechnologies, a field of great topicality, with the greatest dynamics and with a revolutionary impact on industry and society for the next decades.

Composite materials, in recent years, are used more and more often in various industrial branches. These are: naval, aeronautical, chemical, in the transport industry, in the manufacture of furniture as well as for decorations, in medicine, in construction, in the context of the modern world, the sports equipment industry (bicycles, protective equipment, skis, etc.). The progressive use in these fields is due to their superior characteristics most of the time, such as the reduction of energy consumption in obtaining them, corrosion resistance, high temperature resistance, wear resistance, tear resistance, etc. [2].

The choice of the material and its processing is a complicated but very important step for the performance required by the end user. The most common composite materials are those with a polymer matrix comprising a wide range of long fibers, short fibers and powders bound together by the polymer matrix.

Matrix - represents the second basic element of composite materials due to its very good chemical, mechanical and electrical characteristics. In the process of forming polymer composite materials, two types of matrices are differentiated (thermoplastic matrices and thermoset matrices). The technique of forming thermoplastic matrices involves melting the raw material followed by polymerization and cooling of the material in the mold. In the case of thermosetting matrices, the polymerization is carried out by adding a hardener (most of the time).

Composite materials represent a permanent new topic among research subjects from the perspective of the multiple possibilities offered by the design of their properties. In this context, the present study proposes to investigate the effect of alternating polymers in the realization of a fabric-reinforced composite. This represents a way of intervention to change the properties of a composite at certain levels (on its thickness, for example). A similar topic was researched by Radu Bosoancă, also at the Research and Development Center for Thermoset Matrix Composites (CCDCOMT). The use of two or more polymers means different qualities of the matrix-polymer interphase but also areas where the two polymers (or two of the polymers) are adjacent forming a junction that ensures (or not) the transition from the properties of one to the properties of the other .

For this study I had to inform myself and I did an extensive bibliographic research to find out if there are any scientific approaches for such an analysis. The realization of the materials was possible because at CCDCOMT we found both the necessary fabrics and polymers. I was quite well prepared (during my master's degree studies) for the formation of the materials, but their variety managed to surprise me. We designed six reinforcement systems and used three polymers to make the composite matrices. So the workload was enormous.

I chose to study and research a subject from the issue of composite materials because composites research tends to be more and more developed at the present time. The creation of reinforced materials had to be completed with an analysis of the polymer junctions of the polymers used for the formation of reinforced composites. For this reason, in this paper, two important parts can be distinguished – the study of polymer junctions and the study of reinforced composites with stratified matrices.

In addition to the mechanical properties (resistance to various types of static tests) the physical properties of such materials are also important. Maybe not necessarily in this case, when three epoxy resins are used, but for cases where the matrix layers would be made of different polymers, obviously with the aim of improving a response of the material to some external action. One can imagine outer layers of more elastic polymers (silicone or polyurethane resins) and inner layers of stiffer polymers. Certainly, in such cases, a more complex study would be necessary both in terms of fabric-reinforced composites and in terms of polymer junctions. The junction of two polymers with different expansion coefficients, for example, can lead to undesirable mechanical effects, generated by internal stresses that occur during heating.

Chapter 1

Researches on Fiber and Fabric Reinforced Composites

1.2. Applications of fiber reinforced polymer composite materials

E. Triki et al [124] studied the dependence of the interlaminar tear strength of E-glass fabric/polyester composite laminates on the ply orientation. According to the results, fabric laminates show much higher GIIC values, fabric composites have inherent roughness, resin-rich regions, and a large fracture surface due to the undulating pattern of yarns and delamination of multiple crack fronts.

Ali Tabatabaeian, and Ahmad Reza Ghasemi [126] studied the curvature changes and mass loss of nano-composite plates with different epoxy resins. The experimental results showed that regardless of the type of resin, the mass of the composite materials decreases with the increase in the number of thermal cycles. It can be concluded that the addition of nanoparticles leads to a decrease in the weight loss percentage of the nano-composites under thermal fatigue conditions. It was observed that the number of thermal cycles is a more noticeable parameter on the percent weight loss of the composites than the addition of nanoparticles.

Bo Yang et al [129] analyzed the nesting effect on laminates. They found that compared to increasing the length of the main flow channel, decreasing the width is a more significant factor in reducing through-thickness permeability. The results also show that a considerable degree of nesting can occur due to unidirectional displacement, the total thickness can decrease by up to 5-6%, and the through-thickness permeability reduction can reach up to 80%. Bidirectional fabric displacement leads to a greater degree of nesting, the total thickness decreases by more than 12%, and the through-thickness permeability decreases by more than two orders of magnitude.

Silvio Leonardo Valença et al [132] evaluated the mechanical behavior of epoxy composite reinforced with plain Kevlar fabric and glass/Kevlar hybrid fabric. Thanks to the values obtained after the mechanical tests, it can be seen that the structures developed with Kevlar and glass fiber hybrid fabrics have transferred the highest values of mechanical strength and specific stiffness, becoming a new alternative for use as a structural laminated composite in the industrial market.

V. Velmurugan et al [134] performed an experimental evaluation of the mechanical properties of natural fiber reinforced polymer composites. The authors found that jute reinforcement with nylon fillers showed higher flexural strength compared to the combination of nylon and spider silk fillers in the flexural test. Reinforcement of the composite with spider silk and nylon fillers with epoxy matrix achieved higher toughness, and reinforcement with jute and nylon fillers with epoxy matrix achieved higher flexural and tensile strengths.

Kyle C. Warren et al [135] investigated three-dimensional woven composites. This extensive experimental study was based on composites reinforced with three-dimensional woven preforms subjected to shear, compression and in-plane shear loading. In addition, a two-dimensional quasi-isotropic woven material was evaluated for comparison. Loads were applied in both the warp and weft directions for tensile and compressive loading. The orthogonal woven material was found to have both higher strength and modulus in tension and compression, although a woven architecture with larger layers was found to outperform the rest of the three-dimensional architectures.

Jun Misumia and Toshiyuki Oyama [140] produced a modified low-viscosity, high-strength epoxy resin by the in situ radical polymerization method to improve the mechanical properties of carbon fiber reinforced plastics. In order to achieve both good mechanical properties including the strength and toughness of the cured resin and reduced viscosity in the uncured resin composition, the “radical in situ polymerization method” was applied to the epoxy resin for the CFRP matrix. The results demonstrated that the “radical in situ polymerization method” can be effective for improving the fracture strength of CFRP laminates while maintaining the low viscosity of the resin composition.

Mireia Olave et al [141] tested the mode I fatigue fracture resistance of woven laminates. Two woven laminates reinforced with T700 carbon fiber and epoxy resin with different pull size (3K/12K) were evaluated. The higher percentage of matrix at the crack front can delay the onset of fatigue. The 3K material shows a higher fatigue delamination threshold value than the 12K material. The differences generated by the nesting effect show no visible changes in the curves. For woven materials, unit cell size and configuration type do not affect the slope of the delamination rate. All types of materials show very similar values.

M. D. Kiran et al [142] evaluated the breaking strength of carbon fiber and epoxy composite with different carbon fiber thicknesses. The composites were fabricated using hand-stretching technique by infusing 200gsm, 400gsm resin and hybrid carbon fabric laminate. The fracture toughness of the hybrid carbon fiber composites was studied using the single-edge notch test method at room temperature (25°C). From the experimental results, it was found that the epoxy composites reinforced with 200gsm carbon fiber resists breaking better compared to the composites reinforced with other fibers.

Sadia Tasnim et al [144] developed lightweight polymer composites containing various solid wastes as fillers. The authors used unsaturated polyester resin as binder and used tire rubber core, recycled polyethylene terephthalate (PET) flakes and fly ash as fillers. The use of jute fabric increased the flexural strength and strength of the polymer composites. Microstructural analysis reveals no additional substance other than the binder and fillers, indicating no reaction of the fillers with the resin in the composite. Polymer composites containing shredded rubber and PET flake fillers exhibit higher strain capacity at maximum flexural load than their composite counterparts containing hybrid fillers.

Sunil Manohar Maharana et al [145] studied the moisture absorption behavior of hybrid composite consisting of jute and Kevlar as reinforcing fibers, fumed silica as nanoadditive and Epoxy Ly-556 as matrix. Following the tests carried out, the authors found that the surface exposure of jute fibers in a humid environment greatly affects the rate of water absorption, and the mass percentage of the filler greatly influences the moisture absorption properties. The moisture absorption rate decreased to 3% of the filler; subsequently, moisture absorption increases due to excess filler.

S. Dai et al [148] fabricated six types of 3D woven composites of carbon fiber and epoxy resins. They studied the influence of fiber architecture on the tensile, compressive and flexural behavior of 3D woven composites. Four orthogonal weaves and two blocking angles were tested with the primary loading direction parallel to the warp direction. The mechanical performance was found to be affected by the distribution of resin-rich regions and the waviness of the load-bearing fibers, which were determined by the fiber architectures. The bond points in the resin-rich regions were found to be the sites of damage initiation in all fabric types under all loading conditions, which were confirmed with both visual observation and correlation strain maps with digital image.

Mehmet Karahan et al [149] performed an evaluation of the internal geometry of 3D orthogonally woven carbon fabric composite material without crimping. According to the results, it was found that the obtained detailed parameters of the internal fiber architecture of a representative 3D orthogonal fabric carbon fiber composite without crimping demonstrate high in-plane yarn straightness and high uniformity of the composite reinforcement geometry. Specifically, typical coefficients of variation in the composite were measured as 3–4% for wire spacing, 4–5% for wire width, 6–8% for wire thickness, and 2–6% for interior fiber volume fraction. These variations are much smaller than the respective variability parameters observed for typical 2D woven carbon fabric composites. There are significant variations in fiber volume fraction between different layers of warp and filling yarns.

N. Blanco et al [150], [151] characterized the intralaminar fracture toughness of woven composite laminates. The intralaminar fracture strength of 5HS-RTM6 carbon fiber fabric and epoxy composite material was experimentally characterized using double tapered compact tension specimen (2TCT). This geometry model was found to achieve lower values for the failure indices described in the first part of the article. Two different material configurations were considered: one with the material warp direction parallel to the applied load direction and the other one with the material warp direction perpendicular to the applied load direction. The values obtained for the intralaminar fracture strength in mode I were similar for both configurations.

Ilyani Akmar Abu Bakar and his collaborators [155] presented a genetic algorithm for the optimization of fabric composites, able to address both the choice of the elastic constants of the constituents and the fabric model. The composites thus obtained show an acceptable strength performance, with considerable values of elastic properties and tightness to the fabric. The best model not only offers high elastic properties, but also could minimize the resistance problem due to a high tightness to the fabric. TexGen and ABAQUS software are ideal for this analysis.

H. M. Y. C. Mallikarachchi [158], examined the micro-mechanical behavior of two-layer plain weave laminates. As a result of the tests carried out, it was proven that the relative positioning of the individual layers influences the axial and direct bending stiffness. In general, staggered arrangement provides higher bending stiffness and lower axial stiffness, which can be useful in certain design criteria.

S. Senthil Gavaskar and S. Madhu [160] studied the torsional and compressive properties of cylindrical glass fiber reinforced polymer composite. The authors used types of fiberglass fabrics that include pure form of unidirectional fibers, veil mats and fabrics. The result of the study shows the influence of different layers of fiberglass fabrics on their strength and the possibility of replacing metal shafts that transmit low powers with composite shafts (GFRP).

In [161], the authors designed a carbon fiber-reinforced trifunctional polymer for strengthening and protecting reinforced concrete structures. In this paper, long-term performance tests demonstrated that CFRP can not only work as a reinforcing material for reinforced concrete (RC), but can also work simultaneously act as a protective coating and anode cathodic protection (ICCP), protecting steel reinforcements from corrosion. The CFRP coating has been shown to be a partial protector, reducing the corrosion of steel reinforcement. At a low current density of $20 mA/m^2$, ICCP-induced CFRP damage was avoided, enabling long-term mechanical strengthening of RC structures.

Marina Bunea et al [180] investigated the low-velocity impact response of fabric-reinforced hybrid composites with layered epoxy matrix. Impact tests were performed with the low weight impact system at 90,629J of energy level. The results showed that the matrix properties have a great influence on the fracture mode of the hybrid composites, while the defect degree of the damaged areas depends on the fiber orientation. The highest impact resistance was obtained in the case of hybrid composites with 0° layer orientation. The researchers observed that composite materials with ply orientation at different angles suffered more severe damage due to the propagation of delamination along the fiber directions.

Bîrsan and his collaborators [181], performed DSC and TMA analyzes for epoxy composites reinforced with carbon fabrics, aramid fiber fabrics, glass fiber fabrics and hybrids with loaded or unloaded layered matrices. The authors found that, in the case of the epoxy matrix, the added fillers reduced the thermal coefficient of linear expansion and had an

In [183], Bosoancă et al analyzed the tensile behavior of four fabric-reinforced composites with four different epoxy resins as matrices. Thermal measurement shows that there are differences between thermally cured reinforced materials and those that are naturally polymerized. The mechanical behavior of the materials, given by the average curves, presents for each material six passages. From these passages, the second corresponds to the elastic response of the composite material, while the sixth represents the elastic response of the fibers. The highest value of the elastic modulus is achieved for the Epiphen RE4020-DE40202 epoxy system and corresponds to the less brittle matrix (for both materials - the one strengthened by heat treatment and the one that is naturally polymerized).

The forming technique could explain the twisted appearance of the 45° tensile tested specimens due to the double corrugation of the fabric layers. The number of 45° specimens of different types (during tensile tests) could be explained by the massive presence of fibers oriented at 45° with respect to the loading direction. Within the CCDCOMT research center, various studies on fabric reinforced materials have been carried out [186]–[200].

1.3. Conclusions

- composite materials show a wide interest for researchers who approach a problem that starts from the matrix, reaches the reinforcement and the characterization of the materials;
- many researches take in consideration composites with polymer matrices - be they thermoset or thermoplastic;
- working models and interpretations of the results are proposed which, within certain limits, are acceptable and here we refer to the ranges of values that some characteristic parameters of the mechanical responses of the composites can take;
- many studies refer to the matrix-reinforcement interphase (or other elements immersed in the polymer) to increase the utility value of the composites;
- I did not find bibliographic references regarding the analysis of the properties of polymer junctions, although in the design of the properties of composites a solution is to use layered matrices;
- some studies carried out at the Research and Development Center for Composites with Thermosetting Matrices (CCDCOMT) aimed at the analysis of composites with a layered matrix consisting of the same polymer but modified differently for certain depths in the composite (the modifications being produced either by the introduction of solvents , either by adding organic or inorganic agents).

Chapter 2

Research objectives

The designability (in the sense that the responses of the composites to certain external actions can be determined prior to their formation) of the properties of composite materials is certainly the most important feature of these materials. As we have shown above, based on bibliographic studies, most authors define composite materials as materials created to satisfy certain conditions. In the case of simple demands this is apparently easy to achieve, but for complex demands there are inter-conditions that can lead to obtaining materials which, although designed for a certain application, fail due to second-order effects, earlier than the level accepted in design. In this sense, the studies carried out at CCDCOMT by Victor Ungureanu, Ana Boboc and, more recently, Radu Bosoancă highlighted the connection between the thickness of the sheet and its resistance to breaking under conditions where the sheet's reinforcement layer was the same.

Another problem, also related to the designability of the properties of composite materials, studied by Radu Bosoancă but also by Marina Bunea, is that of the properties of materials reinforced with fabrics but with a heterogeneous matrix (with an elasticity gradient, respectively, matrices modified with powders) - this problem, is similar somehow, with the design of a composite sandwich. As stated by Adrian Cîrciumaru, the creation of a composite with special properties may involve, at a given moment, the use of two or more polymers to form a single composite and without them being mixed before the creation of the composite.

After discussions with the members of the guidance committee, I understood the importance of the study (proposed and based on my previous experience) related to the behavior - especially mechanical - of the areas of materials formed by joining two polymers, which I called polymer junctions. This study can also prove to be of some use in the case of repairing composite structures, given the fact that usually large structures (wind turbine blades) are repaired by patching (reinforced patches glued to the structure by means of a polymer).

A study for two completely different polymers (eg epoxy resin and silicone resin) would have been difficult to undertake in this new direction so we decided that this study would refer to the junctions between two polymers of the same class (epoxy resins). All epoxy resins for commercial use (for casting, lamination, coating, etc.) have the same basic constituents (the diglycidester of bisphenol A) but the recipes of the mixtures are secret and, regardless of the efforts of Professor Adrian Cîrciumaru, we have not been able to obtain more data about chemical components of resins or hardeners.

The use of two (or more) polymers to obtain a reinforced material means, in fact, obtaining a reinforced composite (with fabrics) and which, between certain layers of reinforcement) has polymer junctions - areas of transition from the properties of a polymer to the properties to the other.

The main objective of the study is related to the analysis of the material properties in the polymeric junction areas and to achieve this objective we established two partial objectives, as follows:

1. the analysis of the properties of bulk polymer junctions (ie polymer junctions obtained by directly joining two polymers (both in the pre-polymer mixture state) and
2. analysis of the properties of composite materials reinforced with fabrics and whose matrix is heterogeneous in the sense that there are three groups of reinforcement layers each immersed in a different polymer.

The preparation of the study was based on:
• bibliographic analysis regarding studies of the same type carried out by other researchers;
• analysis and discussion of research topics already completed at CCDCOMT, together with the coordinator and members of the guidance team;
• familiarization with the methods of forming composite materials used at CCDCOMT;
• analyzing the properties of epoxy resins and understanding the small differences between their properties.

The achievement of the first objective stated above supposed the achievement of partial goals, each corresponding to a stage of the study:
• establishing the manner of formation that allows obtaining polymer junctions;
• establishing the type of mold that allows obtaining samples for all types of tests (tensile, bending, compression);
• formation of reference materials, as well as ensuring the necessary samples for the tests mentioned above;
• the effective formation of materials and their consolidation by applying thermal cures;
• extracting the samples;
• the actual performance of the mechanical tests and the interpretation of the obtained results;
• carrying out thermal and thermomechanical tests and interpreting the results of these tests;
• the interpretation of all experimental results and the formulation of conclusions so that it is possible to move to the second objective.

As in the case of the first objective, also in the case of the second it is necessary to achieve some intermediate goals that are constituted in research stages:
• identification of the type of mold that allows obtaining materials with a matrix composed of three polymers (two polymer junctions for each material);
• establishing the number of plates (material) formed so that it is possible to obtain samples for mechanical tests;
• establishing the types of fibers used for reinforcement (in fact, fabrics) so that it is possible to obtain as large a number of experimental data as possible;
• establishing the number of fabric layers (the same) used to form a material;
• the actual formation of the materials followed by their consolidation through heat treatment;
• analysis of electromagnetic properties of materials;
• extracting the samples necessary to carry out the mechanical, thermal and thermomechanical tests;
• performing mechanical tests - traction, bending, compression - and interpreting their results;
• formulation of final conclusions and themes for the continuation of the study.

Chapter 3

Materials and experimental methods

3.1. Polymer junctions

Based on the experience gained at the Research and Development Center for Composites with Thermosetting Matrices (CCDCOMT) the study, as we stated, is oriented towards the analysis of the properties of materials (polymeric or composites with polymeric matrices) that present junctions and we decided to use three epoxy resins that have also been studied in other researches. One of these resins – Epiphen RE40-DE4020 [201] – is the one on which all the early studies at CCDCOMT were carried out, while the other two Epoxy Resin C [202] and Epoxy Resin HT2 [203] were studied later. Anyway, this is the first study in which the analysis of the junction areas between these polymers is proposed.

The method of forming junction materials was based on the semi-transparency of the polypropylene tubes which allows the visualization of the level at which the liquid is inside the tube. For the specimens required for the tensile tests, the middle of the height of the tube was marked and the two polymers were placed in the molds (with the help of a syringe whose piston was operated very slowly). The first polymer was introduced up to the middle of the height of the cylinder, and the second one to the fill the mold. Thus the marked area (on the outside of the tube) becomes the junction area between the two polymers. In order to obtain the specimens needed for the bending tests, two marks were drawn on the outside of the tubes (each at 60mm from the end of the tube) and all three pre-polymer mixtures were introduced into the tubes – the first up to the first mark, the second between two marks and the third from the last mark to the open end of the tube. In this way, two polymer junctions appeared in each material formed.

By the same method we of course also formed the control materials (ie the three expoxy resins used) this time filling the tubes with the same pre-polymer mixture.

After repeated trials we have established an effective method that ensures sufficient time for molding the polymer mixtures. This method consists of using the mechanical stirrer at a speed of 200rot/min, with the addition of the hardener after dipping the vane into the epoxy resin in the mixing vessel. This regime was maintained for ten minutes and ensured, firstly, the homogenization of the mixture and, secondly, the elimination of gases.

Totally atypical, I left at the end of the section dedicated to obtaining samples for studying the properties of polymer junctions, precisely the mixing method. This makes sense because we used the same blending technique to form fabric reinforced materials where we formed polymer junctions.

3.2. Reinforced materials

At CCDCOMT there is a tradition of forming and characterizing polymer matrix composites and fabric-reinforced materials from the most common fibers used in today's world of modern materials – glass fibers, carbon fibers, aramid fibers

The purpose of the study is related to the analysis of the behavior of polymer junctions both in polymer materials as such and in the case of reinforced composite materials. For this reason, having the studies of our colleague Ana Boboc at our disposal, together with the members of the study coordination team, we determined that it would be appropriate to form materials with six types of reinforcements and, for each material, an inhomogeneous matrix in which to form polymer junctions. Each designed type of reinforcement is made of 15 layers of fabric. Every five layers of a material are imbued, before being placed in the mold, in another pre-polymer (corresponding to the three types of epoxy resins presented at the beginning of this chapter) so that a first polymer junction appears between layers 5 and 6 of reinforcements and, the second between layers 10 and 11. I also set each type of polymer to be in the middle of the material flanked by the other two. In the following, a material will be named (abbreviated) specifying the reinforcement class (AM, BM, CM, DM, EM or FM) followed by the sequence of placing the polymers in the mold ECH (junctions E/C and C/ H), HEC (H/E and E/C junctions) and CHE (C/H and H/E junctions).

In the case of the present study, we used eight types of fabrics, from glass fibers, carbon fibers and aramid fibers. Two of these fabrics were used for all the formed materials and they are making up the core of the composite (a package of nine layers of which eight are of glass fiber fabric and one – the middle one – is of carbon fiber fabric. In fig. 3.3. are shown images of the two fabrics used to form the core of the composite - the photos were edited by Mr. Adrian Cîrciumaru. Both fabrics are plain fabrics (warp thread over weft thread) and have appreciable specific densities compared to the other fabrics used. Placing the fabric layer of carbon fiber (electrically conductive layer) in the middle of the core was made to investigate a future possibility of finding information about the loading state of the composite by electrical measurements.

Fig. 3.1. Fabrics used for the core of composite materials

All six reinforcements therefore have the same core structure (the antisymmetry of layers 5 and 6 with their pair – relative to the median plane – layers 10 and 11 can be observed). Otherwise, from the point of view of the materials used, the symmetry of 4-7 with 9-12 is observed. The orientations of the layers are relative to the longer side of the glass mold and correspond to the angle between this direction and the direction of the warp threads (fascicles) of the reinforcing fabric. With these we can describe the arrangement of reinforcement layers for all six types of reinforcement.

The way we used the name of the fabrics is the same as the one used by Mrs. Ana Boboc (in the study she carried out) because from that study all of us who made and tested materials understood that it is the manner that provides the most information. Thus the letter or letters represent the material of the fibers (S glass, C carbon, A aramid) and the numbers represent the specific density (in g/m^2). The CA combination indicatwe a hybrid carbon fiber and aramid fiber fabric.

Table 1. Reinforcement structure of AM materials

Layer number	Material and orientation
01	S163 (0°)
02	S163 (30°)
03	S163 (-30°)
Core	
13	S163 (-30°)
14	S163 (30°)
15	S163 (0°)

Fig. 3.2. Fabric S163

Table 2. Reinforcement structure of BM materials

Layer number	Material and orientation
01	CA188 (0°)
02	CA188 (30°)
03	CA188 (-30°)
Core	
13	CA188 (-30°)
14	CA188 (30°)
15	CA188 (0°)

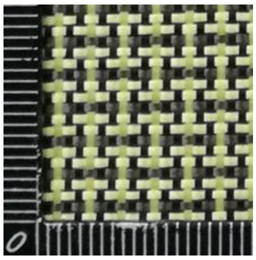


Fig. 3.3. Fabric CA188

Table 3. Reinforcement structure of CM materials

Layer number	Material and orientation
01	A61 (0°)
02	A61 (30°)
03	A61 (-30°)
Core	
13	A61 (-30°)
14	A61 (30°)
15	A61 (0°)

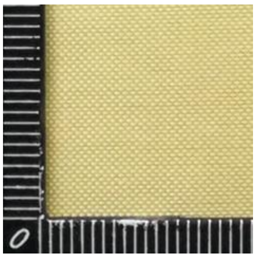


Fig. 3.4. Fabric A61

Table 4. Reinforcement structure of DM materials

Layer number	Material and orientation
01	CA68 (0°)
02	CA68 (30°)
03	CA68 (-30°)
Core	
13	CA68 (-30°)
14	CA68 (30°)
15	CA68 (0°)

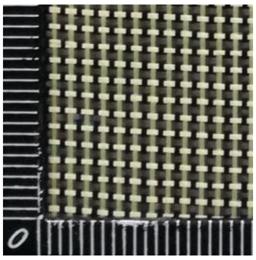


Fig. 3.5 Fabric CA68

Table 5. Reinforcement structure of EM materials

Layer number	Material and orientation
01	CA107 (0°)
02	CA107 (30°)
03	CA107 (-30°)
Core	
13	CA107 (-30°)
14	CA107 (30°)
15	CA107 (0°)

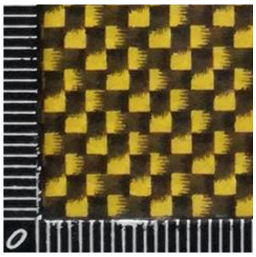


Fig. 3.6. Fabric CA30

Table 6. Reinforcement structure of FM materials

Layer number	Material and orientation
01	C120 (0°)
02	C120 (30°)
03	C120 (-30°)
Core	
13	C120 (-30°)
14	C120 (30°)
15	C120 (0°)

Fig. 3.7. Fabric C120

The necessary (calculated) amounts of each type of pre-polymer were prepared to ensure the formation of three materials at the same time – i.e. all materials in a class were formed at the same time, following the sequence of resins to ensure the two types of junction mentioned above for each type of material. HT2 resin, denoted H, was made first (has the longest gel time) and was kept in the thermostatic bath until the other two were prepared). The second was resin C, also kept in the thermostatic bath until the mixture of resin E was made.

The extraction of the samples from the molds was carried out 21 days after casting, which is seven days longer than the polymerization time recommended by the resin manufacturer (14 days). The plates obtained were also strengthened by applying the thermal treatment described when obtaining the junctions, a thermal treatment that was applied in an oven with free air circulation.

After consolidation, samples were extracted from each material for the various mechanical or thermal tests. Extraction was performed using a high-pressure water jet cutting machine. The specimens for the tensile tests are those provided in the ISO 178/2001 standards, and the bending ones are according ASTM D 790-03.

The formed materials were also tested to determine the coefficient of linear thermal expansion (TMA tests), the samples being extracted with diamond corers driven by a drilling machine - fig. 3.14., having cylindrical shapes with the length of the generator (height) of the cylinder equal to the thickness of the material (for this, the edges of the plates remaining after cutting the specimens for tensile, bending and compression tests were used. From the same edges and using the same cutting method, specimens were extracted for DSC analysis (for determination of specific heat) but delamination that occured destroyed the samples.

Fig. 3.8. Material from which samples were extracted for the TMA study

3.3. Test methods and equipment used

3.3.1. Tensile tests

To carry out the tensile tests, as shown above, we used the method recommended by the ISO 178/2001 standard (ASTM D 790-03), in the case of tests on fabric-reinforced materials, although the respective standards do not refer to reinforced polymeric materials and there is, at least at CCDCOMT, a controversy based on arguments in favor of using *dumbbell* specimens versus using parallelepiped specimens. So all mechanical tensile tests (on the reinforced materials) were done on the Instron 8802 customer machine with a maximum load cell of 25kN, with hand-tightened jaws.

For the tests that targeted the mechanical properties of the polymer junctions, we still used hand-tightened clamps (the same load cell), but the clamps were changed, replacing the flat-clamp ones with those that the test machine manufacturer produced for CCDCOMT for clamping cylindrical samples. Both types of tests were performed at loading speeds recommended by the aforementioned standard, 5mm/min, and the machine software application was programmed to terminate the test at a 20% load drop.

3.3.2. Compression tests

Compression tests were performed on the same machine for all materials formed and shown above. In this case, the clamps needed to hold the samples were replaced by two plates and the loading sense of the machine cell was reversed. For the tests performed to study the polymer junctions we used the recommendations of the ASTM D695_15 standard (which refers to the testing of rigid plastic materials), while for the fabric reinforced materials we used the recommendations of the ASTM D3846 standard (which refers to the plane shear strength of the materials reinforced plastics). Like other colleagues before me I have found that the standards refer to materials widely used in industrial applications and that the materials designed and manufactured at CCDCOMT cannot easily fit into the material categories provided for in the standards.

3.3.3. Bending tests

The bending tests were carried out on the same universal testing machine but with the change of the specimen holder and the punch for applying the load for the three-point bending test. All tests were carried out according to the ASTM D7264 standard but for cylindrical bar specimens (in the case of the junction study) and parallelepiped specimens (in the case of fabric-reinforced materials tests), respectively. The advance speed of the punch was also set to 5mm/min (fig. 3.15.).

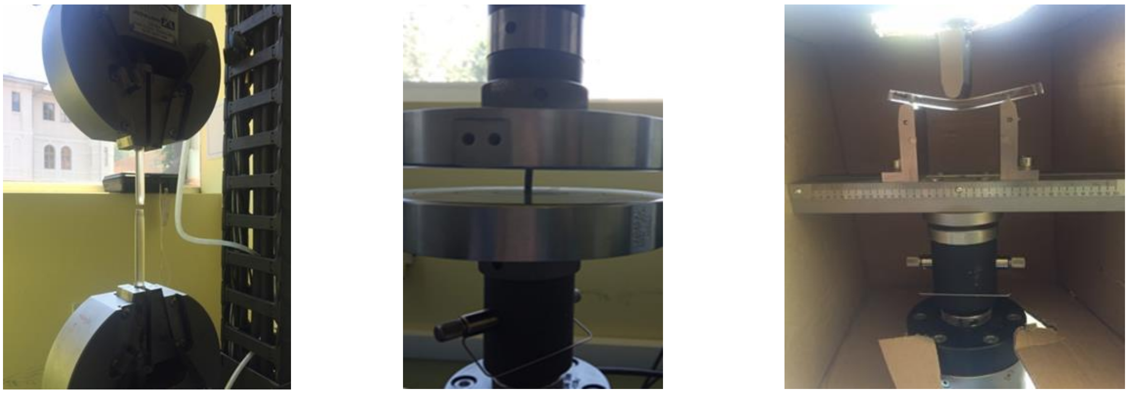


Fig. 3.9. Bars used for mechanical tests

3.3.4. Thermal tests

In the case of the current study, the main purpose of the thermal tests was related to the determination of the specific heat value of the formed materials, knowing that during mechanical stress part of the energy is transformed into thermal energy (heating of the tested material) and, in some cases it might be interesting to evaluate the mechanical released energy by heating mechanism.

Tests were performed on a DSC 1 machine (Mettler Toledo) and evaluated with the software application (*Star*e) provided by the equipment manufacturer. The thermal test cycle consisted of heating the material from 25°C to 125°C, holding at 125°C for three minutes and cooling from 125°C to 25°C, specific heat determinations being made on both heating and cooling. The heating and cooling rates, respectively, were set at 10°C/min, according to the standard recommendations – fig. 3.16.

Fig. 3.10. Mettler-Toledo DSC 1 Differential Scanning Calorimeter

3.3.5. Thermomechanical tests

The dimensional stability of a material is one of the most important properties in the design of composite structures. In these conditions, the coefficient of linear thermal expansion of a material becomes an essential parameter. It is known that some fibers commonly used to reinforce polymers have, in the transverse direction, negative coefficients of expansion, that is, they contract when heated. This can be an advantage (looking for a balance between the expansion of the matrix and the contraction of the fibers) ensuring the constancy of the dimensions (at least in the a direction perpendicular to the reinforcement plane) but it can also be a huge disadvantage in the conditions where the transverse contraction of the fibers can lead to the destruction of the fiber-matrix interphase, the one that is decisive for the macroscopic response of the material (it is the one that ensures the transfer of external loads from the matrix to the fibers).

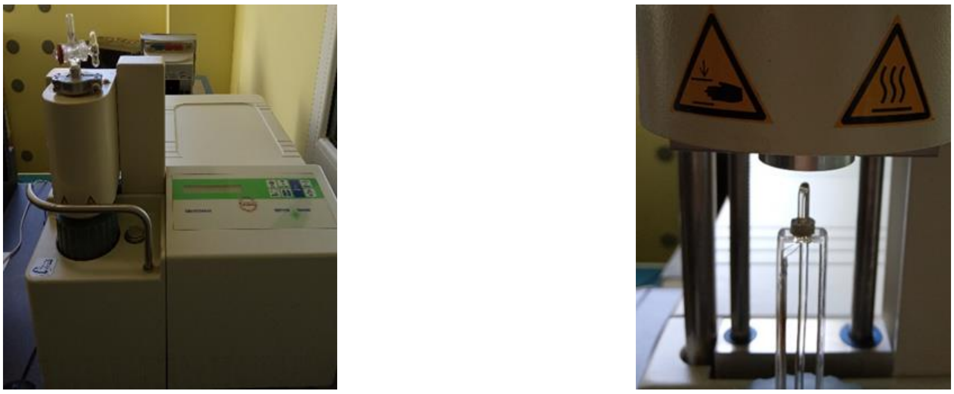


Fig. 3.11. Thermomechanical analyzer TMA/SDTA 840, Mettler Toledo

To determine the values of the coefficient of linear thermal expansion of the fabric reinforced materials and with layered matrix (to obtain the junctions) we used the TMA/SDTA 840 equipment (Mettler-Toledo) controlled by the *Star*e software application which also allows the evaluation of the value of the analyzed parameter - fig. 3.17. As in the case of the DSC analysis, we determined the values of the coefficient of linear thermal expansion during the (controlled) heating of the material and its (natural) cooling. The heating rate was set at 10°C/min – ASTM E831 standard and they were only made perpendicular to the reinforcement plane.

3.3.6. Electrical measurements

To determine the electromagnetic parameters of the reinforced composite plates, we used the standard method recommended in electrotechnics for the analysis of insulating plates and which involves the use of a measuring cell - fig. 18. all results being read, at different fixed frequencies, on an RLC-meter. Colleagues from CCDCOMT who worked before me have created an application that allows the direct recording of results in excel tables, which greatly facilitates the method.

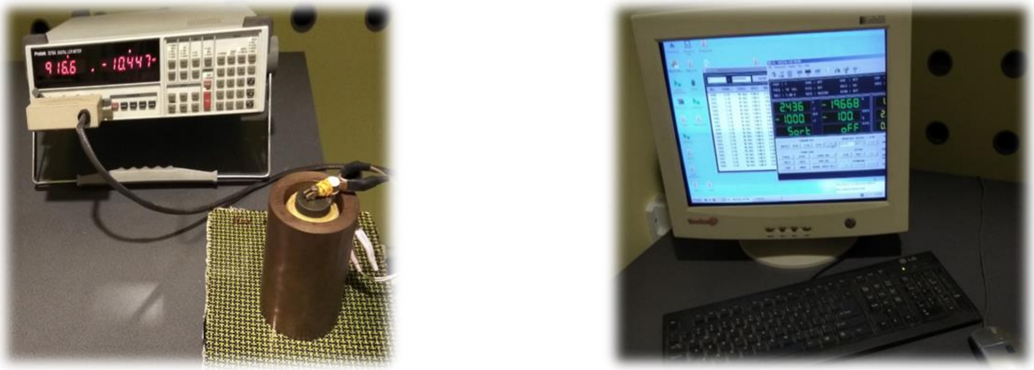


Fig. 3.12. Protek RLC meter and measuring cell. Application interface made at CCDCOMT

3.4. Conclusions

- we made polymer materials to obtain junctions between two epoxy resins;
- we established the casting method so as to ensure optimal conditions for handling the pre-polymers - for the samples cast in cylindrical molds;
- to ensure the samples needed for the tests, we made two types of casting in cylindrical molds – one with two resins (for tensile tests) and one with all three resins (for bending and compression tests);
- we formed fabric reinforced materials in six different configurations of the reinforcement but keeping the same core for all materials;
- we cut and prepared six sets of reinforcements for each configuration of reinforced material - two plates for each configuration of the matrix;
- for each reinforcement configuration, the polymer matrix was layered to obtain – between layers 5 and 6 and, respectively, 10 and 11 (core layers) the three types of possible junctions;
- on the formed plates we performed electrical and electromagnetic tests;
- we extracted the samples necessary for the mechanical, thermal and thermomechanical tests;
- we established the testing conditions of the materials (according to the standards).

Chapter 4

Analysis of tensile tests results

4.1. Epoxy resins and materials with junctions

Epiphen RE4020-DE4020 epoxy resin is an epoxy resin with an extremely wide range of applications – starting from protective coatings, passing through lamination and ending with casting. The other two resins used are special purpose resins being used mainly in the aeronautical industry for the construction of small recreational aircrafts. Other studies at CCDCOMT have shown that the two resins (C and HT2) are stiffer than Epiphen resin. As we have already shown in the previous chapter. To simplify the description of the tested materials Epiphen RE4020-DE4020 resin will be indicated by E, epoxy resin C by C and epoxy resin HT2 by H and their junctions CE, CH and HE, respectively.

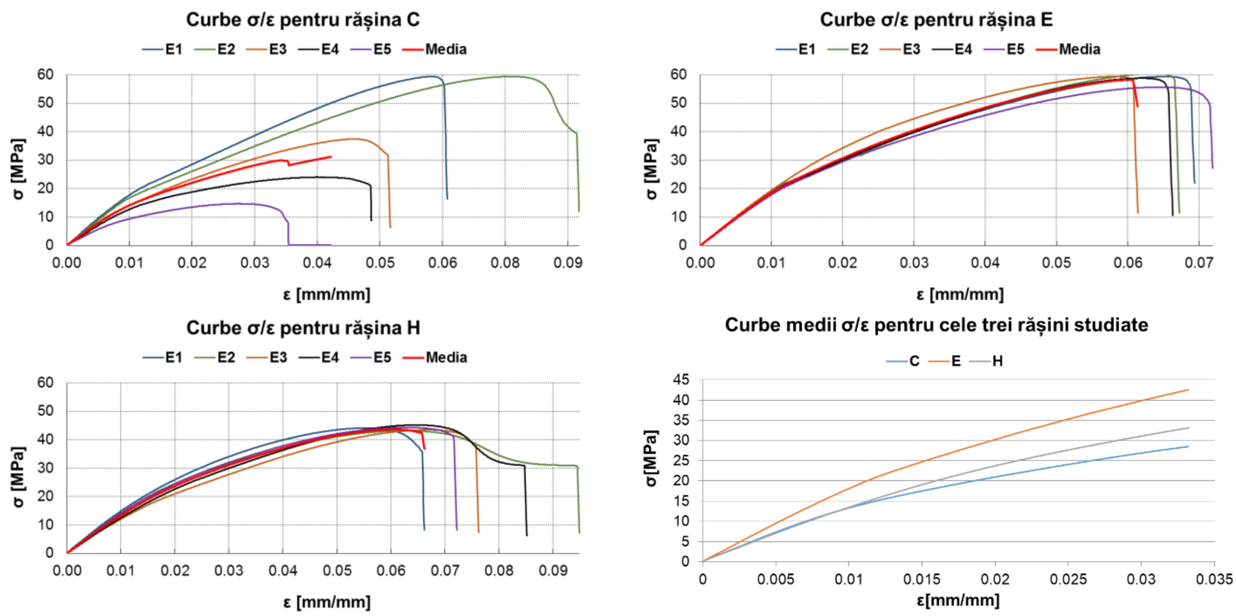
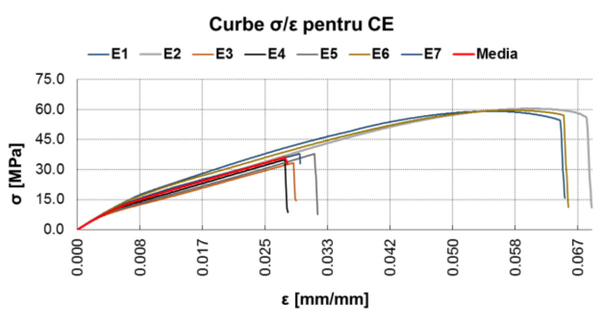


Fig. 4.13. σ/ε curves for the three epoxy resins

The tensile tests for the characterization of the three epoxy resins analyzed throughout the study - fig. 4.1. indicates that C-type epoxy resin is more brittle (the results obtained for the five tested specimens are scattered). Being a resin used for coating or lamination, its most important property is adhesion, even if the manufacturer provides, in the technical sheet, a number of characteristics for the bulk material obtained by casting.



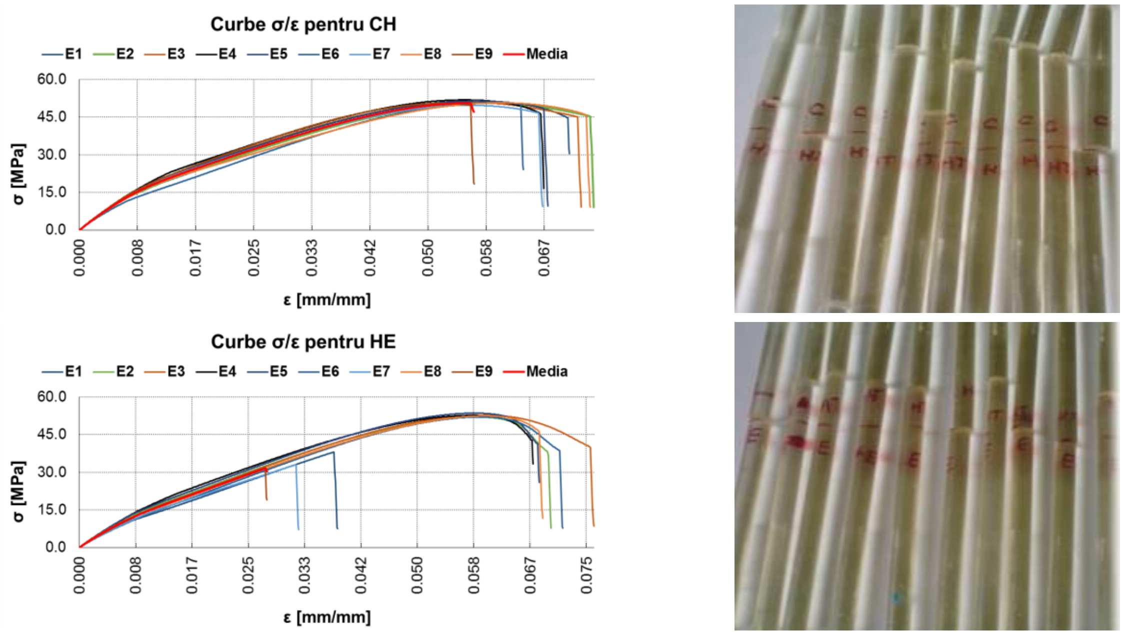


Fig. 4.14. σ/ε curves for materials with junctions

In a discussion with the members of the guidance committee, I looked for answers regarding the dispersion of the results obtained, and it can be said that this comes from the time of the formation of the respective material. As the molding process progresses, the prepolymer mixtures are increasingly viscous, which certainly leads to differences in the behavior of the final materials. It would probably have been interesting to mark each test piece so that ensuring control on the casting moment as well. Another aspect is related to the fact that the cylindrical tubes were loaded by means of syringes.

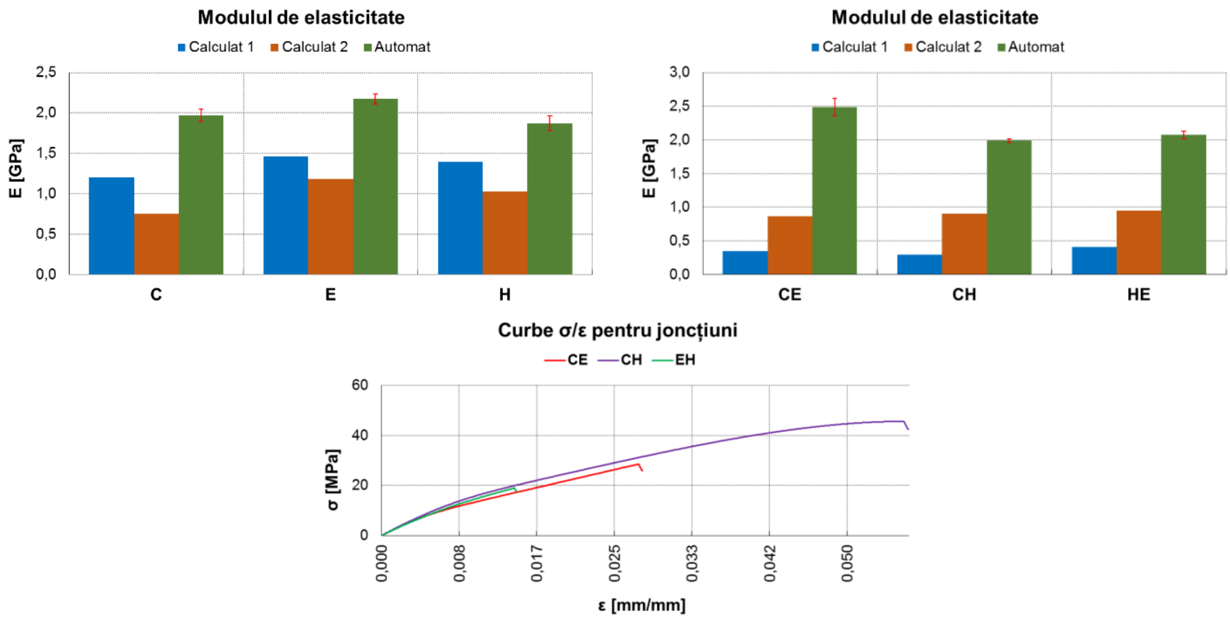


Fig. 153. Tensile modulus of elasticity and average curves of materials with junctions

As for the modulus of elasticity of materials with junctions, they are shown in fig. 4.3. I must state that it is about the elastic moduli evaluated on the first linear segments of the σ/ε curves (between ε=0.000 and ε=0.005 – calculated 1 and between ε=0.010 and ε=0.020 – calculated 2). This evaluation (on two areas of the σ/ε curves) is related to how the reinforced materials evolve and was made after analyzing the experimental data related to the reinforced materials. What is important is the fact that on the second level of the curves the modulus of elasticity has a lower value than the other two analyzed values (calculated 1 which corresponds to the beginning of the test and automatic which corresponds to the entire analysis domain). The data provided by the software application of the test machine, as we stated previously, refer to the modulus of elasticity throughout the analysis domain (until the specimen breaks), as explained by Radu Bosoancă [204].

4.2. Conclusions – materials with junctions (tensile tests)

- testele de tracțiune efectuate pe epruvete realizate din cele trei rășini epoxidice analizate au demonstrat că rășinile C și H sunt mai fragile (C chiar mai fragil decât H) în comparație cu rășina E;
- modulele de elasticitate determinate pe primele zone linaire ale curbelor σ/ε sunt apropiate de valorile determinate de producătorii rășinilor, ceea ce înseamnă că au fost respectate toate recomandările privind utilizarea acestora;
- în timpul testelor epruvetele ce conțineau joncțiuni s-au rupt – de cele mai multe ori – în partea constituită din rășina mai fragilă;
- sunt foarte puține cazurile în care epruveta a cedat în zona joncțiunii ceea ce înseamnă că alăturarea celor doi polimeri (încă din faza de pre-polimer a acestora) nu afectează cu nimic răspunsul global al epruvetelor;
- materialele cu joncțiune CH prezintă o valoare a modulului de elasticitate superioară modulelor de elasticitate ale celor două rășini;
- este posibil ca rezultatele să fie influențate de contaminări ale probelor – amestec dintre urmele de rășină rămase pe pereții cilindrului de la plasarea în acesta a primei rășini și cea de-a doua rășină;
- tensile tests performed on specimens made of the three epoxy resins analyzed demonstrated that resins C and H are more brittle (C even more brittle than H) compared to resin E;
- the elastic moduli determined on the first linear segments of the σ/ε curves are close to the values determined by the resin manufacturers, which means that all the recommendations regarding their use have been followed;
- during the tests, the samples containing junctions broke - most of the time - in the part made up of the more fragile resin;
- there are very few cases in which the sample failed in the junction area, which means that the joining of the two polymers (even from their pre-polymer phase) does not affect the overall response of the samples;
- materials with CH junction have a value of the elastic modulus higher than the elastic moduli of the two resins;
- it is possible that the results are influenced by contamination of the samples – a mixture of the resin traces left on the walls of the cylinder after placing the first resin and the second resin in it;

4.3.Fabric reinforced composites with layered matrix

As we have shown in chapter three, layered matrix materials have been formed into six reinforcement variants that differ only in the type of fabric used for the outer layers of each material (three on each side). All materials have the same core, that is, an identical distribution of a number of nine fabric layers.

The results of the tensile tests will be presented (in the form of σ/ε curves) and will be accompanied by images of the tested specimens. From left to right, the samples are ordered in the order of testing (from 1 to 8), but we preferred not to present the grip regions in the bars in order to have more details of the fracture zones.

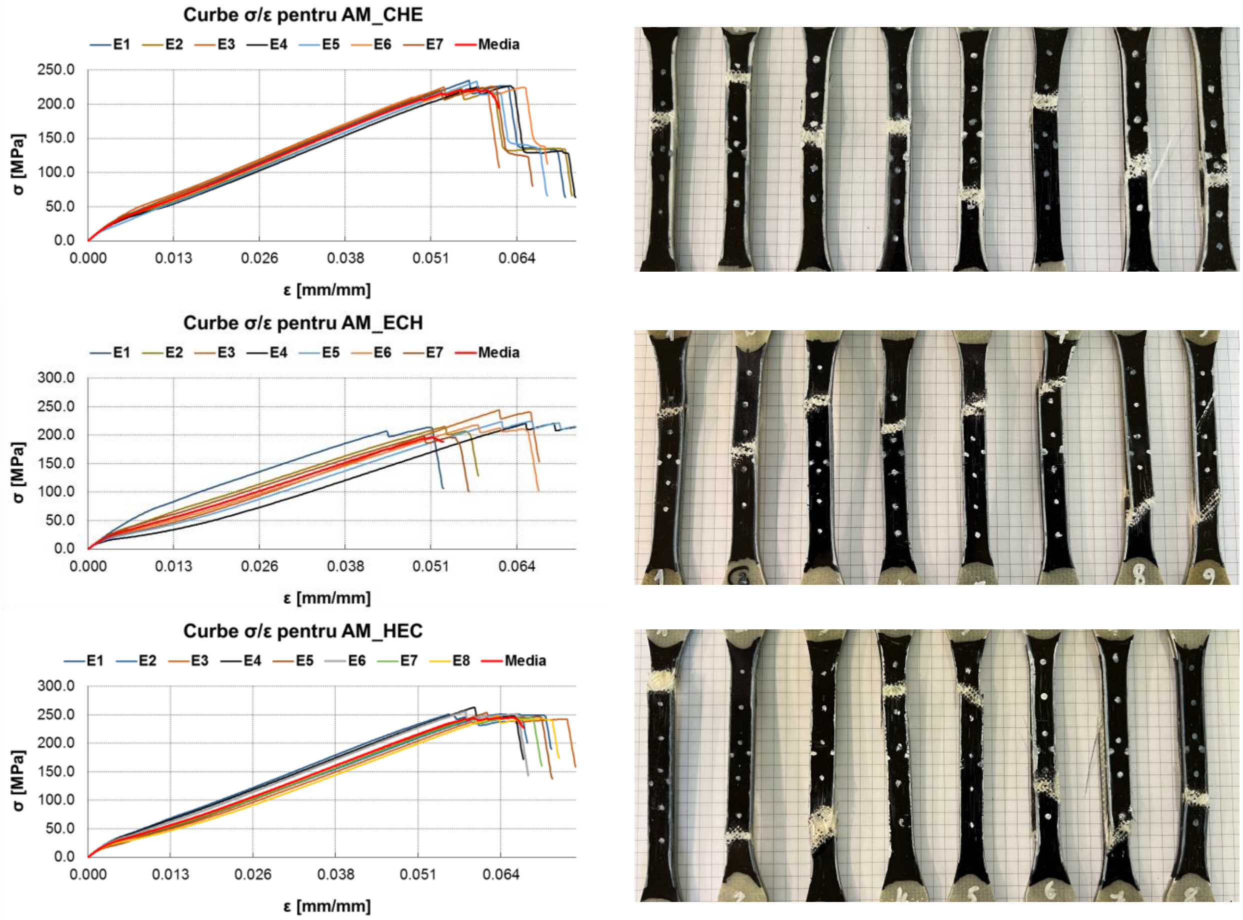


Fig. 4.4. σ/ε curves and tested specimens for AM materials

Although the σ/ε curves show several decreases in the stresses (corresponding to the successive breaking of layers or bundles of layers) the specimens were not broken (i.e. separated into two different pieces) because the tests were terminated when the load was reduced by more than 50% of the maximum reached value. Apparently the outer layers are fractured but the fractures also affect the core of the materials.

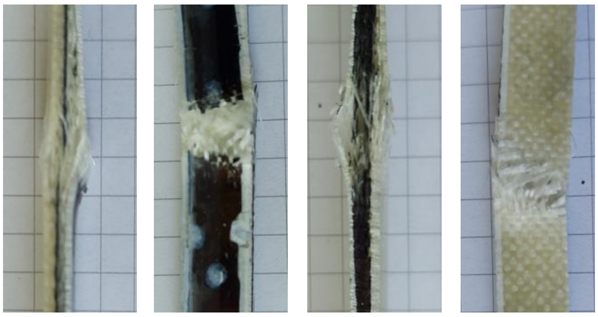


Fig. 4.5. Photo analysis AM_CHE

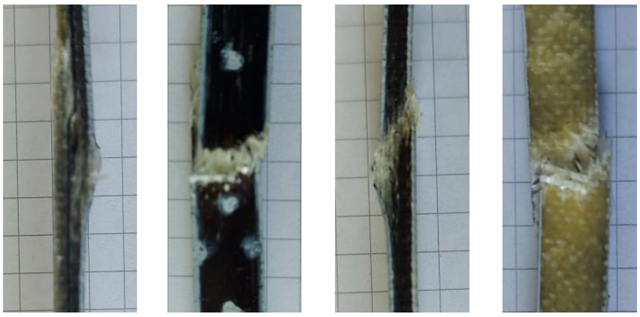


Fig. 4.6 Photo analysis AM_ECH

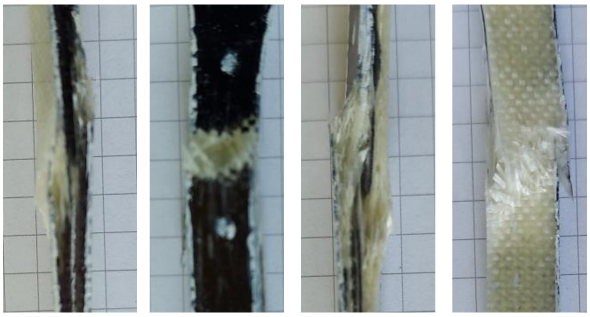


Fig. 4.7. AM_HEC photo analysis

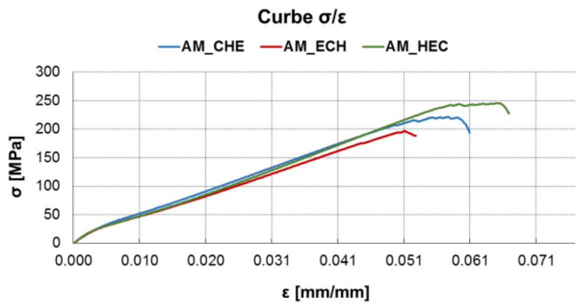


Fig. 4.8. Average σ/ε curves of AM materials

It can be observed that most of the tested specimens are deformed in a plane containing the median plane of the reinforcement, but deformations perpendicular to this plane also occur (which cannot be reproduced in the general images of the specimens). Regarding the first type of deformations, it could be attributed to a misalignment of the specimen in the grips, that is, there is a deviation of the axis of the specimen from the direction of loading. During the tests such an error is almost normal (fatigue of the operator is the best explanation) but it would not justify the deformation of all the specimens. For the second type of deformation it is very clear that it is determined by the structure of the material and the properties of the reinforcements and resins

In fig. 4.9. the average σ/ε curves for the AM materials are shown and it can be seen that the differences are quite small, the material having the lowest response is ECH with resin E in the first five layers and resins C and H in the last so they may be affected by the increase in viscosity of pre-polymer mixtures during lay-up. Best answer, corresponds to AM_HEC material, with E resin in the core and the more brittle resins on the outside.

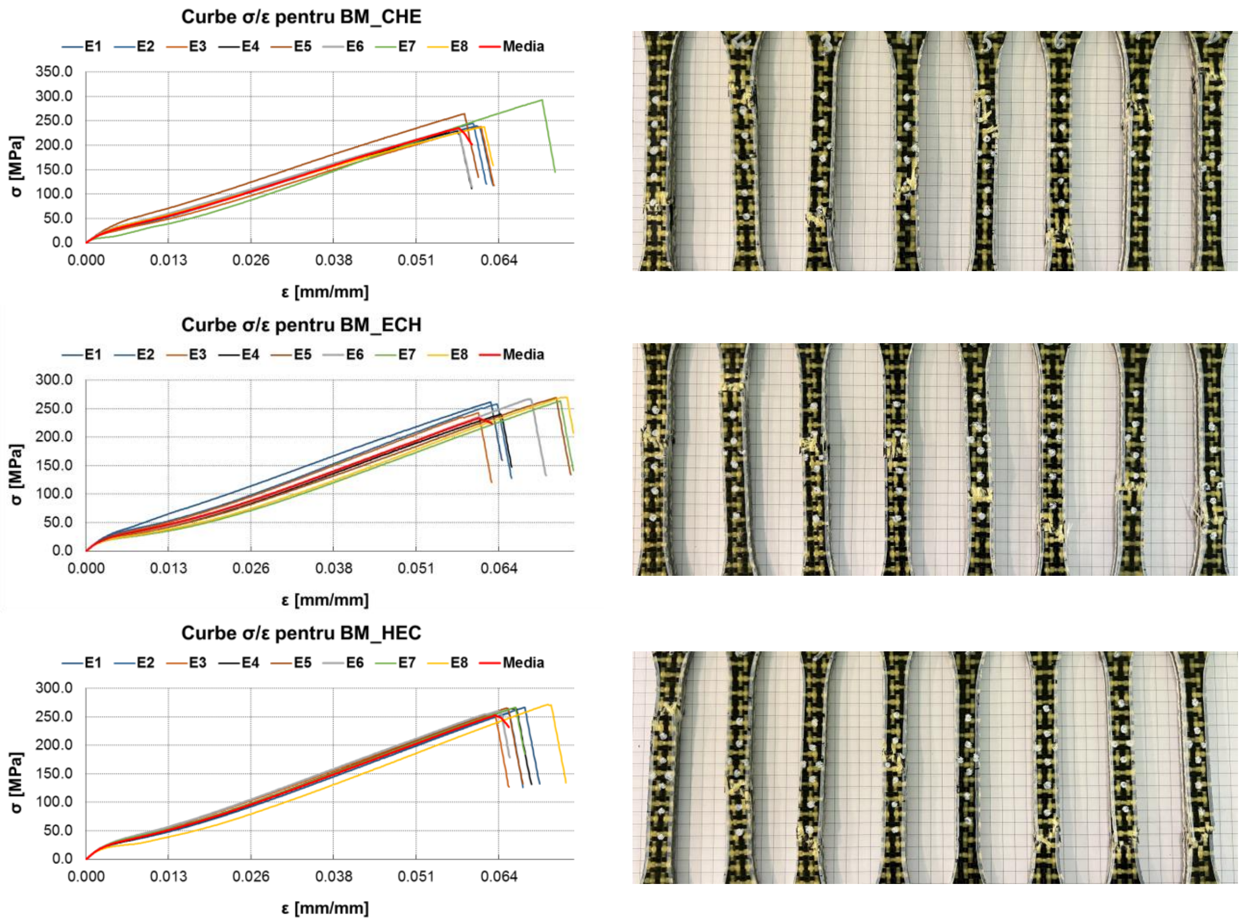


Fig. 4.9. σ/ε curves and tested specimens for BM materials

Unlike the AM materials, the lateral deformations of the BM materials samples are less obvious – fig. 4.9. The weakest responses correspond to CHE matrices and the smallest dispersion of responses is recorded for HEC matrix materials (as opposed to AM materials). From here it can be concluded that the influence of the outer layers is very important from the perspective of the eventual stronger adhesion of the resins to the carbon and aramid fibers. Another factor to consider is related to the thickness of the outer layers (greater in this case than in the case of AM materials).

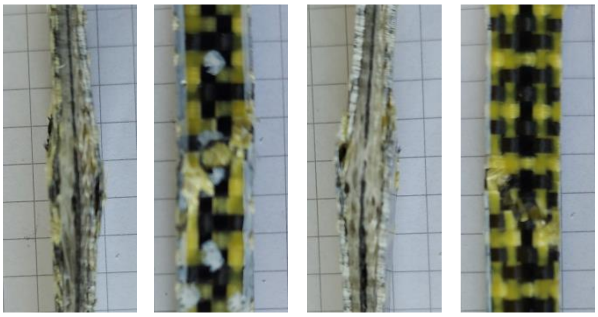


Fig. 4.10. Photo analysis BM_CHE

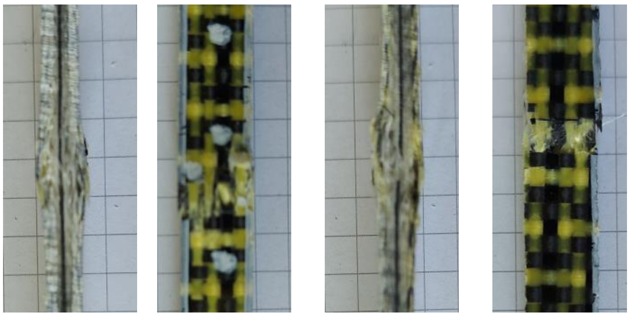


Fig. 4.11. Photographic analysis BM_ECH

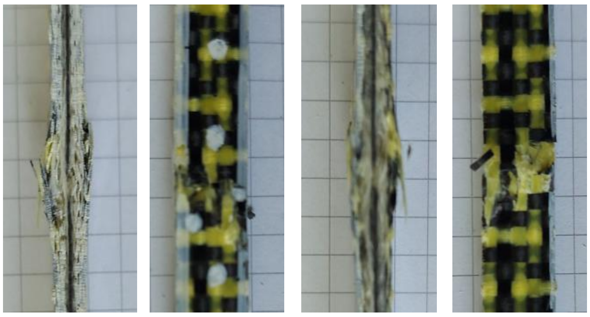


Fig. 4.12. BM_HEC photo analysis

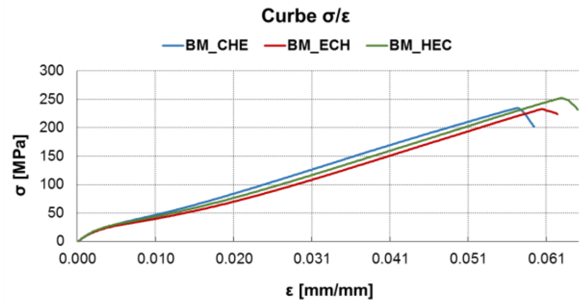


Fig. 4.13. Average curves σ/ε BM materials

Unlike the AM type materials, the photographic analysis of the fractures (fig. 4.10 – 4.12.) does not reveal significant differences between the three matrix types.

CM materials are materials for which the outer layers are made of aramid fiber fabric with a specific density of only 61g/m2 and a thickness of only 100µm (the thinnest fabric used).

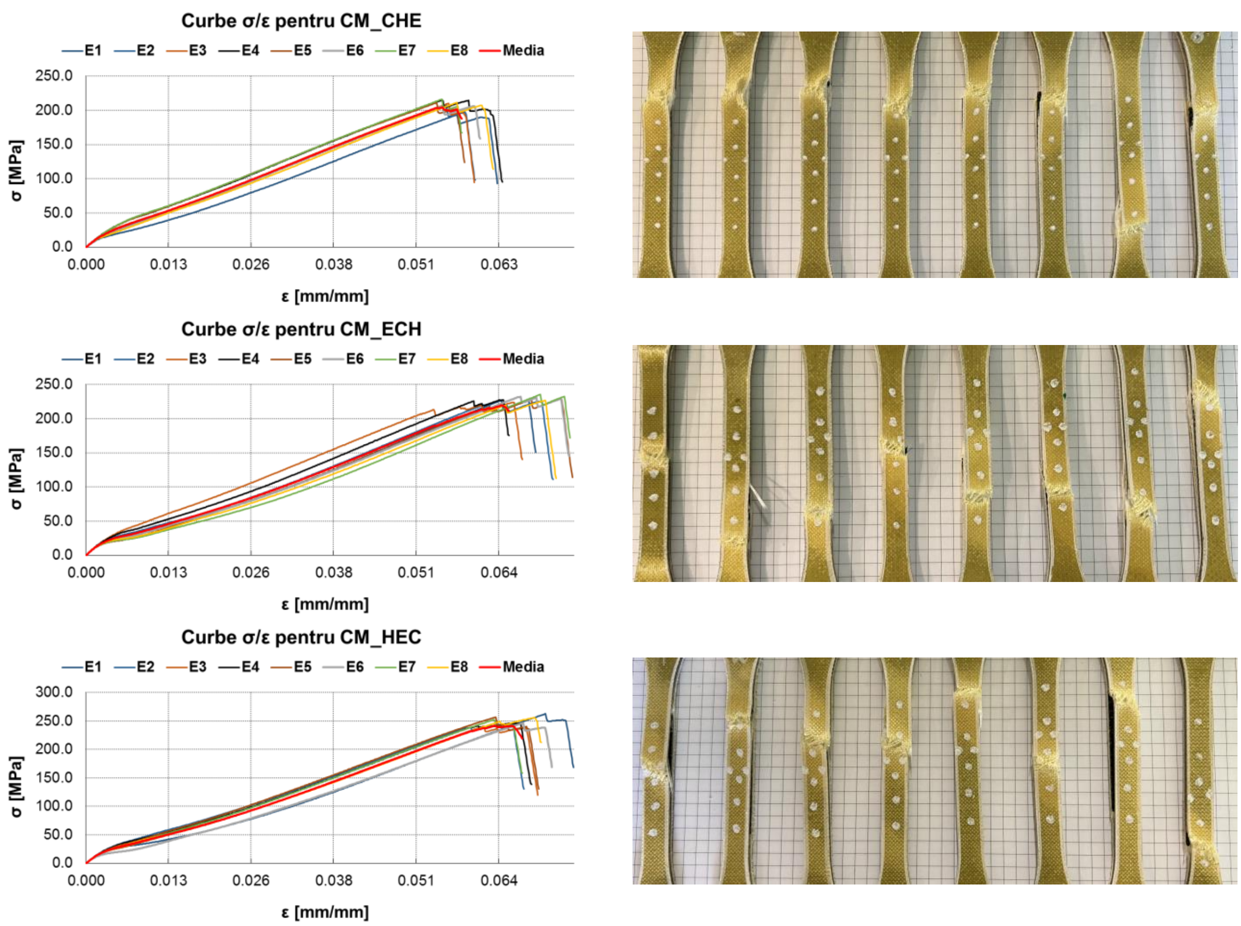


Fig. 16 σ/ε curves and tested specimens for CM materials

In fig. 4.14. the σ/ε curves for the CM materials and the appearance of the tested specimens are shown. For the CM_ECH material, in the first sample, effects are also observed in the immediate vicinity of the ends of the engagement zone and these can be attributed to the differences in the thickness of the sample (much more obvious if the outer layers are very thin). Since it is the only one of all the samples tested (for all CM variants), it can be considered an isolated case. In the other cases, things are different: the CM_HEC materials have predominantly breakage in the engagement area (except for samples with numbers 5, 7 and 8). In the case of the CM_ECH specimens they all broke in the engagement zone, while for the CM_CHE specimens it is observed that they fail at one of the ends of the engagement zone.

As in the previous cases, a better picture of the effects on the samples can be obtained by doing the photo analysis of the tested samples (fig. 4.15. – 4.18.) and, respectively, by doing the comparative analysis of the average stress-strain curves (fig. 4.19.) .

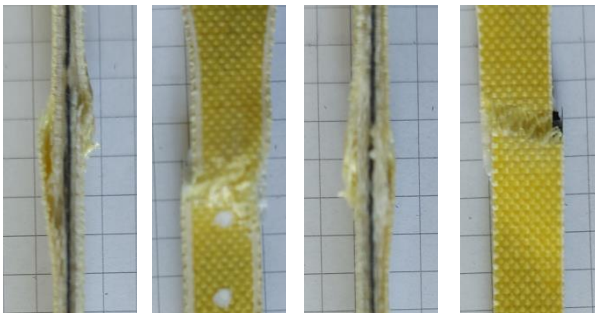


Fig. 4.15. Photo analysis CM_CHE

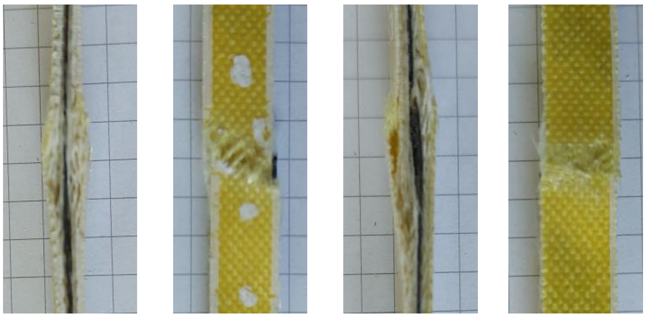


Fig. 4.16. Photo analysis CM_ECH

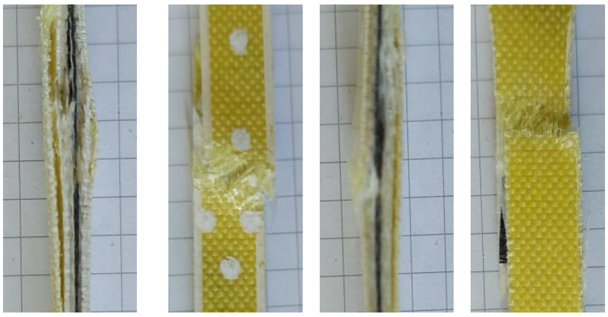


Fig. 4.17. Photo analysis CM_HEC

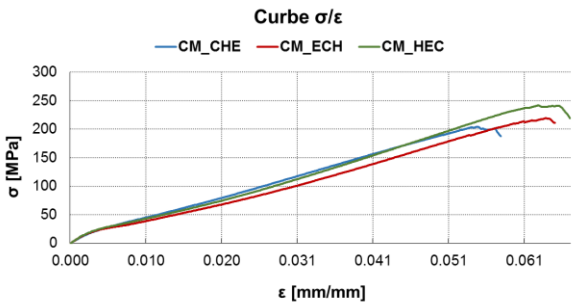
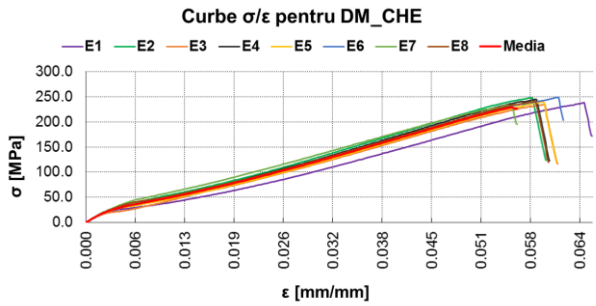
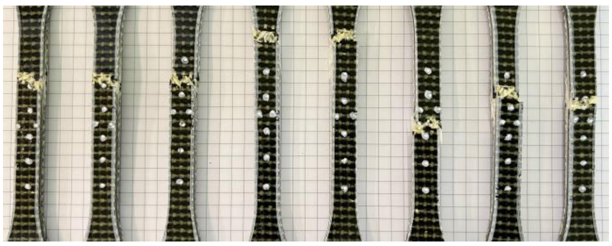


Fig. 4.18. Average curves σ/ε CM materials

The tensile test results for DM type materials are shown in fig. 4.19., in the left column and it can be seen that the dispersion of the data is much higher than for all other materials. Such a result cannot be attributed exclusively to defects in the materials, especially since, in all cases, the fractures of the specimens appear in their employment areas (fig. 4.19., right column). Furthermore, the specimens appear less affected in terms of lateral deformations (compared to other previously studied materials). The largest dispersion is, again, recorded for the ECH matrix.





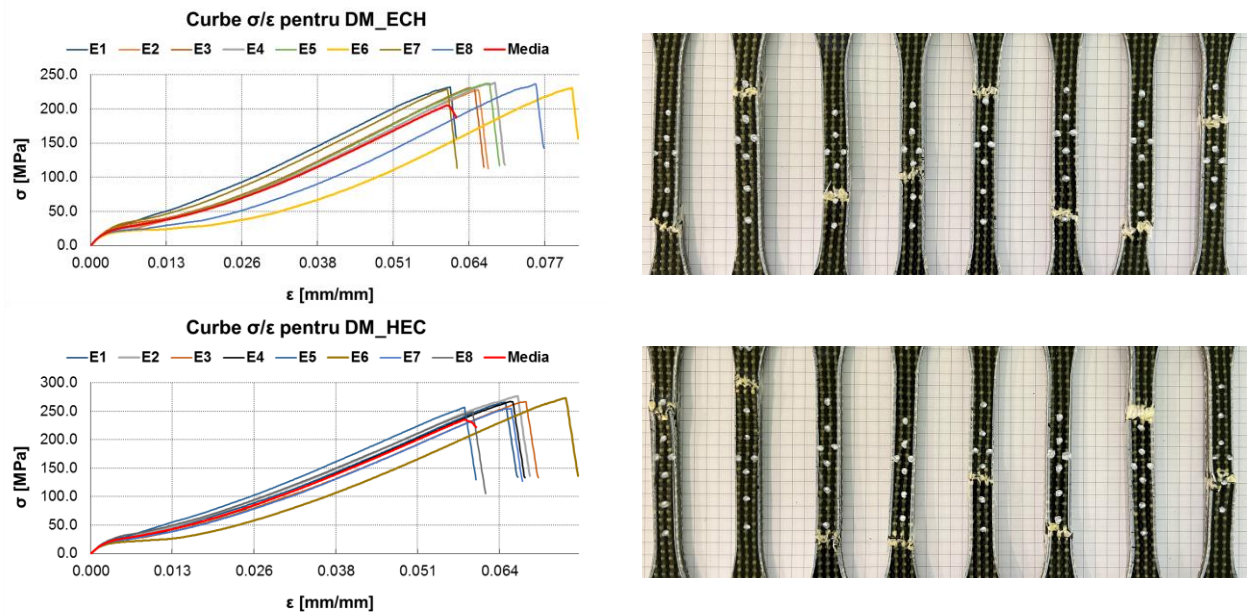


Fig. 4.19. σ/ε curves and tested specimens for DM materials

In fig. 4.20. – 4.23. the images of the fractures of the material are reproduced (according to the previously stated protocol) and small antero-posterior deformations of the specimens can be observed which can be attributed to the preservation of the physical integrity of a part of the core (CM_ECH case) and the expansion of the reinforcement (fibers) due to the immobility of the matrix – in this case, the polymer junctions are subjected to compression which, depending on the properties of the matrix (compressive elastic modulus), leads to the massive fragmentation of the polymer.

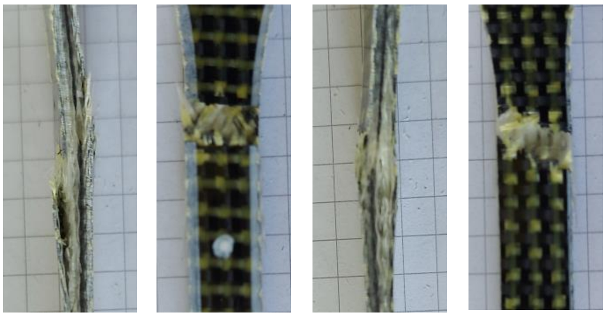


Fig. 4.20. Photo analysis DM_CHE

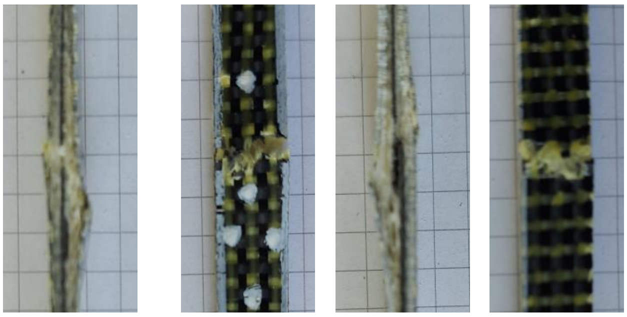


Fig. 4.21. Photo analysis DM_ECH

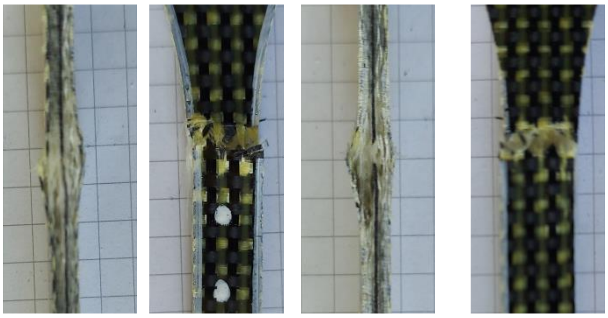


Fig. 4.22. DM_HEC photo analysis

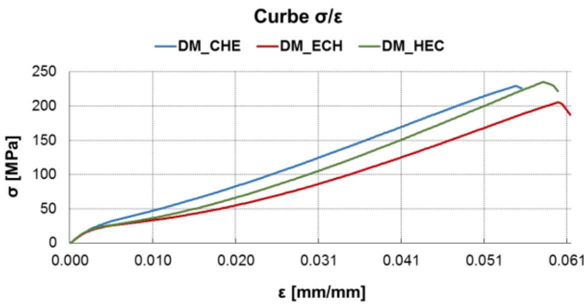


Fig. 4.23. Average curves σ/ε DM materials

The next class of materials is more special because the outer layers are not made of fiber fabrics but of an ordered felt of carbon fibers and aramid fibers supported by a felt of glass fibers. For such reinforcement, the response of the material is difficult to predict. In fig. 4.24. the σ/ε curves and tested specimens for the EM material class are presented.

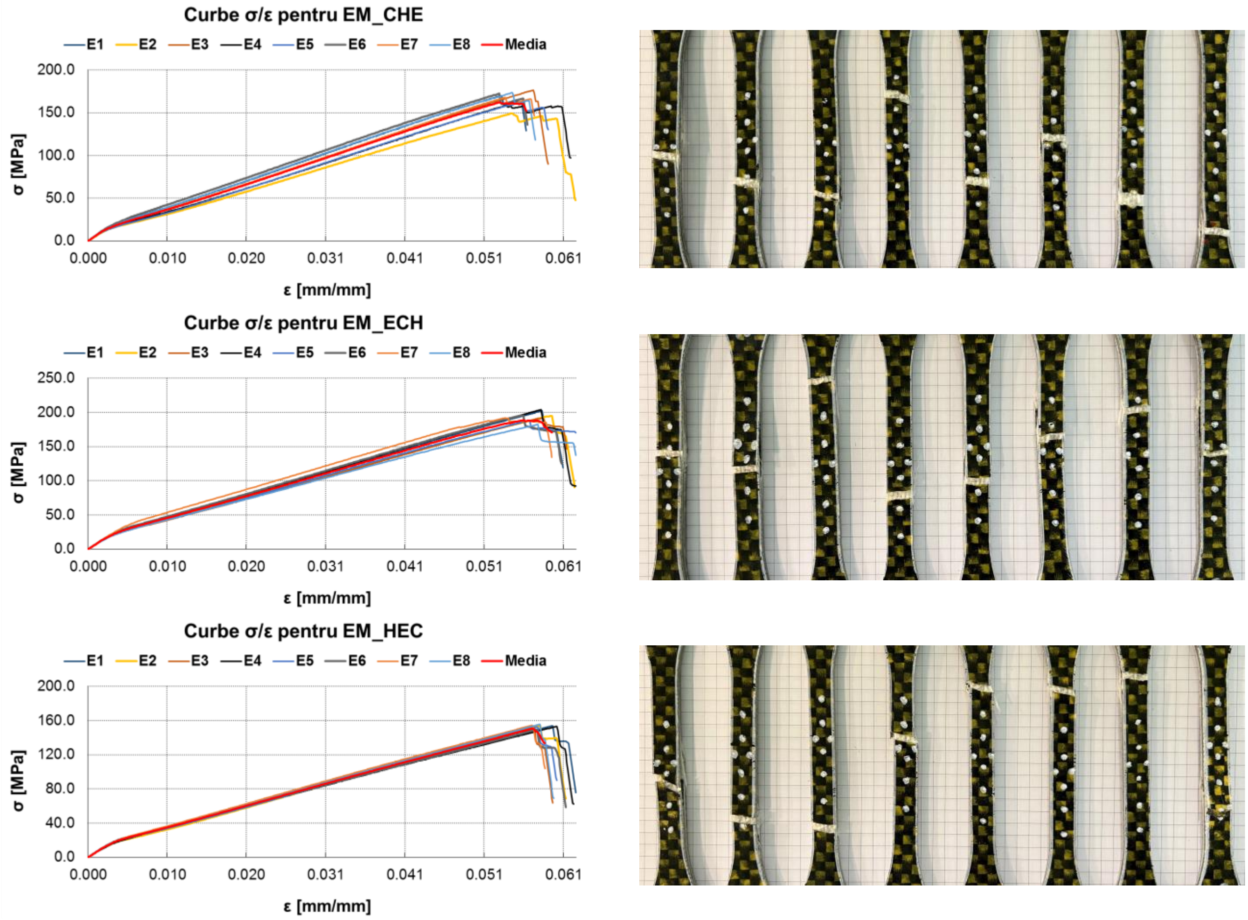


Fig. 4.24. σ/ε curves and tested specimens for EM materials

The material responses are highly clustered (σ/ε curves) for any of the three matrix variants, with the highest dispersion for the CHE matrix and the lowest for the HEC matrix. A reduction in the maximum effort is observed (compared to the materials analyzed so far) which can be easily explained by the absence of the ordered distribution of fibers in the outer layers.

In all cases (as can be seen from the analysis of the photographs of the specimens) the outer layers failed together leaving the first core layers (glass fiber fabrics) exposed. Since there is no order of the fibers in these layers, they yielded differently on the two sides of the specimen (until now the fracture zones coincided on the two sides of the specimens) - fig. 4.25. – 4.26. These layers respond as homogeneous and isotropic layers, similar to the veneer applied to wood or the melamine layer on chipboard.

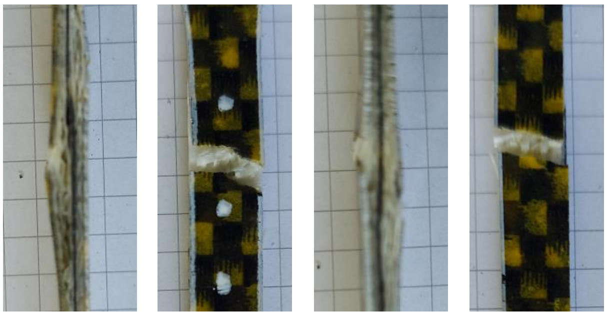


Fig. 4.25. Photo analysis EM_CHE

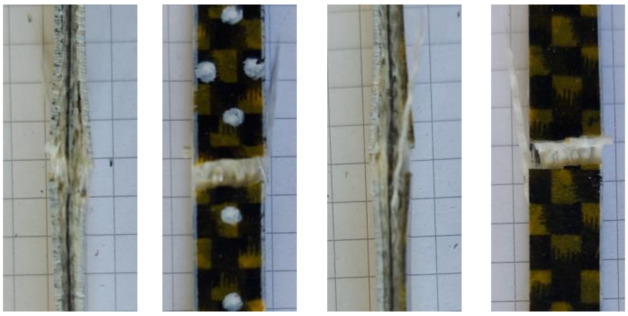


Fig. 4.26. Photo analysis EM_ECH

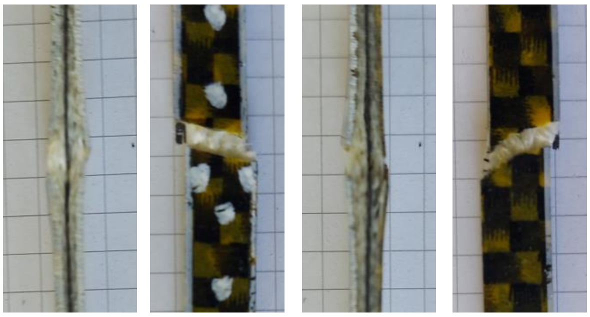


Fig. 4.26. EM_HEC photo analysis

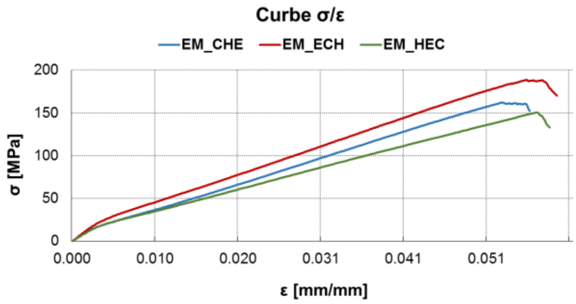


Fig. 4.27. Mean curves σ/ε EM materials

In fig. 4.29. the stress/strain curves and images of the tested specimens for the FM material with the three epoxy matrix variants are shown. The first observation is related to the fact that the maximum stress is higher than all the corresponding values obtained for the materials analyzed up to this point. Many of the specimens break in the immediate vicinity of one end of the engagement zone. In contrast to the previously analyzed cases, in the case of FM materials, there are large dispersions of the results recorded for two of the matrix variants (ECH and HEC).

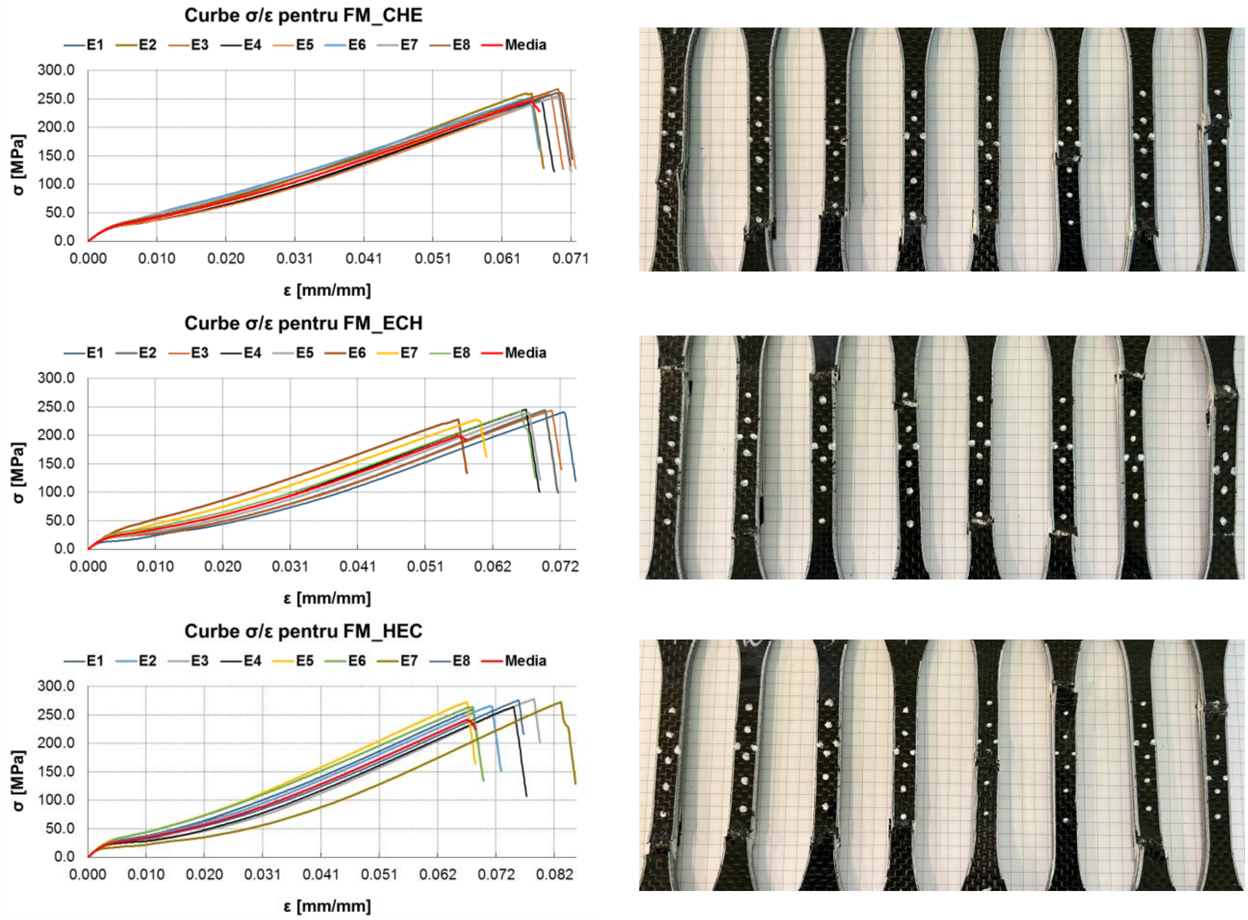


Fig. 4.29. σ/ε curves and tested specimens for FM materials

In this case too, lateral deformations of the specimens are observed (the two fragments resulting from the fracture move laterally in relation to each other) but, on the stress-strain curves, no areas of repeated fractures are visible - the material responds like the BM and DM materials (those where there are carbon fiber bundles in the reinforcement layers).

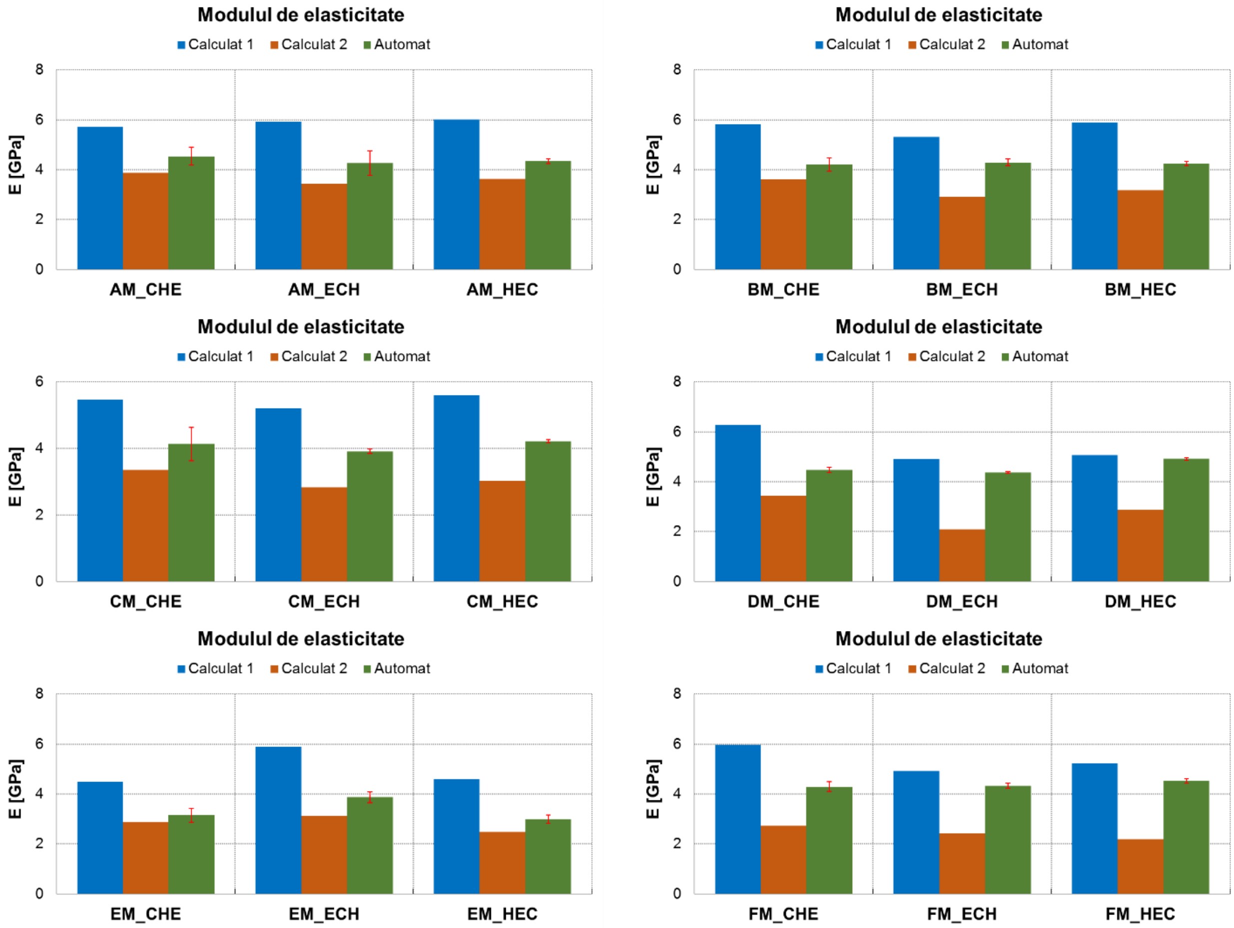
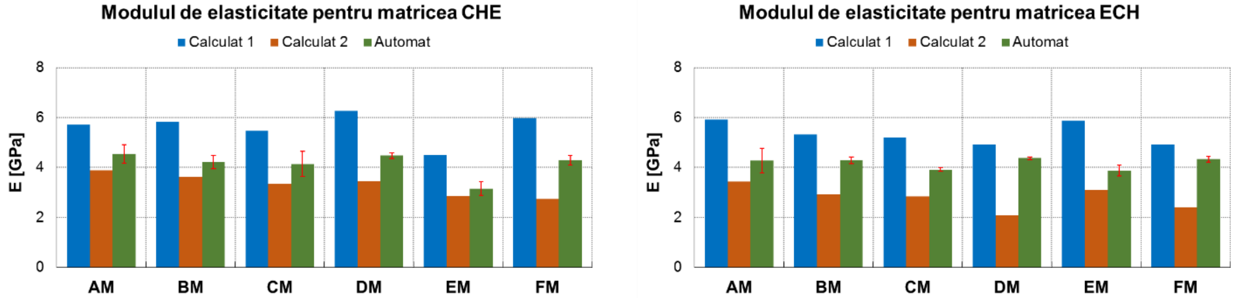


Fig. 4.34. Tensile elastic modulus of materials – class analysis

In fig. 4.34. the values of the tensile elastic modulus of the materials are shown according to the type of reinforcement. The reinforcements of AM materials are made of glass fiber fabrics (except for the middle layer made of carbon fiber fabric) and, assuming that the nature of the polymer-glass fiber interphase is the same regardless of the type of polymer and the characteristics of the glass fibers in the two fabrics, it can be explained that all materials in this class have practically the same elastic modulus.

The highest value of the elastic modulus is recorded for DM_CHE which has a very thin mixed fabric (aramid fibers and carbon fibers) in the outer layers. The lowest value – EM_CHE which has in the outer layers the CA30 material we discussed earlier. Theoretically there should not be significant differences between the materials that have E resin on the outside, because the other two (more fragile) resins form packs of 10 layers of reinforcement that should determine the behavior of the material.

In fig. 4.35. a comparative analysis of the elastic moduli of the materials (calculated and automatic) is presented but on matrices (not on materials, as before).



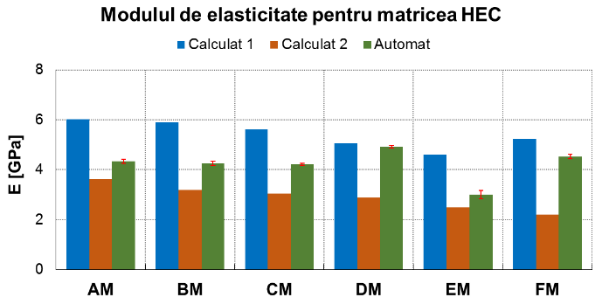


Fig. 4.35. Tensile modulus of elasticity of materials – matrix analysis

The data presented in graphic form in fig. 4.35. suggest a similar behavior of CHE or ECH matrix materials and a different one for HEC matrix materials. In addition, as can be seen from the photographic analyzes of the samples, presented above, in the case of the latter materials, the expansion of the samples in the fracture area is symmetrical with respect to the middle layer of the reinforcement. This means that the presence of the two junctions CE and HE in the core of the material balances the behavior of the specimen after fracture. In the other two cases, as we stated previously, joining resins C and H produces a rigid matrix that determines the behavior of the specimen (before and after fracture) affecting 10 out of the 15 layers of reinforcement.

4.4.Partial conclusions – tensile tests – reinforced materials

- the thicknesses of fabric reinforced materials with layered matrix (containing two polymer junctions) are different and the differences are generated by the properties of the fabrics used for reinforcement in the outer layers;
- during tensile tests for reinforced materials, the polymer junctions are not stressed in the same direction as in the case of polymer materials containing junctions, but in a direction perpendicular to it so that the results obtained for polymer materials with junctions (elastic moduli, for example) they cannot be used to explain the phenomena that occur in reinforced materials subjected to tensile tests;
- in principle, the axial stress of the samples of reinforced materials determines the transverse stress of the junctions (perpendicular to the plane of the junction), i.e. a compression stress;
- all the stress/strain curves (for any reinforced material and for any sequence of polymers in the matrix) show, at the beginning, a very short linear zone that corresponds to the response of the material, after this the matrix fails and the response is given by the reinforcement along with other phenomena of matrix fracturing and fragmentation;
- a dependence of the material's response on the thickness of the outer layers of the reinforcement can be identified (the properties of the fabrics used in these layers - AM, BM, FM cases) but also on the nature of the fibers from which the fabrics used as reinforcement in these outer layers are made (AM cases and FM and BM and DM, respectively);
- the polymer junctions (CE, CH and HE) are inside the core of the reinforcement of the composite material and it can be found, for all materials, that the layers of the fabric made of glass fiber bundles fails;
- as a result of fracturing the glass fibers (reduced elastic modulus), they move away from their positions in the material, generating the effect of expanding the reinforcement in the area of the fracture;
- for CHE or ECH matrix materials (where rigid matrices are adjacent) the two packages of outer layers of the reinforcement generally fractures at different levels while, for HEC matrix materials, the outer layers fractures at the same level on the two sides of the material;

- for all the studied materials, we did not find delaminations (following the analysis of the photos), with the exception of the materials with thin fabrics in the outer layers (CM and DM), as I stated, in the case of EM the behavior is different since it is not a proper fabric;
- for all matrix types the (automatic) modulus of elasticity of the EM material is the lowest and, to some extent, given the way the material fails, it could represent the modulus of elasticity of the reinforcement core;
- the above observation is useful when it is necessary to explain how the fibers are pulled out from the matrix - in fact they are fibers located in the center of the bundles and are not very well trapped in the polymer (unlike the case of thin fabrics);

Chapter 5

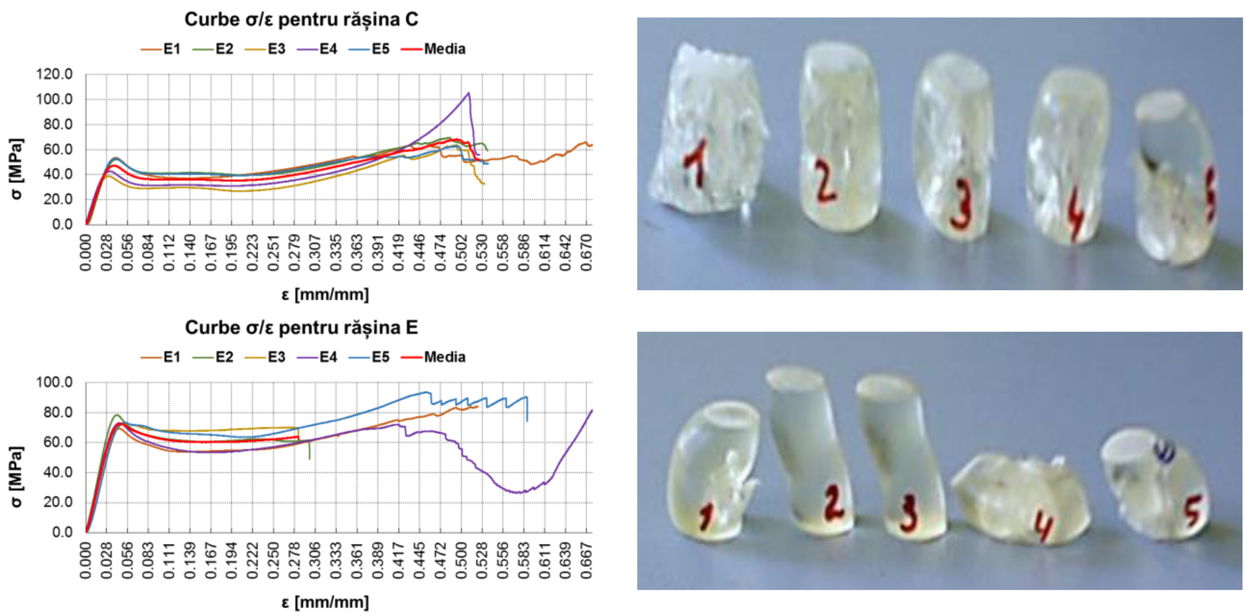
Analysis of compression tests results

5.1. Epoxy resins and materials with junctions

In the analysis of the mechanical properties of the studied materials, the compression tests have a special meaning given the fact that, as we mentioned in chapter 4, when the fabric reinforced materials and matrices containing two junctions are tested in tension (stretching) the distribution efforts leads to a compression stress of the junction areas, compression exerted by the adjacent layers of reinforcement.

As in the case of the tensile tests, the analysis begins with the study of the compression of the epoxy resins used in the study and, as in the case of the tensile tests, they were carried out together with my colleague, Mrs. Irina Țîcau, to whom, once again, I thank. Five samples were tested for each resin and the results obtained are shown in fig. 5.1. It can be seen, from the analysis of the images next to the graphic representations, the different way in which the three resins respond to compression stress.

In the case of resin C, it can be observed that all five tested specimens remained in a vertical position between the two plates and longitudinal cracks appeared in them (fragmentation). In the case of resin E, two of the samples slipped and the applied forces were no longer axial, generating the extraaxial deformation of the samples (the shape of the letter s) without, however, showing cracks. For the other three samples, cracks are observable (different in appearance from those observed in the case of resin C), for samples 1 and 5 also following sliding and for sample 4 with total fragmentation (with multiple observable events on the last part of the σ/ε curve. In the case of resin H, one of the samples has slipped (sample 1) taking the shape of the letter s, samples 2 and 3 are massively fragmented and samples 4 and 5 have a similar appearance to samples 1 and 5 of resin E but with a higher level of fragmentation greater than theirs.



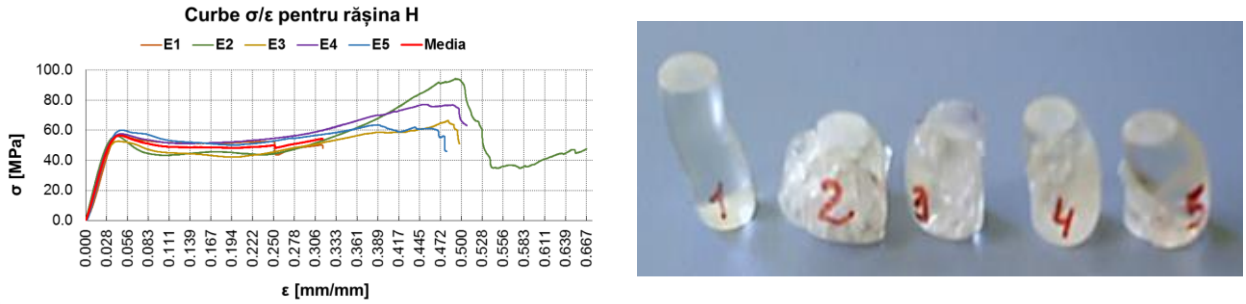


Fig. 5.1. Stress/strain curves for the studied resins and images of the tested specimens (compression)

According to the way the specimens fail in compression, the same findings can be made as in the case of tensile tests. Resin C is the most brittle, followed by resin H and finally the least brittle, resin E. One can also sees massive fragmentation – a large number of fragments resulting from stress – of the resin the more it is brittle (rigid). This observation is related to what was stated in chapter 4 with reference to how the reinforced composite specimens fracture and the effects of fracturing – the expansion of the fiber bundles due to the fragmentation of the resin.

In fig. 5.2. the average curves for the three analyzed resins are shown and it can be seen that the amplitude of the responses is the same as in the case of tensile tests (fig. 4.3. Chapter 4), with the most important response from resin E and the smallest from resins C.

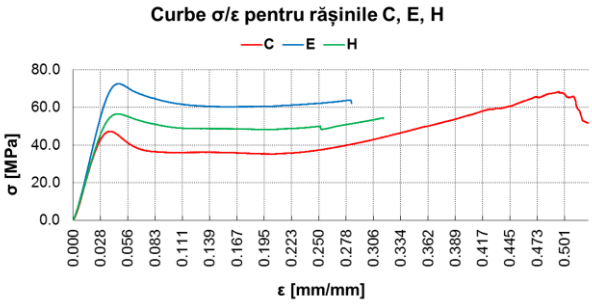
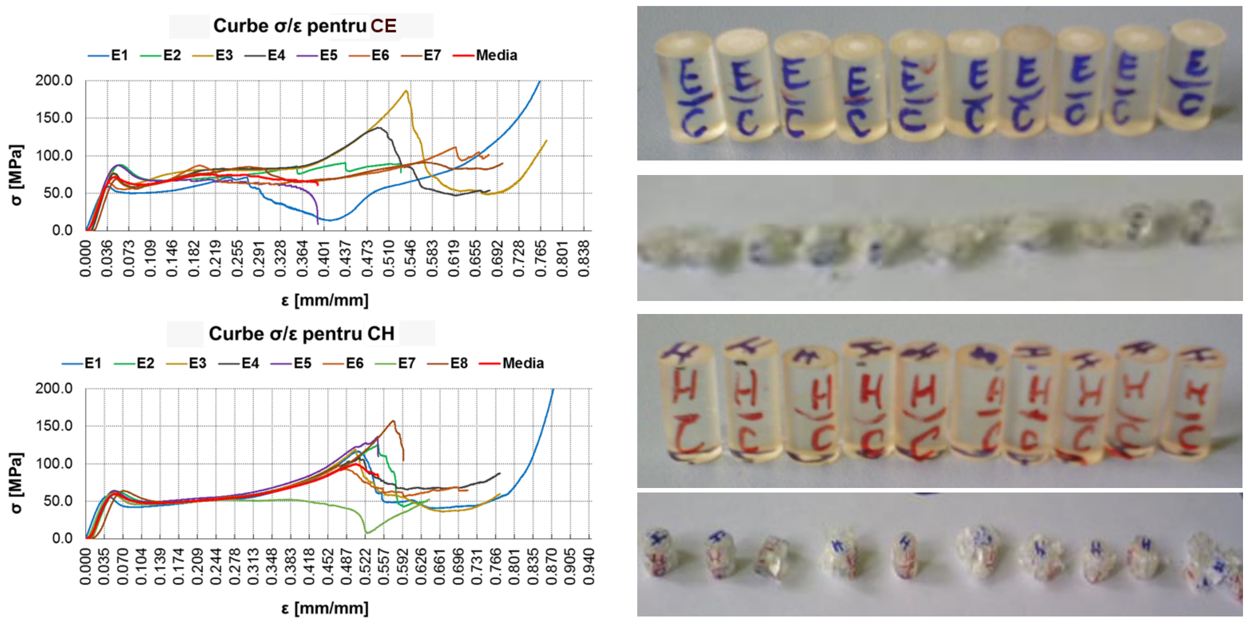


Fig. 5.2. Average stress-strain curves for the three studied resins (compression)

Regarding the polymeric materials containing junctions, the tests were carried out under the same conditions as the samples made from the three analyzed resins and the results are shown in fig. 5.3.



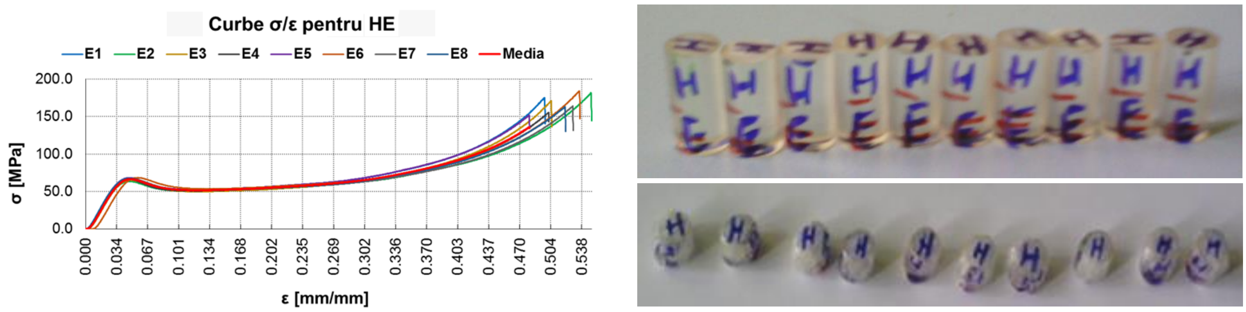


Fig. 5.3. σ/ε curves for jointed materials and specimens before and after testing (compression)

In the case of these tests, the samples slipped less between the platens and, as a result, the tests continued until the destruction of the samples as can be seen from the images presented. The highest effort corresponds to the CE junction, for the other two junctions the efforts are comparable (within the limit of elasticity) but with visibly different slopes of the stress/strain curves.

In the case of materials with junctions the fragmentation is much more obvious than in the case of the study of the used resins. The presence of C resin (in the two types of junctions it forms) affects the response of the tested samples, CE junctions being the ones with the most dispersed responses (the most brittle and the least brittle of the resins).

The compressive elastic modulus (calculated, as in the case of tensile tests, on the first linear zone and on the linear zone following the inflection point on the stress/strain curves) are shown in fig. 5.4. for each material containing a junction along with the elastic moduli of the two polymers forming the junction.

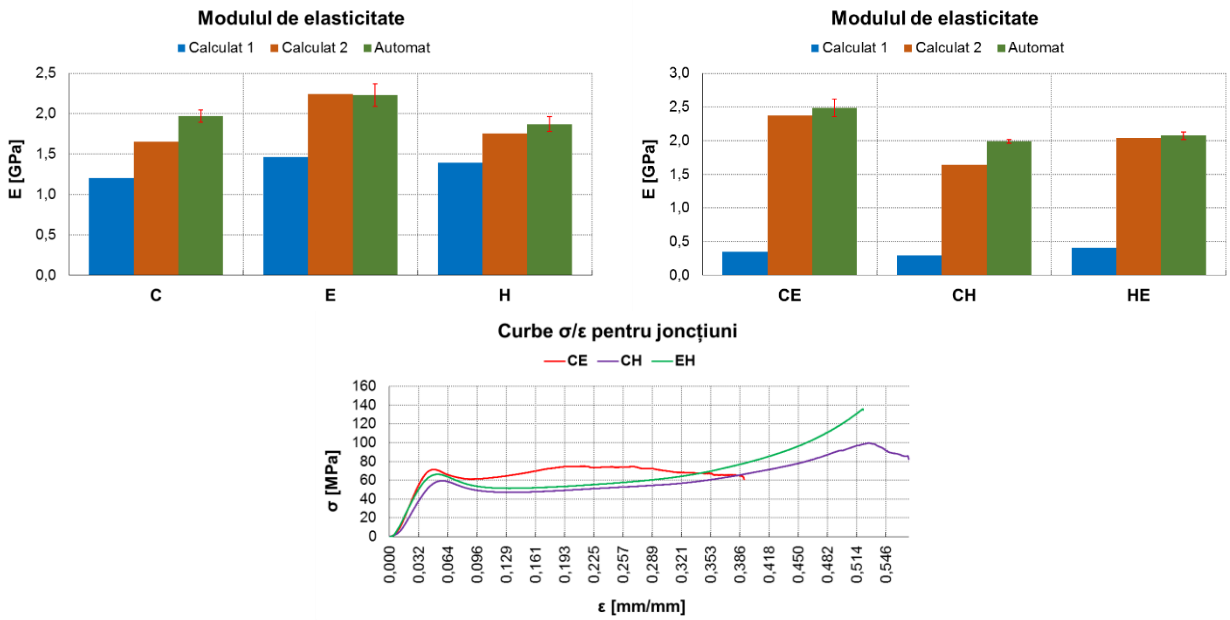


Fig. 5.4. Elastic moduli and average σ/ε curves of materials containing junctions (compression)

In fig. 5.4. it can be seen that the weakest response to compression corresponds to the CH junction (junction between the stiffest polymers) while the junctions containing resin E have similar behavior. It is expected, in this respect, that reinforced materials containing the CH junction will behave differently from those containing the CE and EH junctions. This has already been highlighted in the case of the analysis carried out on the results of tensile tests.

5.2. Conclusions – materials with junctions (compression)

- testele de compresiune realizate atât pe polimeri cât și pe materiale conținând joncțiuni polimerice relevă o fragmentare masivă a probelor atât pe direcția aplicării efortului cât și pe direcție perpendiculară pe direcția aplicării efortului;
- în condițiile în care testele de tracțiune au indicat fragilități diferite ale celor trei rășini epoxidice (cu C cea mai fragilă și E cea mai puțin fragilă) materialele au un comportament afectat de aceste proprietăți, în ceea ce privește fragmentarea dar și în ceea ce privește răspunsul elastic, modulele de elasticitate la compresiune și tracțiune sunt aproximativ egale doar pentru rășina H (este vorba despre valorile calculate ale modulelor de elasticitate);
- valorile modulelor de elasticitate la compresiune evaluate prin intermediul aplicației software care controlează mașina de teste sunt mult mai mari decât cele determinate (calculate) pe zona de răspuns elastic deoarece, pe de o parte mașina nu detectează momentul în care proba nu mai răspunde elastic și, pe de altă parte, deoarece evaluarea modulului de elasticitate se face prin raportarea efortului la sfârșitul testului la deformația înregistrată în același moment fără a ține cont de modificarea ariei secțiunii transversale a epruvetei;
- cel mai bun răspuns la compresiune îl au materialele care conțin joncțiuni CE și EH (joncțiune între un polimer rigid și unul mai puțin rigid).
- the compression tests performed both on polymers and on materials containing polymer junctions reveal a massive fragmentation of the samples both in the direction of the application of the effort and in the direction perpendicular to the effort direction;
- in the conditions where the tensile tests indicated different fragility of the three epoxy resins (with C the most fragile and E the least fragile) the materials have a behavior affected by these properties, in terms of fragmentation but also in terms of the elastic response, the compressive and tensile elastic moduli are approximately equal only for resin H (these are the calculated values of the elastic moduli);
- the values of the compressive elastic modulus evaluated through the software application that controls the testing machine are much higher than those determined (calculated) on the elastic response zone because, on the one hand, the machine does not detect the moment when the sample stops responding elastically and, on the other hand, because the evaluation of the elastic modulus is done by relating the effort at the end of the test to the deformation recorded at the same moment without taking into account the change in the cross-sectional area of the specimen;
- the best response in compression is found in materials containing CE and EH junctions (junction between a rigid polymer and a less rigid one).

5.3. Fabric reinforced materials with layered matrix

In the case of the compression tests we tried to apply the stress in the reinforcement plane and obviously the biggest challenge was to place the specimens between the compression plates. This was not always possible because cutting the samples led to obtaining almost parallelepipedal samples with a square base and having a height equal to the thickness of the material. In these conditions, most of the time, the strain was applied extraaxially and it is expected that the results of the determinations will be strongly influenced by this. Anyway, even if we will not consider the results of the precise determinations, the effect of compression on the samples (loading parallel to the reinforcement plane) can, at least, lead to the qualitative analysis of the phenomena that occur in the material.

In fig. 5.5. the σ/ε curves for the three AM materials are shown, along with images of the specimens after testing.

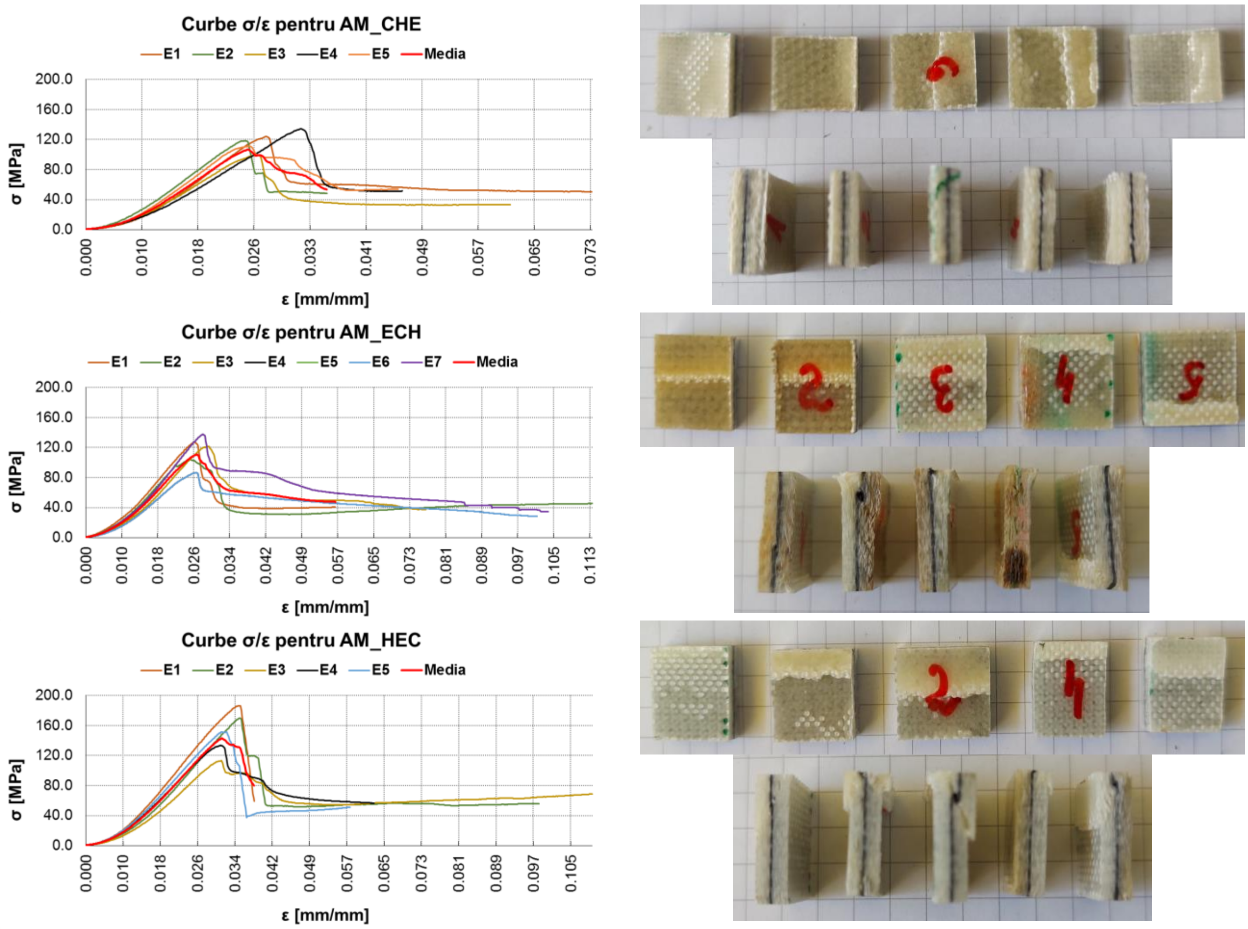
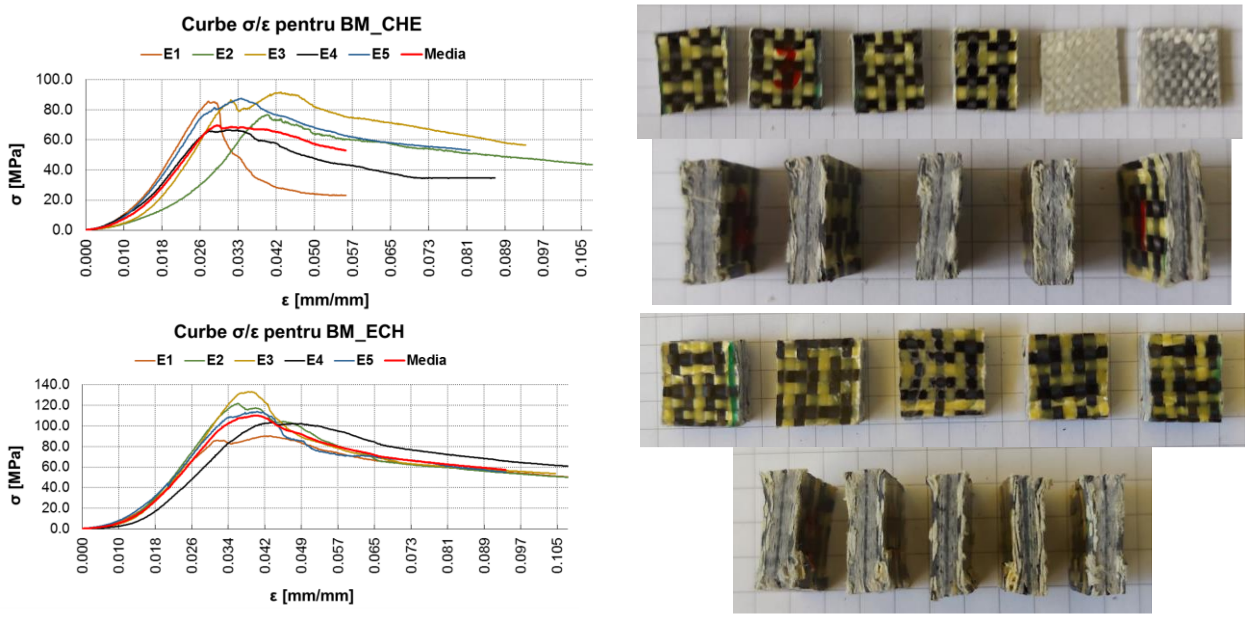


Fig. 5.5. Stress/strain curves and images of tested specimens (compression) – AM

The compression behaviors (σ/ε curve profiles) are dispersed precisely because of those exposed in the opening of this subchapter. The starting segments of the curves (which should have been linear) are curved and correspond to the range necessary for the deformations that make the specimens sit perfectly between the plates. After the zones of effective loading, events corresponding to partial fracturing of some layers are observable (in many cases), after which the samples slide and the tests are interrupted.

For AM-type materials the outer layers are thick layers made of woven glass fiber bundles (stiff fibers) and the effects visible in the images consist mostly of the fracturing of these layers.



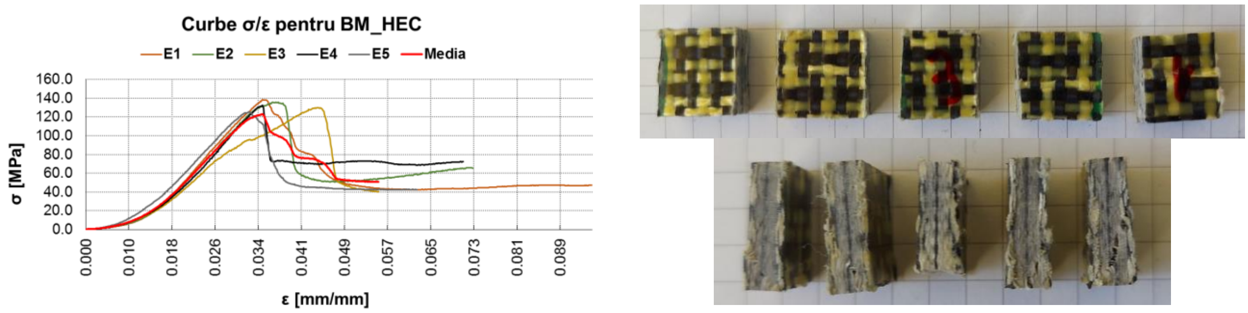


Fig. 5.6. Stress/strain curves and images of tested specimens (compression) – BM

In fig. 5.6. the stress/deformation curves and the images of the samples tested from the BM materials are presented – materials which, like the AM materials, have reinforcing layers made of thick fabrics. This time the outer armor layers are made of the hybrid fabric made of carbon fiber bundles and aramid fiber bundles.

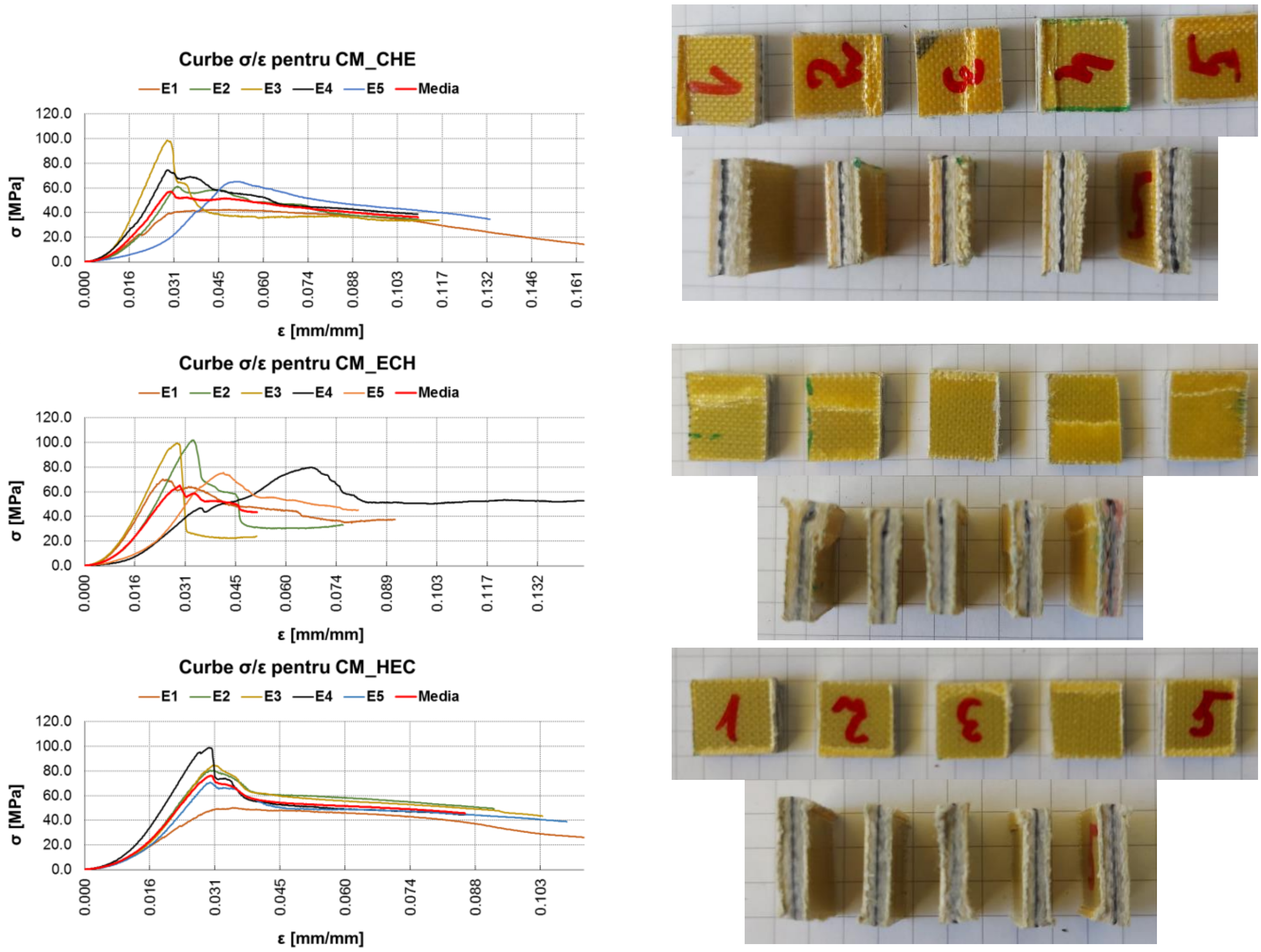


Fig. 5.7. Stress/strain curves and images of tested specimens (compression) – CM

For CM-type materials (fig. 5.7.) fracturing of the outer layers can be observed, but this fracturing can be determined by the fact that the cutting faces of the specimens are not plane-parallel and, until the specimen is placed, the outer layers are deformed under an action extraaxial after which the efforts are taken over by the core of the material. In the case of CM_ECH materials, fracturing of the core layers of the material is also visible, as we found with AM materials, but, most of the time, the core remains unaffected. For the CM_HEC material the smallest dispersion of the experimental data is found, but this is also valid for the AM and BM materials with the same HEC matrix.

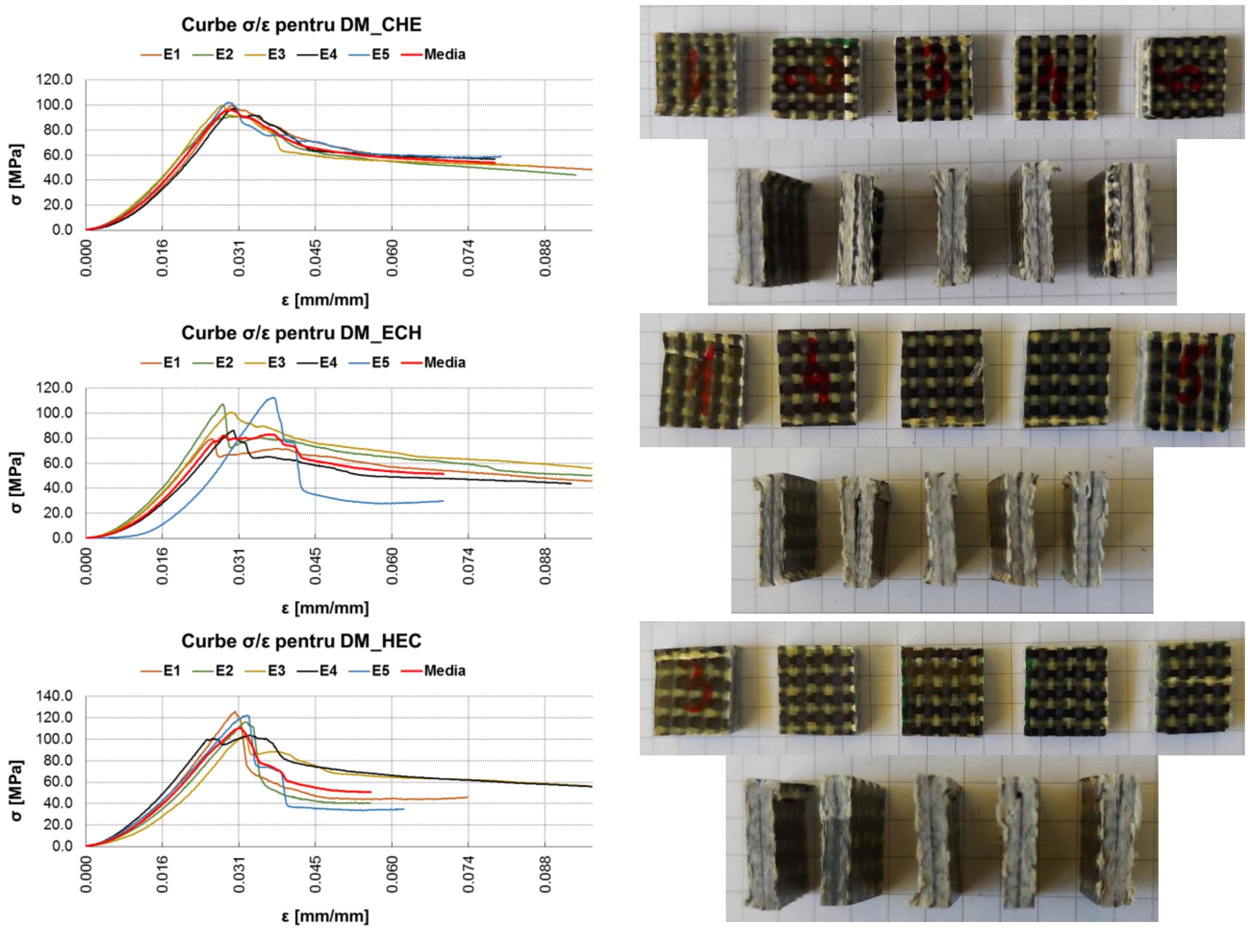
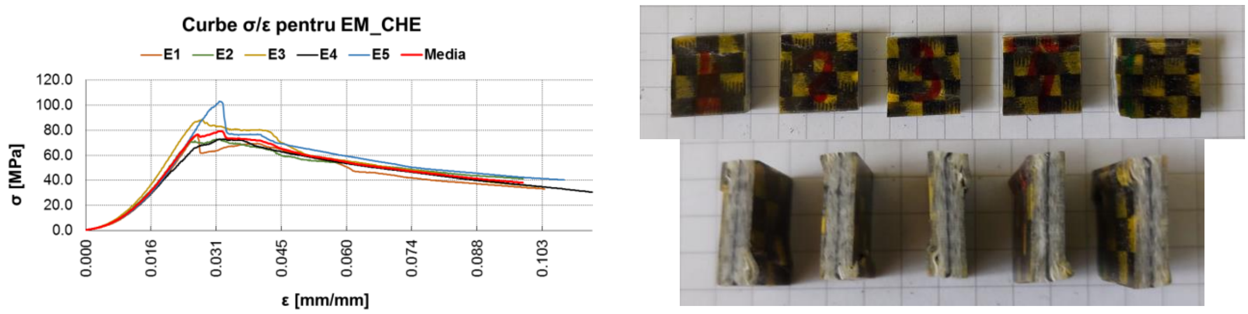


Fig. 5.8. Stress/strain curves and images of tested specimens (compression) – DM

In the case of DM type materials (fig. 5.8.), the appearance of the samples after testing is similar to that of the samples from the BM material, with the damage to the outer layers (which this time are thin). Fractures (with sliding of the resulting fragments) of the core of the material are also observable, a sign that the efforts are taken over by the core and the outer layers do not have much influence. As in the case of CM materials (also with thin outer layers), their fractures are observed in the vicinity of the edges of the samples (even if in this case these fractures are not easily visible in the photographs due to the color pattern of the fabrics).

EM-type materials are materials with very thin outer layers of reinforcement but which, unlike all other materials analyzed, are not made of a fabric but of a felt. In the case of tensile tests, we have seen that packages of three outer layers of these materials all fail at once in a direction perpendicular to the direction of loading of the specimen. In fig. 5.9. the stress-strain curves and the appearance of the specimens tested in compression for EM materials are shown.



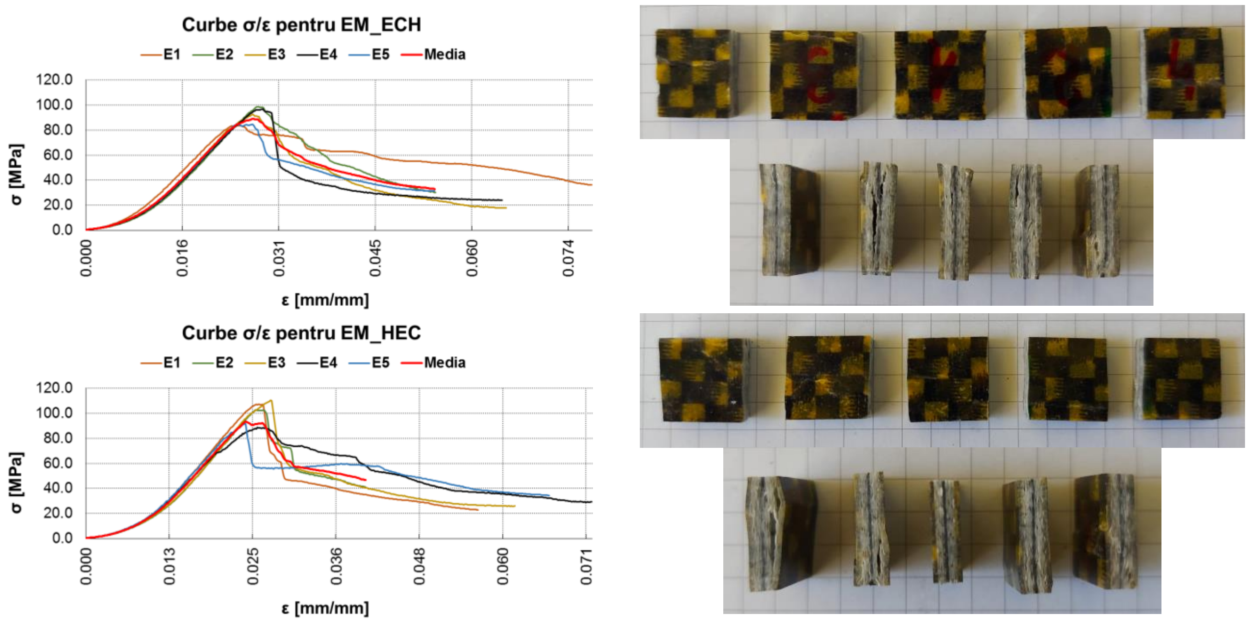
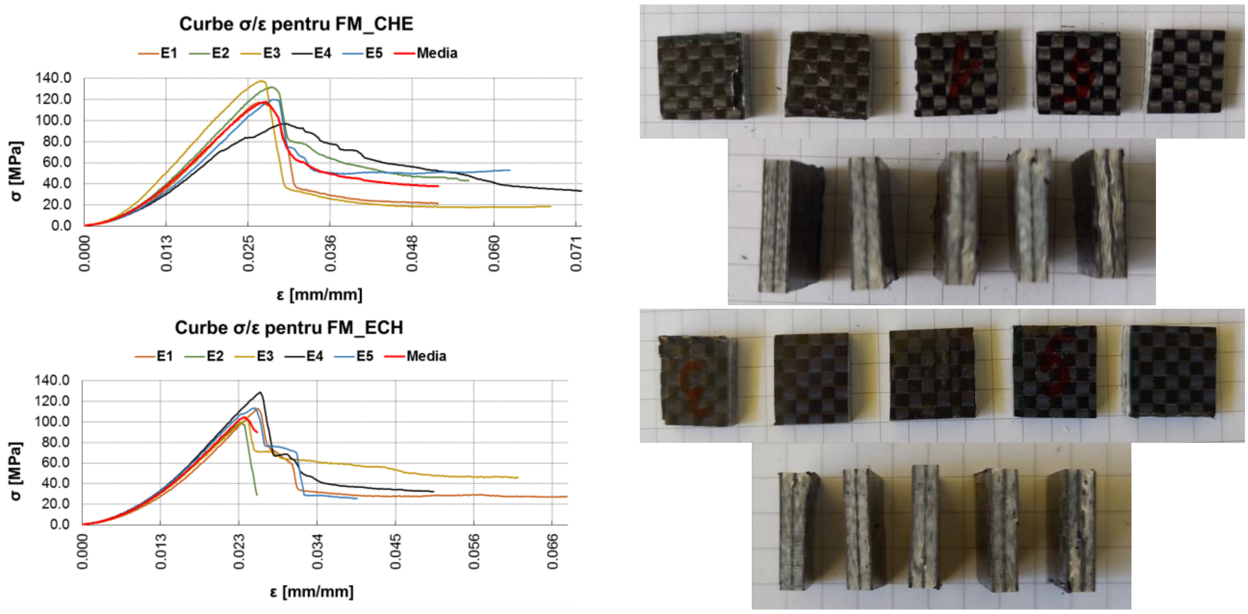


Fig. 5.9. Stress/strain curves and images of tested specimens (compression) – EM

Delaminations inside the material are easily visible, most likely caused by the fact that, practically, the outer layers of reinforcement do not take over the compressive stress, and then it is distributed on the core of the reinforcement made of glass fiber fabric (stiff in the longitudinal direction). In the case of the EM_CHE material, the delaminations are at the level of the adjacency between the outer layers and the first layers of the core. In the case of the other two types of matrices, the delaminations appear both inside the core and, apparently, at the level of the junction between two polymers (samples 4 and 5 of EM_ECH and samples 1 and 2 of EM_HEC).

The fact that the responses of the materials are much more grouped than in the case of the other materials (the dispersion of the results is much lower) validates the hypothesis that the outer layers do not take over from the compression stress and the response of the materials is that of the core and this response depends on the predominant polymer (H – in the first case, C – in the second case, E – in the last case). It is as if the material consisted only of the core and if there were no imperfections generated by shearing the samples, probably the answers would strictly depend on the nature of the internal matrix, the quality of the polymer junctions (their elastic properties) and obviously the quality of the polymer-fibers interphase. Even if the test results are affected by the cutting imperfections (the quantitative ones) the information obtained in relation to the behavior of the material is interesting.



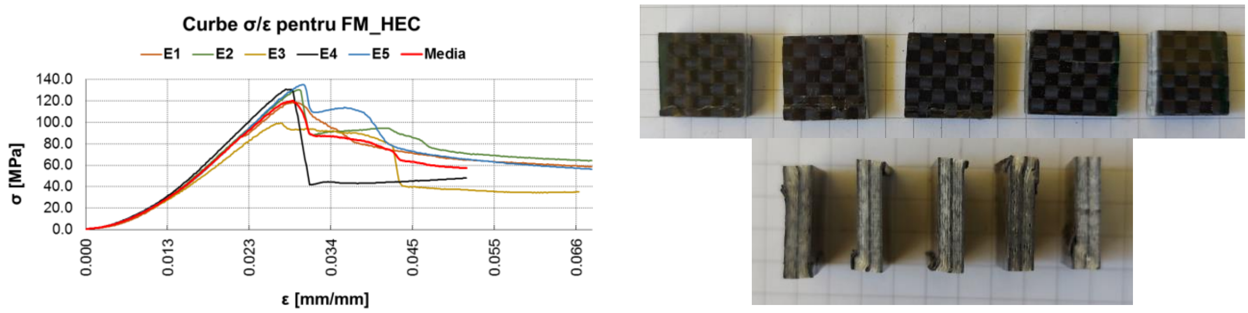
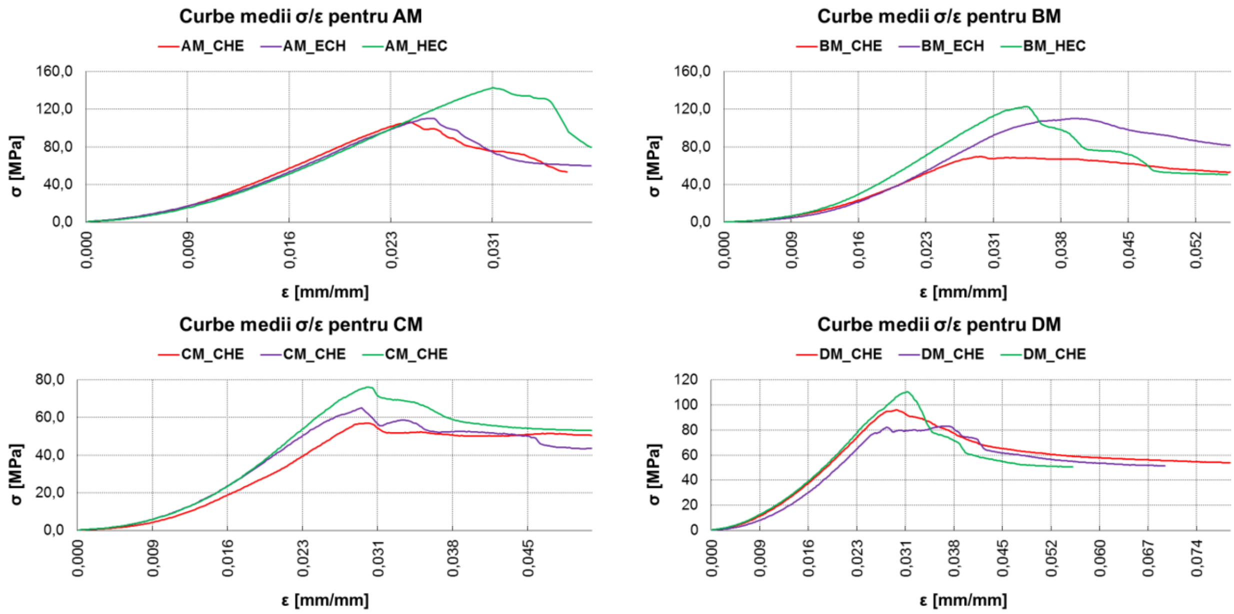


Fig. 5.10. Stress/strain curves and images of tested specimens (compression) – FM

In fig. 5.10. the evolutions and the images of the samples from the FM type materials in the compression tests are presented. FM materials are thick materials with homogeneous outer layers (carbon fiber fabric) and should behave like AM and BM materials where part of the compressive stress is also taken up by the outer layers. In the case of FM materials, internal fractures and local internal delaminations produced by these fractures can be observed. As in the case of AM and BM materials, it is possible to observe (on the surfaces of the tested specimens) areas of curvature of the outer layers without, however, having a very large extension (as in the case of CM materials, for example). There are no visible delaminations between two types of fabric in the reinforcement, nor any that could correspond to the complete breaking of a junction between the polymers. Thus, we can consider that at the level of the junctions, the mixture of the two polymers leads to the appearance of a layer (of unknown thickness) along which the transition is made from the properties of one polymer to the properties of the other polymer. Junction thickness is difficult to determine as long as there are no directly observable properties of the polymers (except perhaps color). Even if there were a technique based on color measurement, it would be difficult to determine the thickness of a junction with epoxy resins.

In fig. 5.11. the average σ/ε curves of the reinforced materials are shown and, with the exception of the BM material (fabric of carbon fibers and aramid fibers in the outer layers), the clustered behavior of the materials with thick outer layers (regardless of the matrix type) and the dispersed behavior can be seen of materials with thin outer layers. In the case of BM materials, again, we can explain this behavior by the fact that the nature of the polymer-fiber interphase depends on the type of fibers (carbon fibers and aramid fibers). A thicker sheath better protects (in axial compression) the core material.



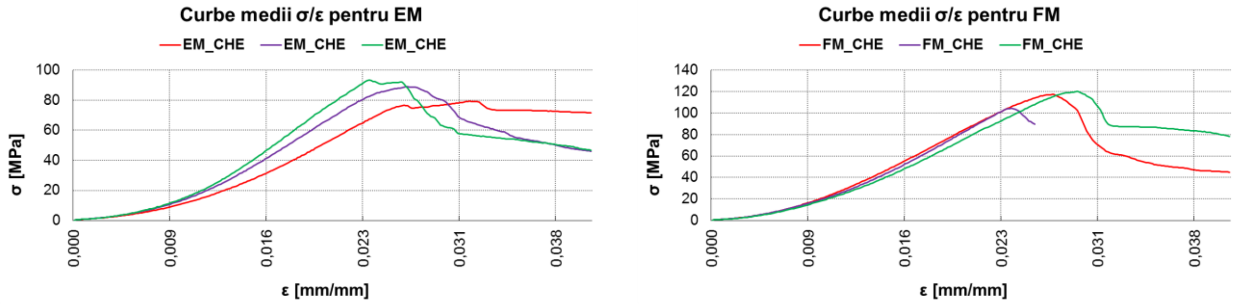


Fig. 5.11. Mean stress/strain curves of reinforced materials (compression)

In fig. 5.12. the values of the compressive elasticity modules are graphically shown – as we have shown above, there are three values – the first which corresponds to the beginning of the test and, theoretically, to the breaking of the outer layers on which the load is inclined (due to shearing deficiencies), the second which corresponds to the elastic response on the second level of the average curve and automatically which is the value returned by the testing machine for the whole test.

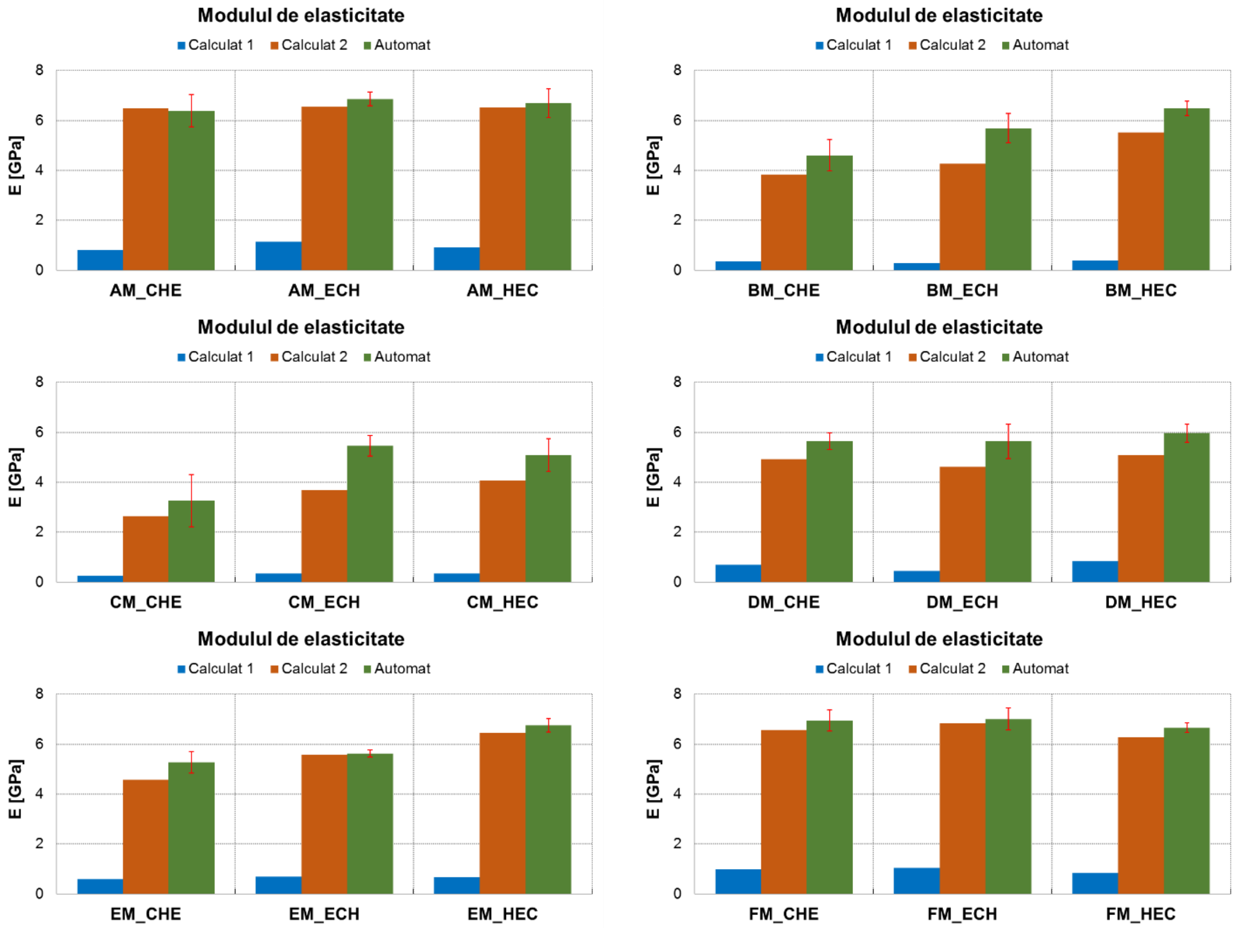


Fig. 5.12. Compressive elastic moduli of materials – analysis by classes

If the junctions were made of polymers of different classes, a determination of the junction thickness would probably be more accurate. For the materials formed and analyzed in this study, it is almost impossible to determine the thickness of the junction. However, it is expected that in the case of polymeric materials with junctions these thicknesses are greater than those in the case of reinforced materials. In the latter case, the junction is formed between the two adjacent layers of fabric imbued with different prepolymer and, due to diffusion, it can - eventually - affect the two layers of reinforcement.

The analysis of the values of the compressive elastic modulus (the three values), according to the type of matrix, is presented, in graphic form, in fig. 5.13. Apparently and within measurement errors, materials containing rigid-rigid (CH) polymer junctions behave similarly (CHE and ECH matrices) while materials with two rigid-less-rigid junctions (HE and CE) exhibit elastic behavior higher (higher values of the elasic modulus). In the case of materials with thick homogeneous outer layers, we can even speak of a coincidence of the values of the elastic modulus (within the measurement errors) regardless of the type of matrix (type of junctions).

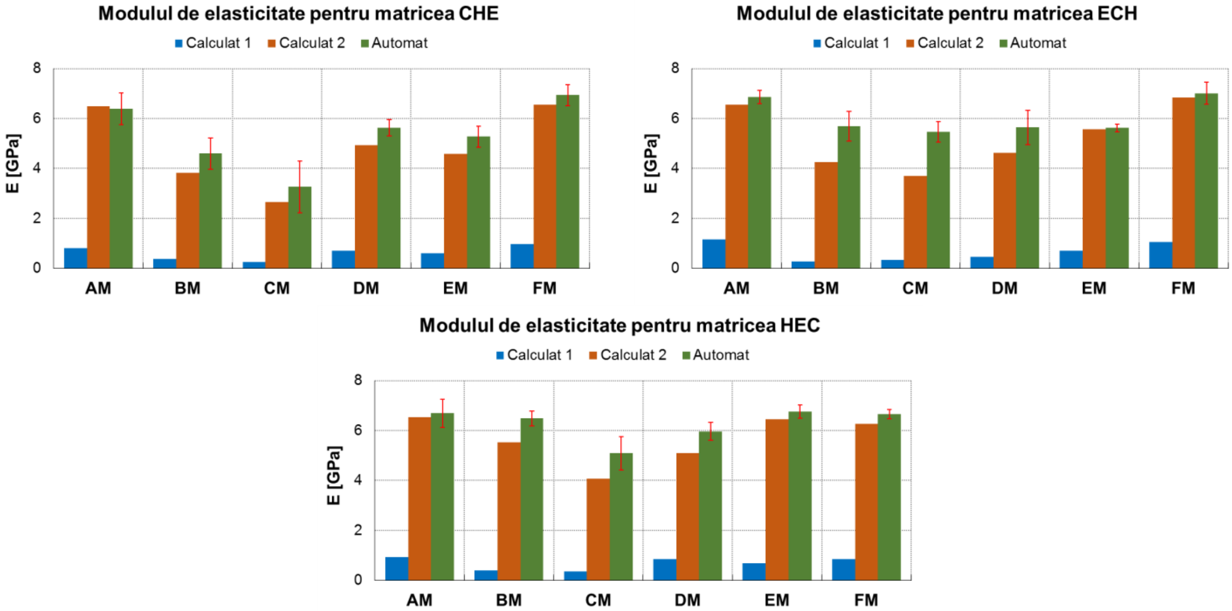


Fig. 5.13. Mean stress-strain curves for reinforced materials (compression)

5.4. Partial conclusions – reinforced materials – compression tests

- most materials give a core-type response, after flattening the edges resulting from cutting;
- a higher strength, accompanied by a higher fragility, is found in the case of AM type materials which are made, except for the middle layer of the reinforcement, from glass fiber fabrics;
- in AM materials, internal delaminations due to buckling (under compression stress) of the fibers oriented in the direction of loading can be observed;
- reinforced materials that have thin fabrics in the outer layers have practically the same type of response because the total surface on which the load is applied to these layers is much smaller than the transverse surface of the core;
- in the case of EM materials (with felting in the outer layers), internal delaminations are found for all types of matrices, but these delaminations are sometimes in junctions and other times at the adjacency between two types of fabrics;
- the elastic moduli calculated on the first linear segment of the σ/ε curves (calculated 1) have very low values compared to the elastic moduli calculated on the second linear area of these curves (calculated 2), for all the materials analyzed and the latter are lower than the values of the automatic elastic modulus.

Chapter 6

Analysis of three-point bending tests results

6.1. Epoxy resins and bonding materials

Testele de încovoiere în trei puncte au fost realizate pe aceeași mașină de teste după înlocuirea bacurilor cu sistemul suport (în două puncte) – poanson. Au fost respectate setările de viteză de înaintare a poansonului – 5mm/min și testele au fost făcute până la ruperea epruvetelor. În mod evident primele materiale supuse încercărilor de încovoiere în trei puncte au fost cele trei rășini epoxidice utilizate, epruvetele fiind de formă cilindrică cu diametrul de 8mm și lungimea de 100mm. Rezultatele acestor teste sunt prezentate în fig. 6.1.

Three-point bending tests were carried out on the same test machine after replacing the trays with the (two-point) support – punch system. The punch advance speed settings – 5mm/min were followed and the tests were done until the specimens broke. Obviously, the first materials subjected to three-point bending tests were the three used epoxy resins, the samples being cylindrical with a diameter of 8mm and a length of 100mm. The results of these tests are shown in fig. 6.1.

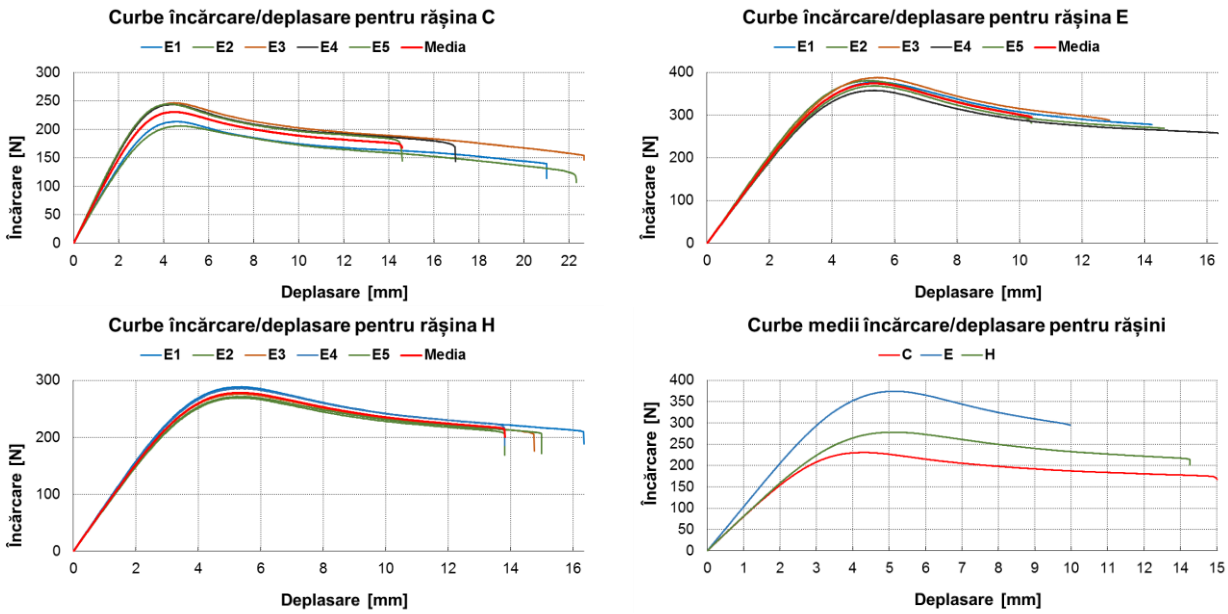


Fig. 6.1. Load/displacement curves for the three studied resins studied (bending)

The highest punch displacement values are recorded for resin C, while the lowest are recorded for resin E. One observation should be made about this, namely that resins C and H break (as can be seen from individual curves) while in the case of resin E, the failure of the specimen is not recorded because the test is stopped following the conditions set for its interruption.

It is interesting that, in the case of the average curves, the maximum values of the loads are observable for displacements between 4mm and 5mm, for all three epoxy resins. The averages, on the other hand, are much closer to the behavior of the individual specimens for all three resins, in contrast to the results recorded for the other test types.

In fig. 6.2. individual load/displacement curves for materials containing junctions and average curves for the three types of junctions are shown.

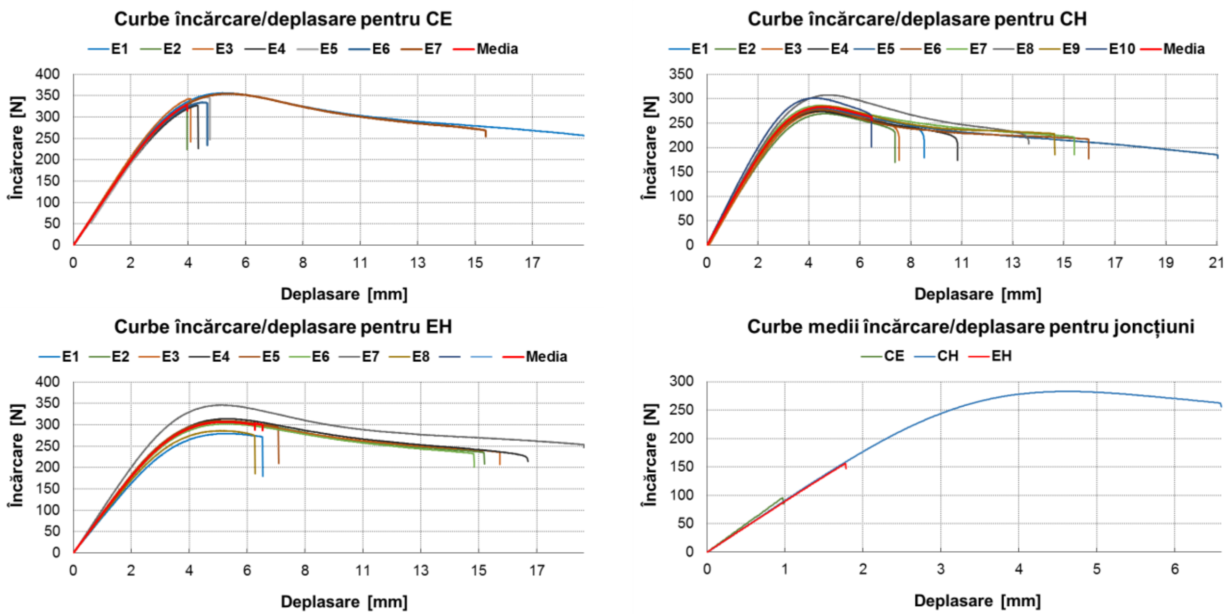


Fig. 6.2. Load/displacement curves for materials with junctions (three-point bending)

The three-point bending tests were performed by placing the punch on the junction area, the stresses are directly related to this area and are not very related to the general elastic properties of the three polymers - in fig. 6.3. are images of the tested samples. All the specimens (with one exception) are broken in the junction area – we showed in Chapter 3 how the specimens were obtained for the bending tests – marked with a line perpendicular to the cylinder generator. What can be easily seen is that the junction center mark is on the E side of the specimens containing the junctions of this polymer with the other two (left image for CE and right image for EH) meaning the specimens broke on the side of more rigid polymer. In the case of the CH junction, the break occurs right in the junction. These observations could shed some light on the junction thickness (which we talked about in the tensile tests), i.e. the distance at which the properties of the two polymers that make the junction overlap to make the transition from one set of properties (of a polymer) to another set of properties (of the second polymer) - this apparent thickness of the junction has a value at most equal to the diameter of the punch. In the case of the CH junction it can be said to be null.

Fig. 6.3. Specimens tested in three-point bending (materials containing junctions – CE, CH, EH)

Among the parameters that the testing machine software can automatically evaluate is the flexural modulus, although we have not been able to understand how this is evaluated (for cylindrical specimens). Therefore, unlike the cases of tensile and compression tests, in the case of three-point bending tests, we present the automatic values of the flexural moduli for the three polymers and for the three materials containing the three types of polymer junctions (fig. 6.4.).

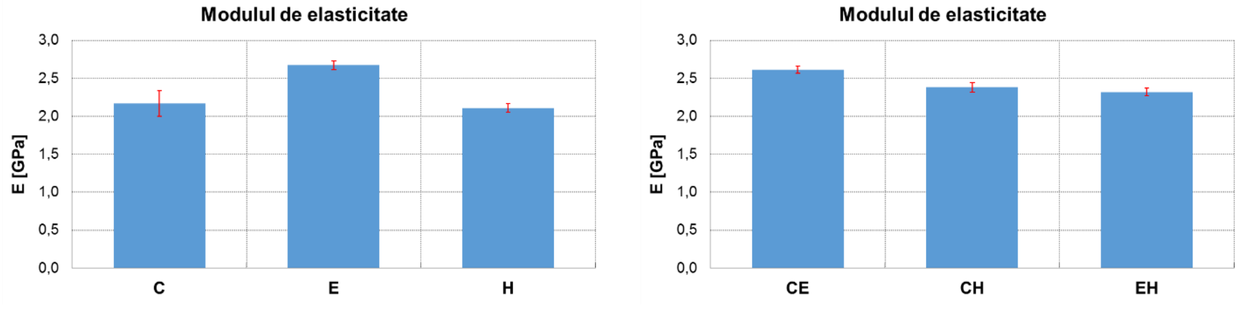


Fig. 6.4. Flexural elastic modulus

As can be seen the flexural moduli of resins C and H are practically equal and the highest value of the modulus is in the case of resin E. This explains quite well the fact that the CH junctions break in the junction area while the others two break in the area of the stiffer polymer. The value of the flexural modulus of the material containing the CE junction is (within the measurement errors) greater than the values of the flexural moduli of the two polymers. The observation is also valid for materials containing the CH junction. The only junction for which the value of the flexural modulus is between the values of the flexural moduli of the two polymers is the HE junction. But, here the experimental errors could be higher due to the contamination that I described previously.

6.2. Conclusions – materials with junctions (three-point bending tests)

- all the tested samples break - in the case of rigid resins (C and H), the break occurs when the punch moves between 14mm and 18mm;
- in the case of specimens made of resin E, the setting of the test machine (testing interruption conditions) does not allow to record the moment when the fracture of the specimen takes place;
- in the case of materials containing junctions, the rupture of the specimens takes place, in all cases (with only one exception), in the vicinity of the junction in the part of the more rigid polymer (junctions CE and EH) or even in the junction for the junction between the two resins with similar stiffnesses;
- the flexural moduli (determined automatically by the testing machine software) show the highest value for resin E and reasonably equal (flexural) values for the other two resins;
- the loading of the samples is done perpendicular to the axis of the sample (the height of the cylinder) and in the plane of the junction, which means that its upper layers are subjected to compression (perpendicular to the plane of the junction) and the lower ones are subjected to tension (perpendicular to the plane of the junction), i.e. exactly under the conditions in which the samples of the materials with junctions were tested in during of compressive tests and, respectively, tensile tests, presented in the two previous chapters;
- because the punch is in direct contact with the specimen, the generation of polymer fragments that were observed in the compression tests where the distance to the junction was comparable to the thickness of the specimen cannot be observed.

6.3. Fabric reinforced materials with layered matrix (three-point bending tests)

The three-point bending tests were carried out on parallelepiped specimens with a length of 100mm, a width of 15mm and a thickness equal to the thickness of the material. For each analyzed material, in part, the samples were loaded from the face that has the polymer described by the first character in the matrix to the face that has the polymer described by the last character in the matrix (for an XM_HEC material, the load is applied from face H to face C) .

Under these conditions, according to the theory of flexural elasticity, each of the three polymers is found, in turn, in the middle layer of the material that remains undeformed.

As in the case of the analysis of the tensile tests, in this case too I chose the specimen marked 4 (from all the sets of specimens tested) to perform a visual analysis (on photographs) of the effects of bending to failure of the materials.

For AM materials, the load/displacement curves and the photos of specimen 4 after testing are shown in fig. 6.5.

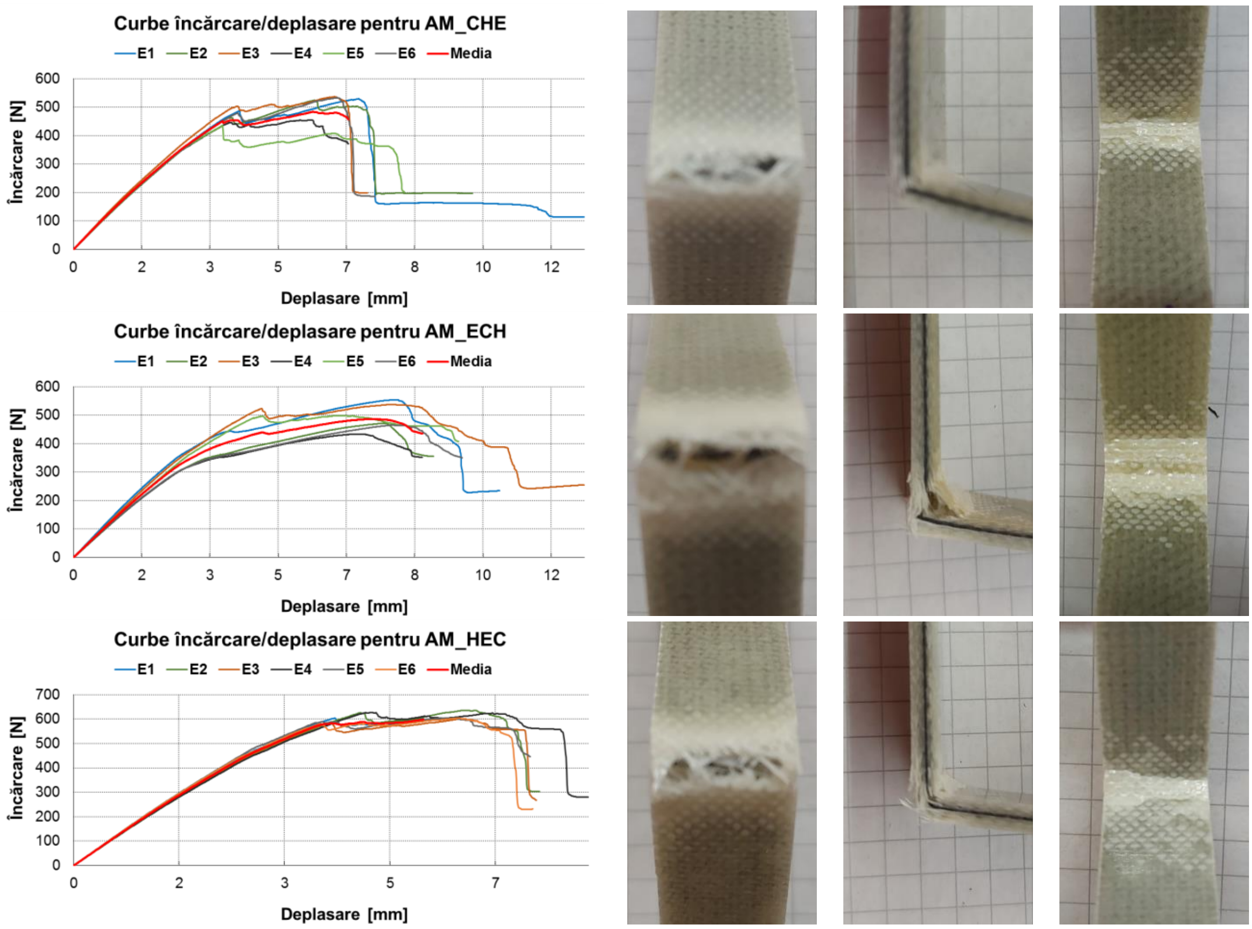


Fig. 6.5. Load/displacement curves and visual analysis for AM materials (three-point bending)

At a first analysis, it can be observed that, in the case of materials containing rigid-rigid (CH) junctions, the dispersion of the obtained results is very large. Regarding the bending effects, it can be seen that the effect in the contact area between the punch and the specimen is the smallest in the case of AM_CHE (no delamination – color change) as in the other two cases. On the opposite faces to the face on which the loading is carried out, the breaking of the layers occurs with the tearing of the fibers out from the matrix (AM materials are materials with thick homogeneous outer layers). For the materials containing the CH junction, complete fracturing of the specimen can be observed, while, for the material with resin E in the center, the middle layer is fractured but no relative displacements of the two fragments resulting from fracturing are observed.

The effects of bending include, as in the previous case, the fracturing of the middle layer of the reinforcement but, this time, the fragments resulting from the fracturing do not move relative to each other.

When rigid resins (C or H) constitute the matrix for the layers opposite to the layers on which the loading is applied, the fracturing of the outer layers accompanies the fracturing of the core glass fiber layers (as can be seen in the cases (BM_ECH and BM_HEC).

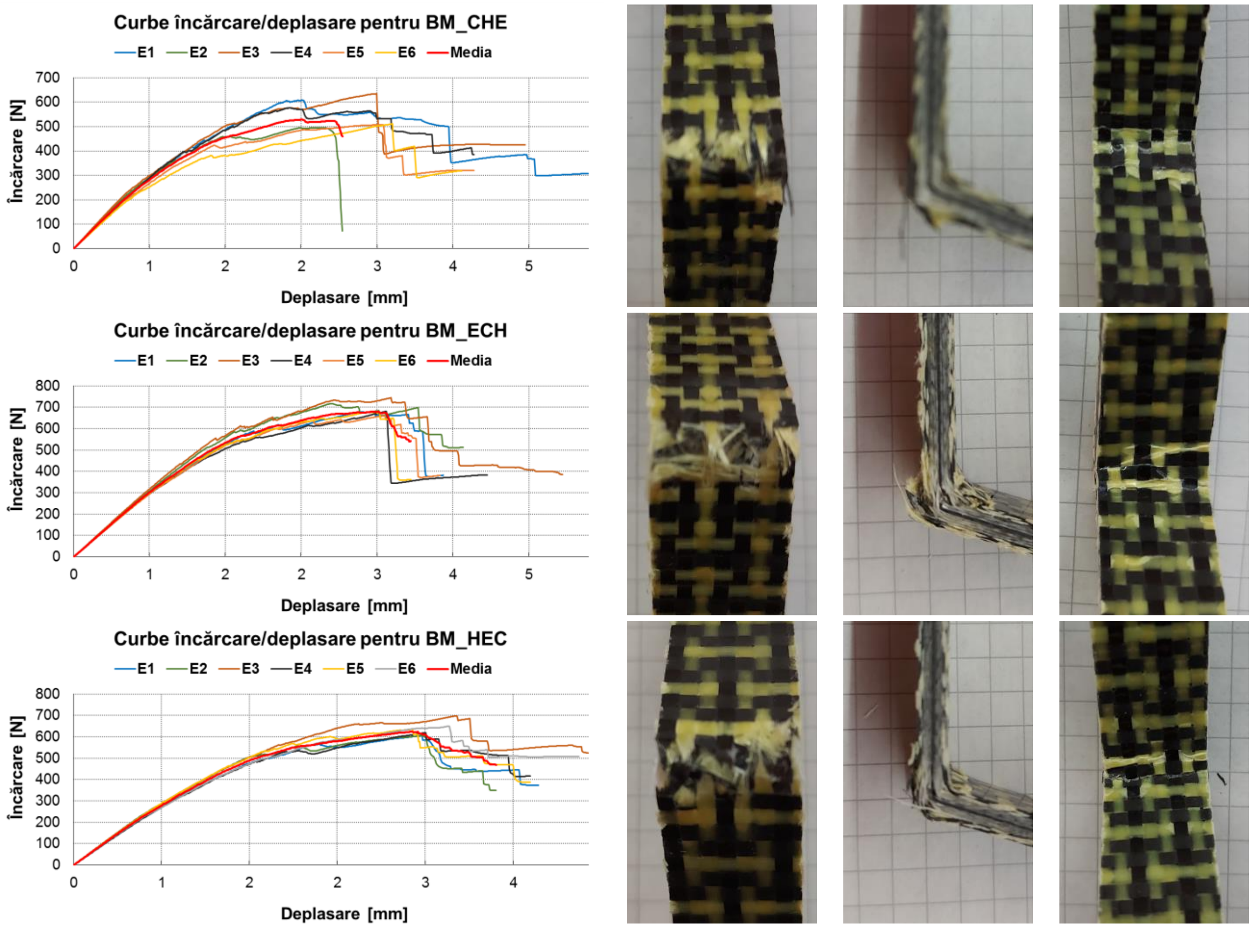
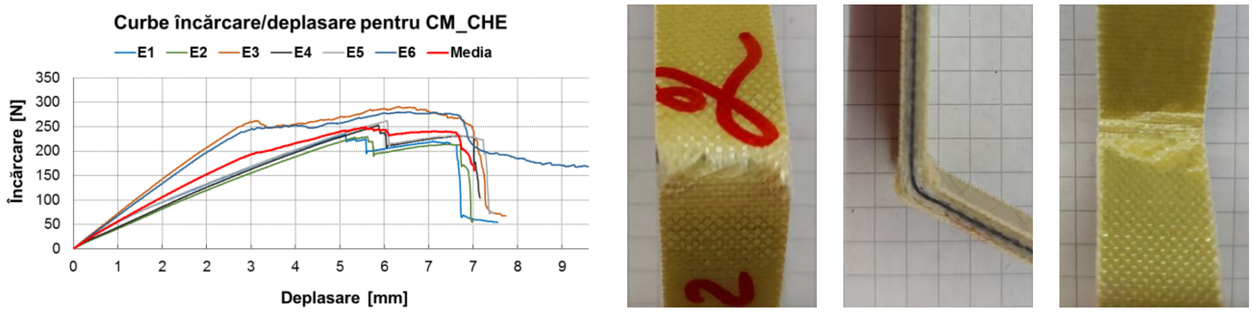


Fig. 6.6. Load/displacement curves and visual analysis for BM materials (three-point bending)

Another effect not observed in the case of AM materials is that of local delamination (visible in the side photographs of the specimens) and this may be a confirmation of the quality differences between the polymer-carbon fiber interphase and the polymer-aramid fiber interphase (as we mentioned in the case of tensile and compression test results). The outer layers are immersed in the same polymer (even if it differs from one side to the other) so the delamination effect cannot be associated with the presence of polymer junctions.

As in the two previously analyzed cases (AM and BM), the individual load/displacement curves are more clustered in the presence of E resin in the middle of the material. For the CM_CHE material, the behavior of specimens 1 and 3 may be due to forming defects.



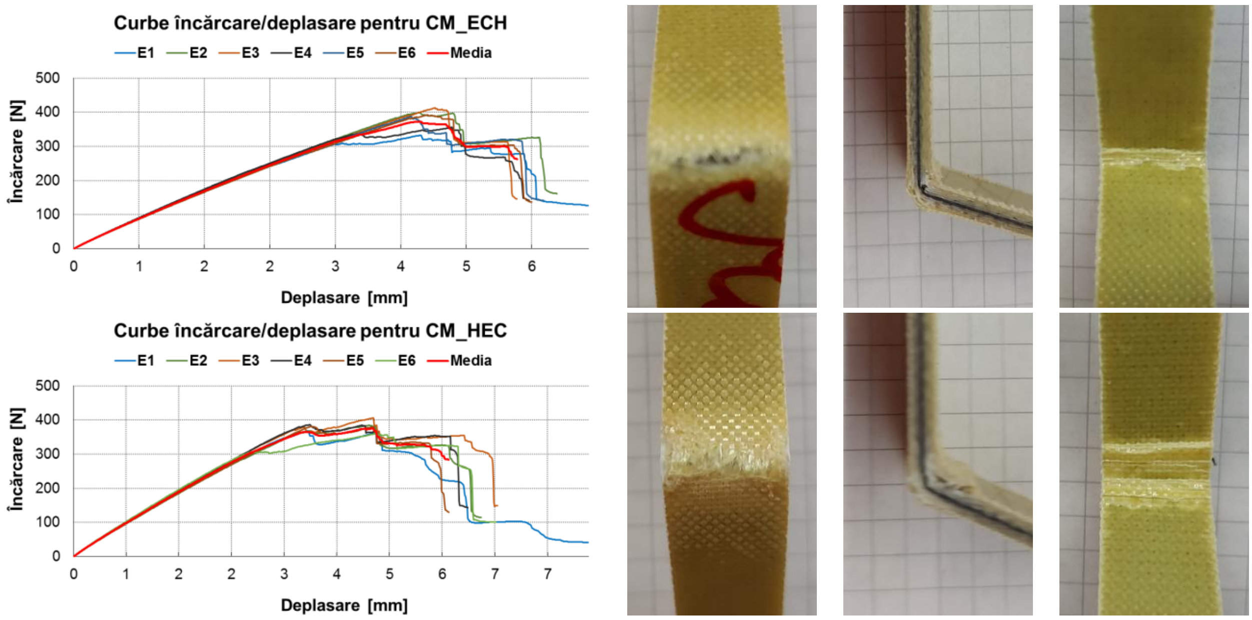


Fig. 6.7. Load/displacement curves and visual analysis for CM materials (three-point bending)

DM materials are materials that have thin fabrics in the outer layers but, unlike CM materials, these fabrics are hybrid fabrics similar to those used in the outer layers of BM materials. Individual experimental data and photographs of the tested specimens are shown in fig. 6.8.

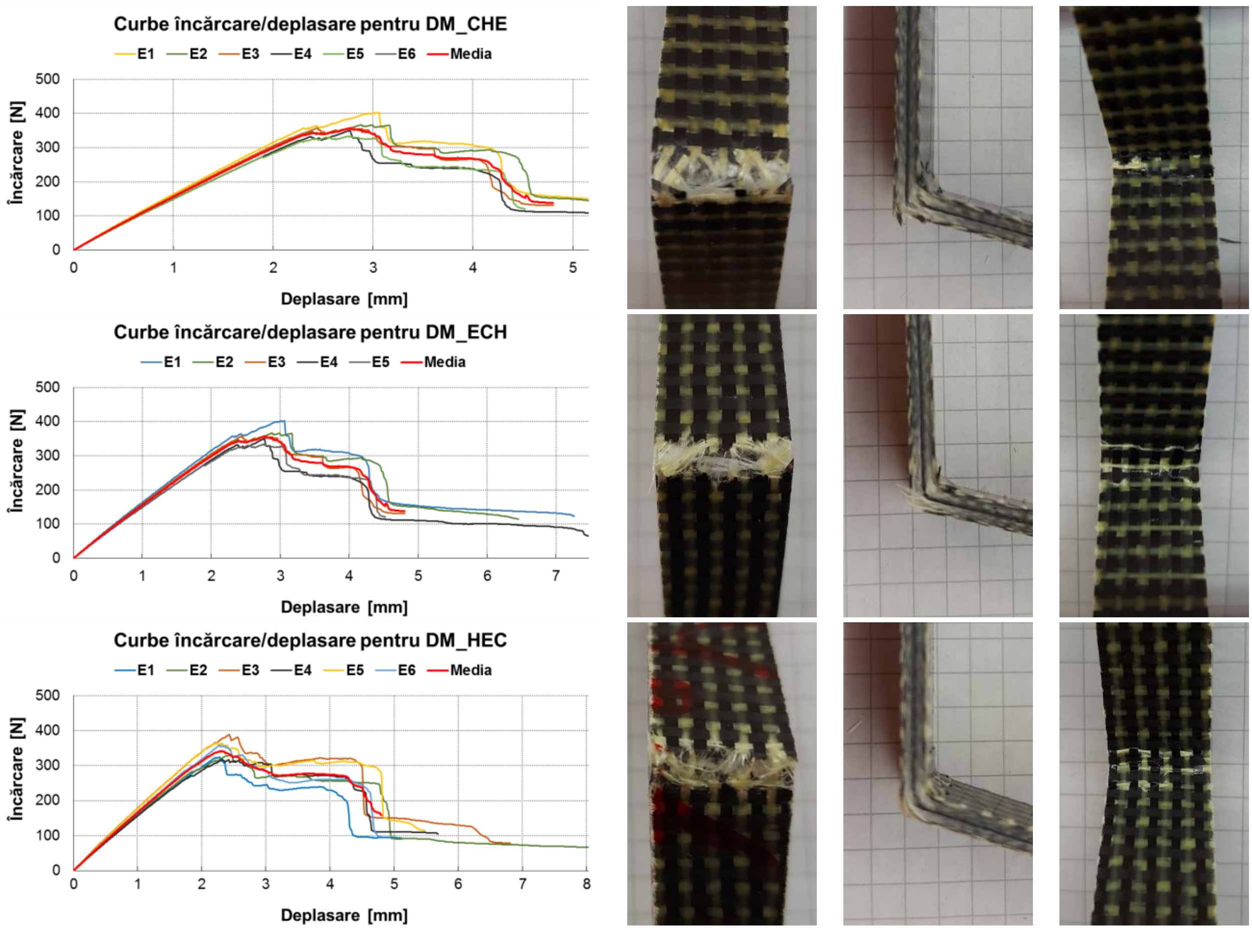


Fig. 6.8. Load/displacement curves and visual analysis for DM materials (three-point bending)

What is remarkable about the bending test results for DM materials is that the individual tests are grouped for all matrix variants, as can be seen in the images above. Moreover, it can be easily observed that the linear area of the mean load/displacement curve for each matrix variant of the DM material passes through the coordinate point (2mm, 300N), i.e. all materials have the same elastic response.

As can be seen, the delamination occurs inside the core (the layers of glass fiber fabric detach from the middle layer made of carbon fiber fabric) and from this point of view the only explanation is related to the existence of a forming defect (the carbon fiber fabric had areas where the pre-polymer did not penetrate – taking into account the order in which the reinforcement layers were placed in the mold).

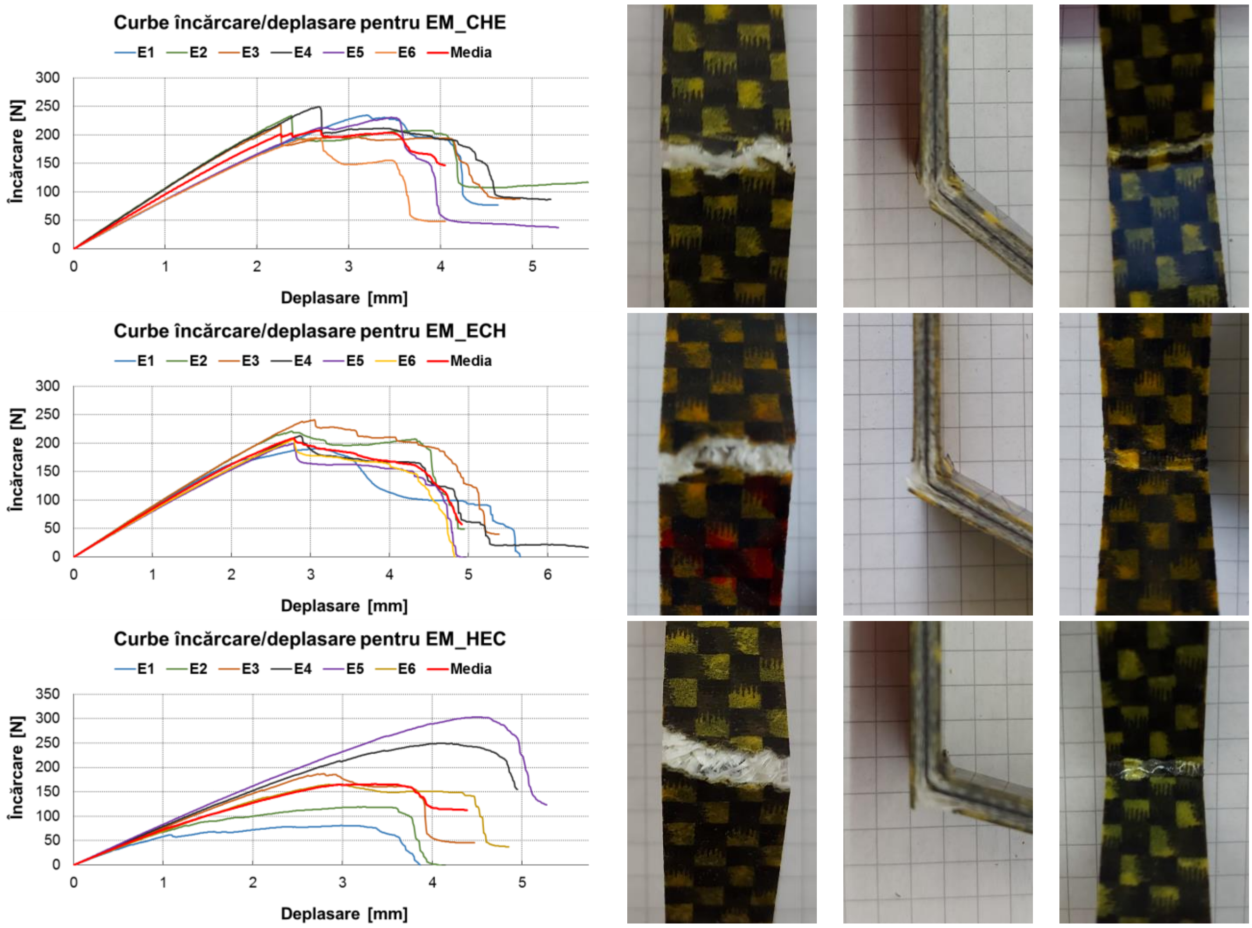


Fig. 6.10. Load/displacement curves and visual analysis for EM (three-point bending) materials

EM materials are special, as we have already mentioned in the two previous chapters, having very thin layers on the outside made of felts of carbon fibers, aramid fibers and glass fibers. Since there is no regular distribution of the fibers, it is expected (as in the case of tensile and compression tests) that these layers contribute very little to the elastic bending behavior of the materials - fig. 6.10.

The fractures of the outer layers are not oriented in specific directions, but rather appear to be determined by the orientations of the fibers in the core. Pull-outs of glass fibers are observed regardless of the nature of the matrix, and also for the faces on which the loading is applied, the effects do not appear dependent on the nature of the matrix.

FM materials are, like AM materials, materials where the outer layers of reinforcement are thick and homogeneous. The results of three-point bending tests for these materials are given in fig. 6.11.

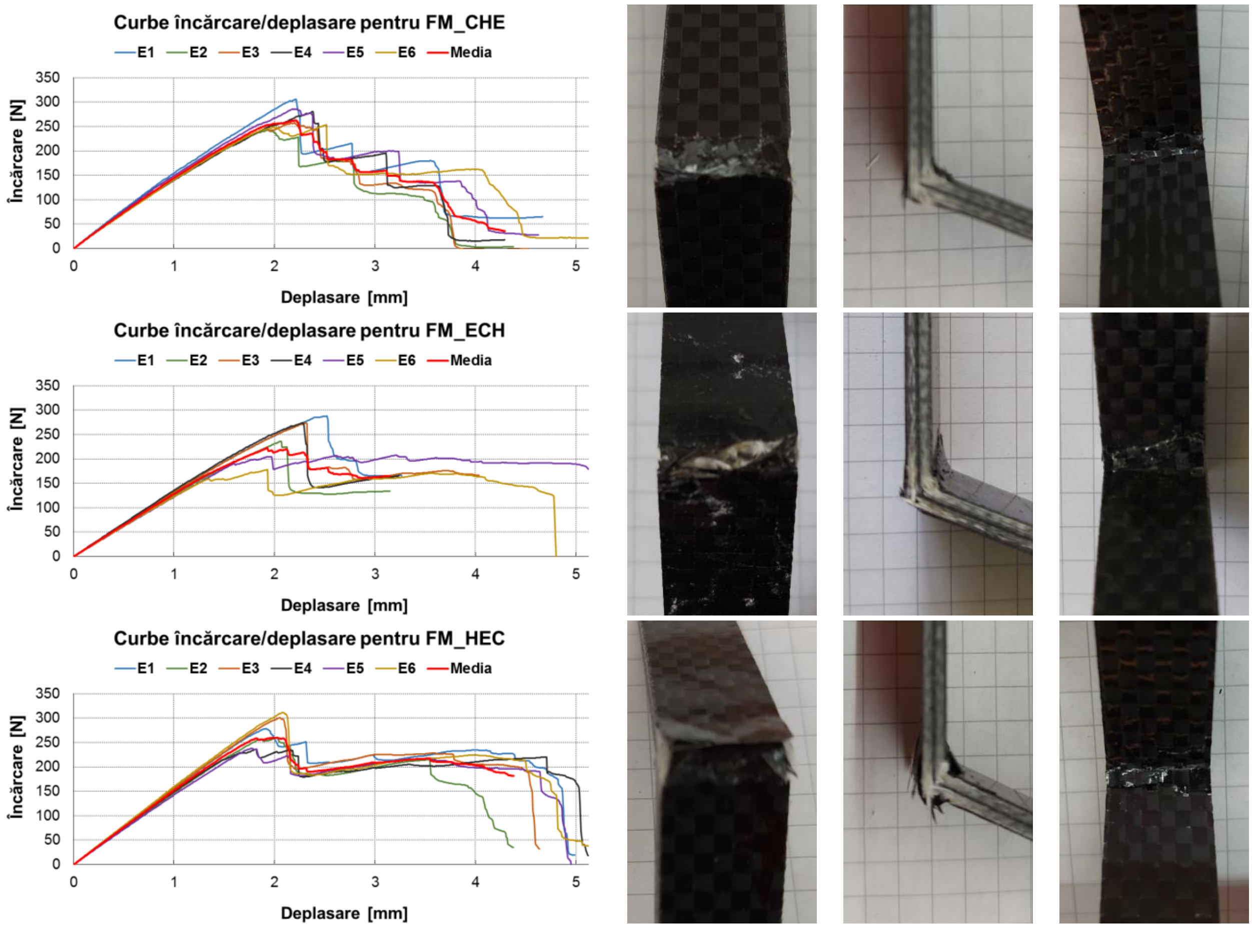
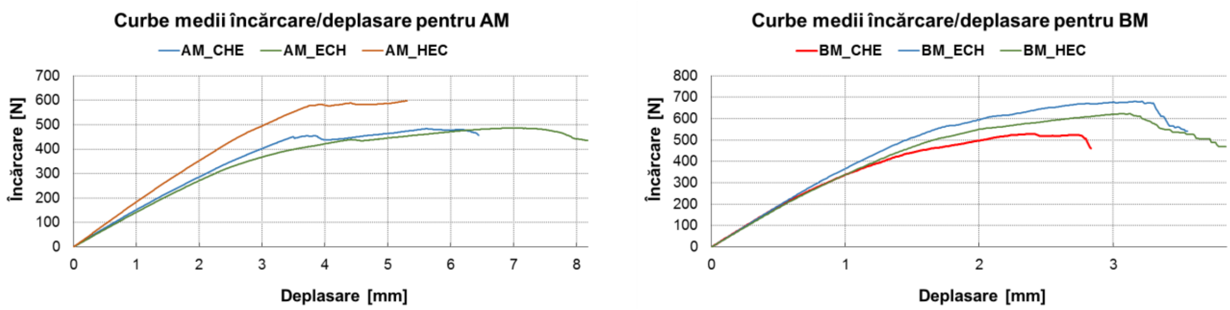


Fig. 6.11. Load/displacement curves and visual analysis for FM materials (three-point bending)

For these materials, the dependence of the effect of the presence of a certain resin in the reinforcement layers on which the loading is applied is visible - more precisely, it can be seen that for resin E on the outside, the layers of carbon fiber fabric (from the side opposite to the side on which the loading is applied – resin C) the outer layers fracture without separating so that the inner layers (glass fiber fabric) cannot be seen (FM_CHE). For resin H on the outside (loading applied to layers immersed in resin E) the fracturing is clear and the fracturing of the adjacent layers made of glass fiber fabric (FM_ECH) can also be observed. In the last case (FM_HEC) the layers on the face opposite to the one on which the load is applied fracture differently and a strong delamination is also visible.

The comparative analysis of the average load/displacement curves for each type of material is presented in fig. 6.12.



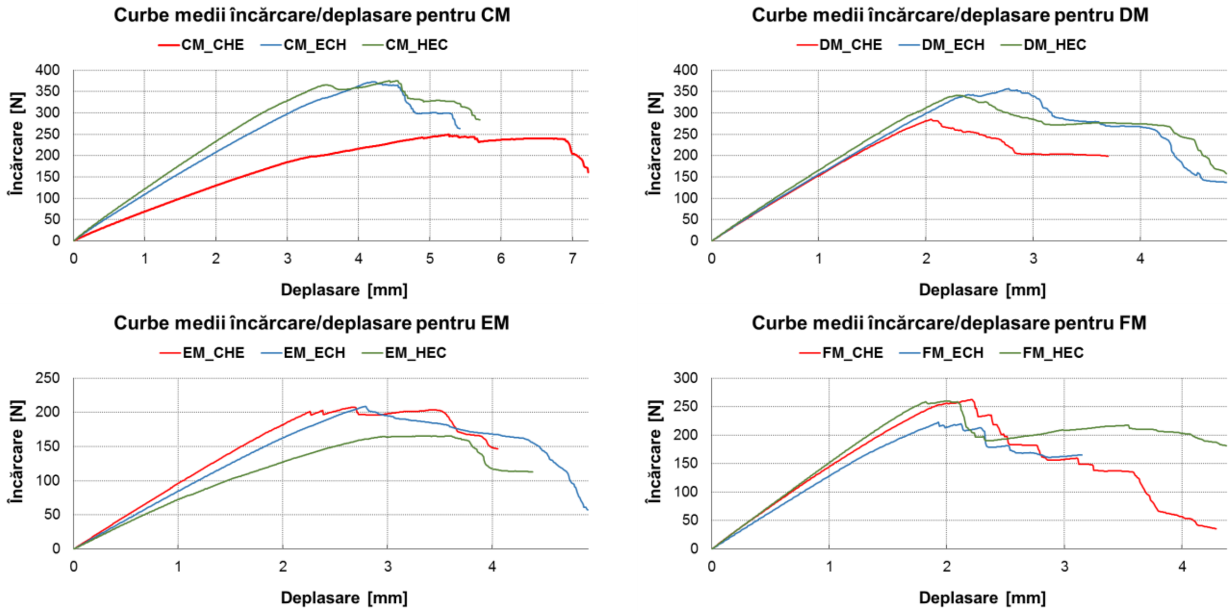


Fig. 6.12. Average load/displacement curves for the analyzed materials (three-point bending)

In the graphs above one can see the different slopes of the linear areas of the curves. These different slopes (different elastic responses) can only be attributed to the alternation of polymers in the matrix (not to the existence of polymer junctions in the material). All tested materials have the same reinforcement and should, after the appearance of the first matrix fractures, that all have a reinforcement-like behavior, which obviously cannot be observed in those presented graphically. There is also the possibility - already mentioned in the analysis of the results of the tensile and compression tests - that, due to the moment at which the reinforcement layers were deposited in the mold - there are differences between the properties (equivalent thicknesses) of the reinforcement layers determined by the viscosity differences of the pre-polymers. The same differences in viscosity can also lead to the inability of the pre-polymer to penetrate to the middle of the fiber bundle in thick fabrics.)

6.4. Partial conclusions - fabric reinforced with layered matrix materials

- the three-point bending tests were performed on standard samples with the application of loading on one side of the materials, namely the side that has the matrix made of the first polymer mentioned in the name of the material XM_CHE – loading from face C to face E;
- AM materials (with outer layers made of glass fiber fabric) are very sensitive to bending tests due to the low bending strength of the glass fibers - in this case the best response is of the AM_HEC material, which contains two junctions rigid polymer - less rigid polymer;
- DM and FM materials have almost identical behavior determined by different causes: for DM thin outer layers of aramid fiber fabric very resistant to shearing and bending; for FM whose outer layers are very thick, the response is mediated by the mutual displacement of the fibers inside the woven bundles favored by the absence of the polymer, which prevents the fibers from fracturing;
- as in the case of tensile or compressive tests, the best responses are those of materials containing E resin in the middle of the matrix, i.e. of materials containing two less rigid-rigid polymer junctions (CE and EH), unlike the others two types of matrices containing a rigid-rigid polymer junction (CH) and a less rigid-rigid polymer junction (CE or EH).

Chapter 7

Analysis of physical test results

7.1. Thermomechanical properties

For the analyzed materials, the two perpendicular directions can be reduced to a single one given the symmetry of the distribution of fabric layers in the reinforcement. Unfortunately, it is not possible to investigate in this direction because it is not possible to cut slices (transverse to the reinforcement plane) narrow enough and with plane-parallel faces that can be placed in the thermomechanical analyzer.

In the representation below (fig. 7.3.), the values of the coefficient of linear thermal expansion are shown in the direction perpendicular to the reinforcement plane, depending on the type of material matrix. And it is easy to see that no comparison criteria can be found that could lead to valuable conclusions (as happened with all mechanical tests).

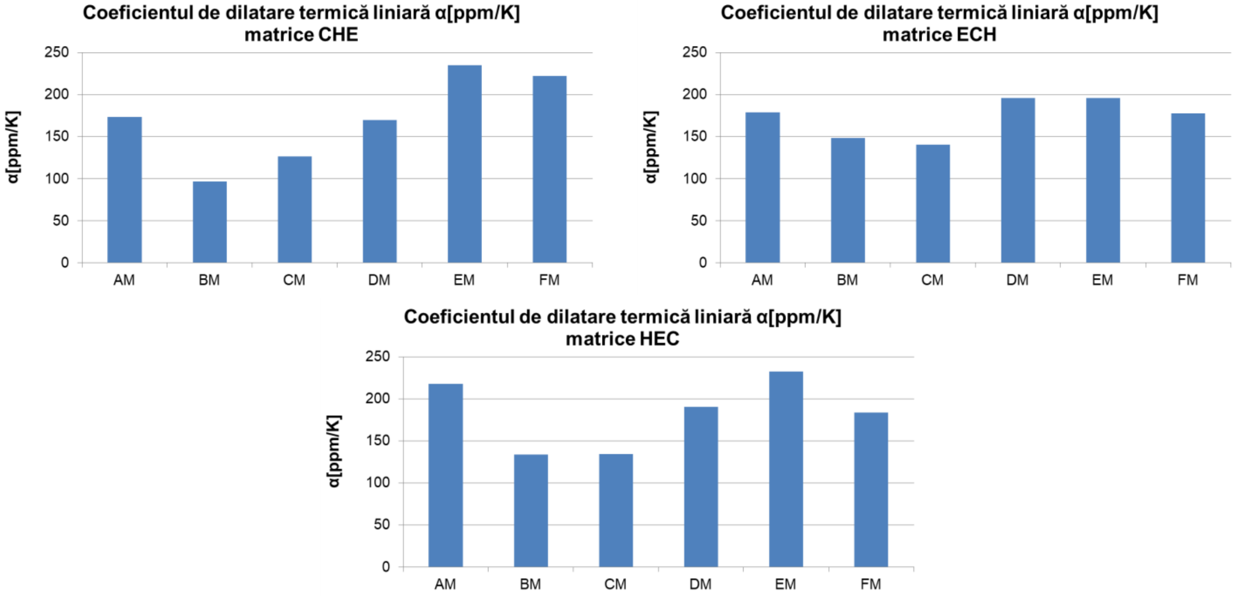


Fig. 7.3. The value of the coefficient of linear thermal expansion - matrix type

7.2. Partial conclusions – thermomechanical tests

- the values of the linear expansion coefficient in the direction perpendicular to the reinforcement plane were determined on the heating part of the analysis cycle;

- the determined values of the linear expansion coefficient indicate that all materials are dimensionally very stable (in terms of thickness), the highest values being of the order of 230μm/m·K, in the analyzed temperature range from 30°C to 200° C (maximum recommended temperature value for epoxy resins);

- due to the fact that aramid fibers shrink when heated, the most thermally stable materials are those that contain fibers of this type in the outer layers whose contraction compensates the transverse expansion of the glass fibers;

- even if theoretically, the thick outer layers include more polymer, a strong dependence of the coefficient of linear thermal expansion on this parameter is not observed.

7.3. Thermal properties

In this study, we also intended to verify the law of mixtures for the evaluation of the specific heat of the formed materials, based on the specific heat values of the components (resins and fabrics). Unfortunately, the extraction of the samples from the materials, which we tried using the same method by which we obtained the samples for the thermomechanical tests, did not lead to favorable results. Due to the thickness of the coring and the small diameter of the sample (4mm) the samples were delaminated (destroyed).

In this context we have only carried out experimental determinations to determine the specific heat values for the components used, i.e. epoxy resins and fabrics. Even so, these determinations highlighted some important aspects that until this moment were not taken into account during the interpretation of the results obtained through other analyses.

The analysis cycle is designed with a first isothermal stage (for 3 min) to ensure thermal equilibrium in the entire volume of the analyzed sample at a temperature of 25°C followed by effective heating at a rate of 10°C/min from 25°C to 125°C, holding (for 3min) at 125°C and finally cooling, also at a rate of 10°C/min from 125°C to 25°C.

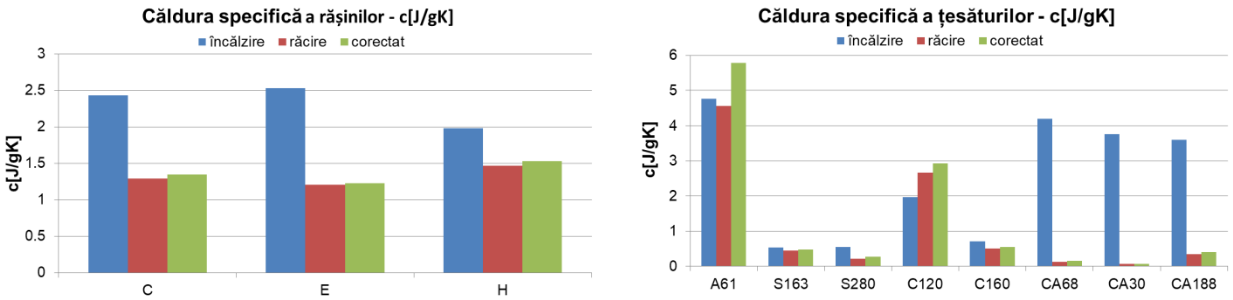


Fig. 17 Specific heat values for resins and fabrics

Table 7 Average mass losses of DSC analyzed samples

Material	C	E	H	A61	S163	S280	C120	C160	CA68	CA30	CA188
Δm[%]	3.99	1.86	4.05	21.33	6.15	19.00	9.13	8.96	13.09	6.17	15.86

A look at the graphic representations in fig. 7.5. immediately leads to the conclusion that there are only two materials for which the corrected specific heat values are higher than those obtained on the material heating segment – A61 and C120. The fact that the specific heat values on the heating segments are higher than the values calculated on the cooling segments is due to the fact that during the heating, all the volatile substances come out of the crucible of the furnace (their vaporization requiring a greater amount of heat than that required to heat the material). When cooling, the released volatile substances no longer return to the crucible, so the amount of heat is lower, however, the calculation of the specific heat value is (automatically) carried out by reference to the initial mass of the sample - which is not true.

7.4. Partial conclusions – thermal properties

- the average values of the specific heat on the heating segment of the measurement cycle are significantly higher than those determined on the cooling segments of the measurement cycles;
- these higher values mean, in fact, higher values of heat quantities and mean that some processes take place in the measuring system (most likely vaporizations) which have as a consequence (measured) the reduction of the mass of the sample;
- the performed thermal analyzes confirms the existence of organic compounds used by fabric manufacturers to stabilize individual filaments (fibers) in the bundles used in fabrics;
- the highest substance loss is recorded for the A61 fabric (aramid fibers) and, at the same time, the same fabric also has the highest specific heat value.

7.5. Electrical and electromagnetic properties

The method used to analyze these properties is presented in [205] and is an alternating current method for three different (fixed) values of the measurement signal frequency. The measurements are made with the help of an RLC-meter and a measuring cell, the material being placed in the measuring system. Plates of reinforced material are placed on a conductive (bronze) table and two (also bronze) coaxial electrodes are placed on top – an active electrode (inner) and a guard electrode (outer). If the measurement is made between the active electrode and the conductive mass – the results characterize the volume properties of the materials, if the measurement is made between the active electrode and the guard electrode – the results characterize the surface properties of the material.

In fig. 7.6. the volume electrical conductivity values of the reinforced materials are shown graphically and it can be seen that all the materials that have carbon fibers in the outer layers (BM, DM, FM) have conductivity values three to four orders of magnitude higher larger than the other materials (AM, CM, EM). Although the EM material also has carbon fibers, but in felting it seems that the electrical conductivity value is influenced only by regular geometric distributions of the carbon fibers.

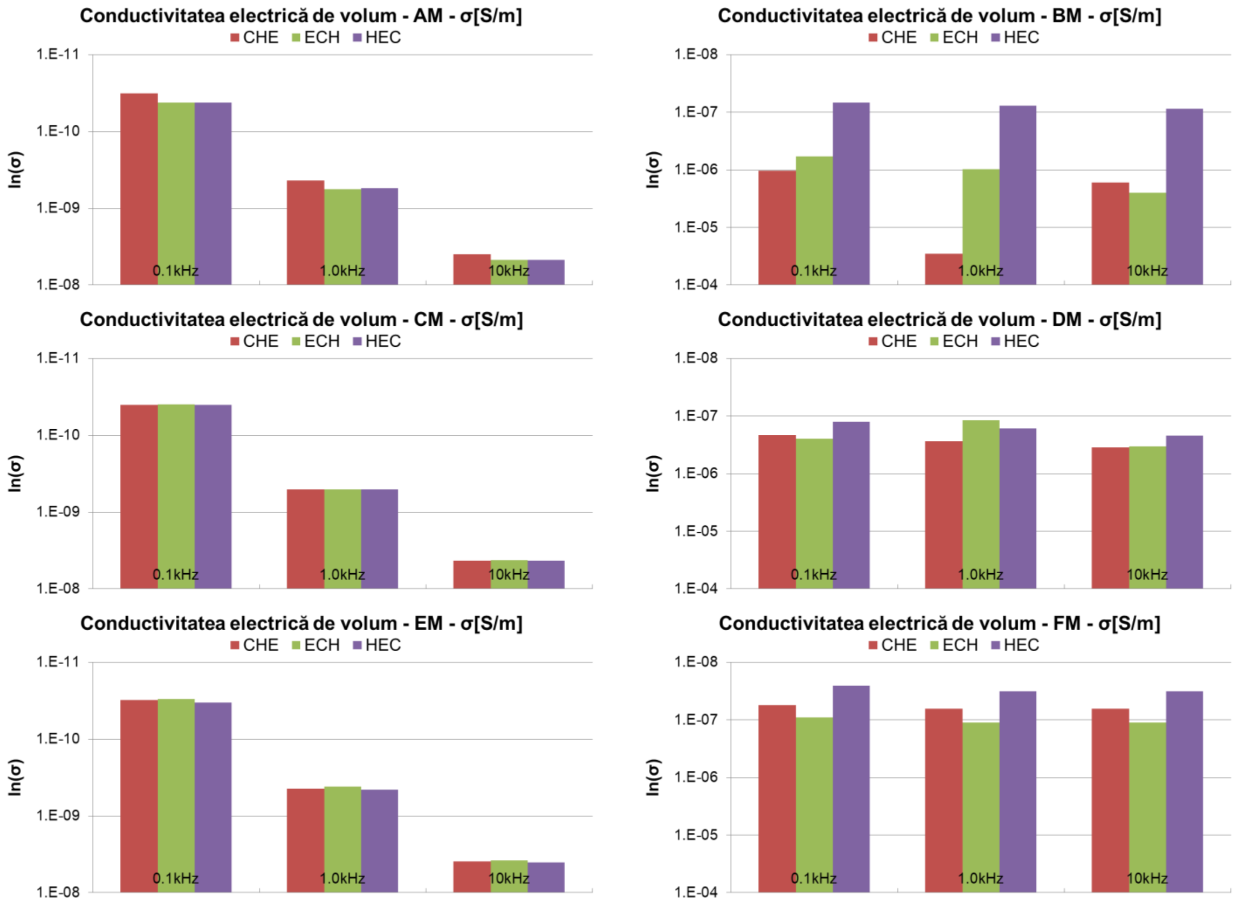


Fig. 7.6. Volume electrical conductivity values for reinforced materials

For materials that do not have carbon fibers in the outer layers, there is no dependence of the electrical conductivity value on the polymer sequence in the matrix. In this case the measurement signal is applied to the face corresponding to the first resin in the name. The small variations that occur with the AM materials may be due to the thickness of the resin layer (the other two materials have thin layers on the outside).

As for the surface electrical conductivity values, it must be said that it depends only on the nature of the layers to which the measurement signal is applied - that is, it also depends on the type of fibers and the polymer that provides the matrix of these outer layers (for all materials the measurement is on the surface whose matrix is the resin corresponding to the first letter in the second part of the material's name - fig. 7.7.

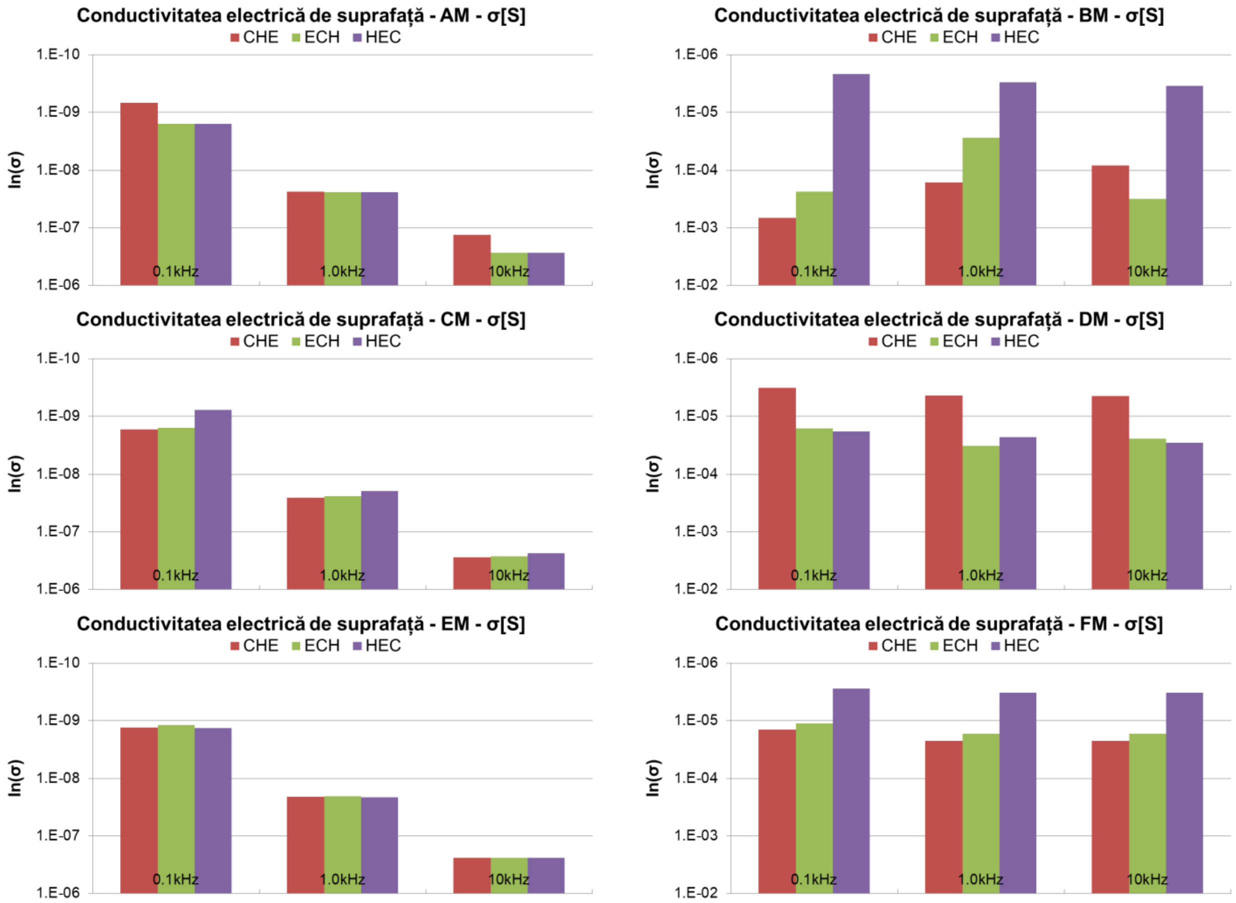


Fig. 7.7. Surface electrical conductivity values for reinforced materials

In the case of materials containing geometrically distributed carbon fibers, it can be said that there is no dependence of the surface electrical conductivity on the frequency of the measurement signal, but it can be easily seen that there is a strong dependence on the nature of the resin, although this dependence is not the same for all the three types of fabrics. However, the electrical conductivity values of these materials (BM, DM, FM) are three to four orders of magnitude higher than those corresponding to materials that do not have carbon fibers geometrically distributed in the outer layers (AM, CM, EM).

7.6. Partial conclusions - electrical and electromagnetic properties

- two electrical parameters were determined – volume electrical conductivity and surface electrical conductivity and two electromagnetic parameters – volume dielectric permittivity and surface dielectric permittivity;
- the measurement system is the same for both sets of parameters and is based on the use of an alternative signal with a pre-set frequency (in the case of the RLC-meter used in the laboratory, three measurement frequencies are available – 0.1kHz, 1.0kHz and 10kHz);
- materials containing regularly distributed carbon fibers in the outer layers present values of volume electrical conductivity and surface electrical conductivity three to four orders of magnitude higher than the corresponding values for materials that do not contain such fibers in the outer layers, these values do not depend on the sequence of polymers in the matrix.

Chapter 8

Personal contributions, conclusions and future research directions

The chosen topic is one that has hardly been researched and that is why everything we have achieved represents a novelty in the field of forming and characterizing composite materials - in a tradition that continues at the Research and Development Center for Composites with Thermoset Matrices (CCDCOMT) at the University The Lower Danube from Galati.

- the working hypothesis for the initiation of this study was to investigate the possibility of using different polymers to obtain reinforced composites;
- the chosen polymers are three epoxy resins and the interest of the study was oriented towards the polymer junction – the area where (due to diffusion) the bonds between the two polymers are made;

• a study in which the junctions are made between two thermosetting polymers with liquid precursors would be extremely interesting, for different classes of polymers.

The forming of the materials, which I achieved with the support of the guidance team and my colleague Irina Țîcău, represents a new solution, even if it is not very convenient and involves extraordinary coordination. We have obtained polymer junctions in quality materials (both in terms of polymer materials and in terms of reinforced materials).

- the tensile tests carried out on polymers with junctions showed that always in the case of less rigid- rigid junctions the materials yield in the area of the more rigid polymer, in the case of rigid-rigid junctions the materials yield in the junction area, which was expected if we think of properties of materials with welded joints.

The way we thought about reinforced materials (from the point of view of reinforcements) is a way to extract as much meaningful data as possible with low material consumption, given that the fabrics used for reinforcement are very expensive. I decided that all the materials would have the same core and only the outer layers would be different. In order to avoid the problems that Radu Bosoancă encountered in the interpretation of his results, we decided that the areas of polymer junctions should be inside the core. The guarantee of the fact that we made the right decision is the fact that from all the tests carried out we identified only two cases of delamination (one in the compression tests and one in the bending tests).

- the fabrics used in the outer layers have different properties and were proposed for the effect they would have on the general properties of the respective material;
- six reinforcement structures were thus defined (AM, BM; CM, DM, EM, FM) each of them being used to make three materials in which the matrices are represented by the three epoxy resins but their alternation is described by a cyclic permutation;
- in this way each of the three epoxy resins is found in the central area of the core and the junctions with the other two polymers are found between layers 5 and 6, respectively, 10 and 11, so also inside the core.

We have identified different, asymmetric behaviors of some reinforced materials - those where the stiffer matrices form blocks with ten layers of reinforcement, and symmetrical of the materials where the less rigid polymer is in the center of the material. We have also identified different behaviors of materials that have thin fabrics in the outer layers compared to those that have thick fabrics on the outside. As a personal contribution, I also mention the photographic analysis of the results of the tests carried out, which allowed the understanding of the response of each individual material.

- the effects of applying axial load depend on the polymers that are outside the tested material and the best answers are given by materials with two less rigid-rigid junctions, in the other two cases there is a rigid-rigid junction that determines how it fractures the test pieces;

- we also carried out a photographic analysis of fracture zones to better understand the phenomena that occur when materials break;
- no delaminations were recorded (with the exception of only two cases) which means, on the one hand, that the chosen method of formation allows obtaining quality materials and, on the other hand, that the polymer junctions resist;
• an interesting study would be related to the creation of similar materials but with only two polymers in the matrix because, in this case, it would be two identical polymer junctions and the answers could be different if the stiffer polymer is on the outside or on the inside;
• another interesting study, which would complement these results, would be that of the microscopic analysis of the effect of clamping in the jaws which, as I stated, in the case of rigid polymers, can lead to crack initiation from the moment the specimen is clamped in the jaws of the machine testing.

Although we did not use standardized test pieces, we performed compression tests - with photographic analysis of the results - to identify how the material responds given the fact that polymer embedded fabrics form a rigid material that, during compression tests with the applied stress in reinforcement plane, they can buckle leading to delamination. We did not observe such phenomena, due to the fact that the faces of the specimens on which the effort was applied were not plane-parallel. From this point of view, I only carried out a qualitative study that allowed me to understand how the outer layers of different thicknesses behave without their destruction affecting the core of the materials.
• a future study should be done on standard samples for the Whyoming method, and it would certainly be interesting to video record all the tests so that the events visible on the σ/ε curves are associated with phenomena occurring at the level of the sample.

We performed a cross-analysis of the results of the three-point bending tests – where we used the data obtained from the tensile and compressive tests to understand and explain the properties of the materials. And this time, the photographic analysis represents an advantage in terms of the interpretation of the obtained results.
- the results of three-point bending tests depend on the thickness and nature of the outer reinforcement layers and on the nature of the polymer that constitutes the matrix of these layers;
• an interesting study that could be done in its continuation would be to load the samples from both sides of the material;
• the analysis of materials with a layered matrix but with only two polymers (two identical polymer junctions) would also be a study that could successfully complement its results.

In the case of thermal tests carried out to determine the specific heat value, we analyzed the three polymers and the six fabrics used for reinforcement. We highlighted the fact that, in the case of fabrics, there are significant substance losses (during testing) that can be associated with substances deposited on the fiber surfaces either to keep their orderly distribution in the fabric or to ensure the adhesion of epoxy resins. We made the correction in the determination of the specific heat by taking into account the measured mass losses.

In the case of electromagnetic tests (performed on reinforced materials) we determined the values of some significant parameters from the electrical point of view - electrical conductivity (volume and surface), or from the electromagnetic point of view - dielectric permittivity (volume and surface). Their determined values do not depend on the sequence of polymers in the analyzed materials, but only on the nature of the fibers in the fabrics that form up the outer layers. What is significant is the fact that some materials (those with aligned carbon fibers in the outer layers) the values obtained indicate the possibility of their use as electrical energy storage elements (capacitors).

• a more interesting study in this regard should aim for an increase in the electrical conductivity of the outer layers (one on each side of the material) and an increase in the dielectric permittivity of the core.

Bibliografie

[1] A. Madra, P. Breitkopf, B. Raghavan, și F. Trochu, „Diffuse manifold learning of the geometry of woven reinforcements in composites”, *Comptes Rendus Mécanique*, vol. 346, nr. 7, pp. 532–538, iul. 2018, doi: 10.1016/j.crme.2018.04.008.

[2] L. Peponi, D. Puglia, L. Torre, L. Valentini, and J. M. Kenny, “Processing of nanostructured polymers and advanced polymeric based nanocomposites,” Materials Science and Engineering: R: Reports, vol. 85, pp. 1–46, Nov. 2014, doi: 10.1016/j.mser.2014.08.002.
[126] A. Tabatabaeian și A. R. Ghasemi, „Curvature changes and weight loss of polymeric nano-composite plates with consideration of the thermal cycle fatigue effects and different resin types: An experimental approach”, *Mechanics of Materials*, vol. 131, pp. 69–77, apr. 2019, doi: 10.1016/j.mechmat.2019.01.017.

[129] B. Yang, S. Wang, și Y. Wang, „Effect of Nesting in Laminates on the Through-Thickness Permeability of Woven Fabrics”, *Appl Compos Mater*, vol. 25, nr. 5, pp. 1237–1253, oct. 2018, doi: 10.1007/s10443-018-9699-8.

[134] V. Velmurugan, D. Dinesh Kumar, și S. Thanikaikarasan, „Experimental evaluation of mechanical properties of natural fibre reinforced polymer composites”, *Materials Today: Proceedings*, vol. 33, pp. 3383–3388, 2020, doi: 10.1016/j.matpr.2020.05.190.

[135] K. C. Warren, R. A. Lopez-Anido, și J. Goering, „Experimental investigation of three-dimensional woven composites”, *Composites Part A: Applied Science and Manufacturing*, vol. 73, pp. 242–259, iun. 2015, doi: 10.1016/j.compositesa.2015.03.011.

[140] J. Misumi și T. Oyama, „Low viscosity and high toughness epoxy resin modified by in situ radical polymerization method for improving mechanical properties of carbon fiber reinforced plastics”, *Polymer*, vol. 156, pp. 1–9, nov. 2018, doi: 10.1016/j.polymer.2018.09.050.

[141] M. Olave, I. Vara, H. Usabiaga, L. Aretxabaleta, S. V. Lomov, și D. Vandepitte, „Mode I fatigue fracture toughness of woven laminates: Nesting effect”, *Composite Structures*, vol. 133, pp. 226–234, dec. 2015, doi: 10.1016/j.compstruct.2015.07.073.

[142] M. D. Kiran, H. K. Govindaraju, B. R. L. Yadhav, B. Suresha, și N. Keerthi Kumar, „Fracture toughness study of epoxy composites reinforced with carbon fibers with various thickness”, *Materials Today: Proceedings*, p. S2214785321013584, mar. 2021, doi: 10.1016/j.matpr.2021.02.271.

[144] S. Tasnim, F. U. A. Shaikh, și P. K. Sarker, „Mechanical properties and microstructure of lightweight polymer composites containing mono and hybrid fillers sourced from recycled solid wastes”, *Construction and Building Materials*, vol. 277, p. 122369, mar. 2021, doi: 10.1016/j.conbuildmat.2021.122369.

[145] S. M. Maharana, A. K. Pradhan, și M. K. Pandit, „Moisture absorption behaviour of nanofiller reinforced jute-kevlar hybrid polymer composite”, *Materials Today: Proceedings*, vol. 26, pp. 775–780, 2020, doi: 10.1016/j.matpr.2020.01.025.

[148] S. Dai, P. R. Cunningham, S. Marshall, și C. Silva, „Influence of fibre architecture on the tensile, compressive and flexural behaviour of 3D woven composites”, *Composites Part A:*

Applied Science and Manufacturing, vol. 69, pp. 195–207, feb. 2015, doi: 10.1016/j.compositesa.2014.11.012.

[149] M. Karahan, S. V. Lomov, A. E. Bogdanovich, D. Mungalov, și I. Verpoest, „Internal geometry evaluation of non-crimp 3D orthogonal woven carbon fabric composite”, *Composites Part A: Applied Science and Manufacturing*, vol. 41, nr. 9, pp. 1301–1311, sep. 2010, doi: 10.1016/j.compositesa.2010.05.014.

[150] N. Blanco, D. Trias, S. T. Pinho, și P. Robinson, „Intralaminar fracture toughness characterisation of woven composite laminates. Part II: Experimental characterisation”, *Engineering Fracture Mechanics*, vol. 131, pp. 361–370, nov. 2014, doi: 10.1016/j.engfracmech.2014.08.011.

[151] N. Blanco, D. Trias, S. T. Pinho, și P. Robinson, „Intralaminar fracture toughness characterisation of woven composite laminates. Part I: Design and analysis of a compact tension (CT) specimen”, *Engineering Fracture Mechanics*, vol. 131, pp. 349–360, nov. 2014, doi: 10.1016/j.engfracmech.2014.08.012.

[152] M. Olave, I. Vara, H. Husabiaga, L. Aretxabaleta, S. V. Lomov, și D. Vandepitte, „Nesting effect on the mode I fracture toughness of woven laminates”, *Composites Part A: Applied Science and Manufacturing*, vol. 74, pp. 166–173, iul. 2015, doi: 10.1016/j.compositesa.2015.03.017.

[155] I. A. Abu Bakar, O. Kramer, S. Bordas, și T. Rabczuk, „Optimization of elastic properties and weaving patterns of woven composites”, *Composite Structures*, vol. 100, pp. 575–591, iun. 2013, doi: 10.1016/j.compstruct.2012.12.043.

[158] H. M. Y. C. Mallikarachchi, „Predicting mechanical properties of thin woven carbon fiber reinforced laminates”, *Thin-Walled Structures*, vol. 135, pp. 297–305, feb. 2019, doi: 10.1016/j.tws.2018.11.016.

[160] S. Senthil Gavaskar și S. Madhu, „Torsional and compression properties of cylindrical glass fiber reinforced polymer composite”, *Materials Today: Proceedings*, vol. 22, pp. 1149–1154, 2020, doi: 10.1016/j.matpr.2019.12.024.

[161] A. Wei, R. Al-Ameri, Y. C. Koay, și M. Y. J. Tan, „Triple-functional carbon fibre reinforced polymer for strengthening and protecting reinforced concrete structures”, *Composites Communications*, vol. 24, p. 100648, apr. 2021, doi: 10.1016/j.coco.2021.100648.

[177] J. Rouzegar și M. Gholami, „Creep and recovery of viscoelastic laminated composite plates”, *Composite Structures*, vol. 181, pp. 256–272, dec. 2017, doi: 10.1016/j.compstruct.2017.08.094.

[178] W. H. Ong, N. Rajic, W. K. Chiu, și C. Rosalie, „Determination of the elastic properties of woven composite panels for Lamb wave studies”, *Composite Structures*, vol. 141, pp. 24–31, mai 2016, doi: 10.1016/j.compstruct.2015.12.017.

[179] L. Wang, B. Zhao, J. Wu, C. Chen, și K. Zhou, „Experimental and numerical investigation on mechanical behaviors of woven fabric composites under off-axial loading”, *International Journal of Mechanical Sciences*, vol. 141, pp. 157–167, iun. 2018, doi: 10.1016/j.ijmecsci.2018.03.030.

[180] M. Bunea, A. Cîrciumaru, M. Buciumeanu, I. G. Bîrsan, și F. S. Silva, „Low velocity impact response of fabric reinforced hybrid composites with stratified filled epoxy matrix”,

Composites Science and Technology, vol. 169, pp. 242–248, ian. 2019, doi: 10.1016/j.compscitech.2018.11.024.

[181] I. G. Birsan, V. Bria, M. Bunea, și A. Circiumaru, „An Experimental Investigation of Thermal Properties of Fabric Reinforced Epoxy Composites", *Mater. Plast.*, vol. 57, nr. 2, pp. 159–168, iul. 2019, doi: 10.37358/MP.20.2.5362.

[183] Radu Bosoancă, Vasile Bria, Claudiu Mereuță, Adrian Cîrciumaru, Iulian-Gabriel Bîrsan, „Tensile Analysis of Fabric Reinforced Materials". Materiale Plastice 56, no4, pp. 705-714., 2019.

[184] Marina Bunea, Radu Bosoanca, Adrian Cojan, Iulian Gabriel Bîrsan, „Thermomechanical and Electrical Properties of Fabric Reinforced Laminates with Filled Stratified Epoxy Matrix", *Materiale Plastice*, vol. 55, nr. 3, pp. 269–273, 2018.

[185] Mara Dimofte, Marina Bunea, Ana Căpățînă, Adrian Cojan, Radu Bosoancă, Adrian Cîrciumaru, „Tensile and Bending Analysis of Fabric Reinforced Graded Epoxy Composites", *Materiale Plastice*, vol. 54, nr. 2, pp. 362–367, 2017.

[186] Vasile Bria., Adrian Cîrciumaru, IG. Bîrsan, „Some Properties of Starch/Epoxy Composites", *Materiale Plastice*, vol. 48, nr. 2, pp. 189–194, 2011.

[187] Marina Bunea, Radu Bosoancă, Cristian Eni, Nicoleta Cristache, Victorita Stefanescu, „The Impact Characteristics of Fabric Reinforced Hybrid Composites", *Materiale Plastice*, vol. 54, nr. 2, pp. 286–290, 2017.

[188] Marina Bunea, Ioan Bosoanca, Radu Bosoanca, Marius Bodor, Adrian Cîrciumaru, „Bending and Compressive Properties of Fabric Reinforced Composites", *Materiale Plastice*, vol. 52, nr. 3, pp. 368–372, 2015.

[189] Ana Căpățînă, Adrian Cojan, Vasile Bria, Adrian Cîrciumaru, IG. BÎRSAN, „Tensile Behaviour of Fabric Reinforced Plies", *Materiale Plastice*, vol. 56, nr. 4, pp. 891–900, 2019.

[190] Gabriel Andrei, Dumitru Dima, IG Bîrsan, Laurenția Andrei, Adrian Cîrciumaru, „Effect of Ferrite Particles on Mechanical Behaviour of Glass Fibers Reinforced Polymer Composite", *Materiale Plastice*, vol. 46, nr. 3, pp. 284–287, 2009.

[191] Victorita Stefanescu, Ana Boboc, Adrian Cojan, Radu Bosoanca, Cristian Muntenita, Marina Bunea, „The Thermal Behavior of Hybrid Fabric Reinforced Composites with Stratified Filled Epoxy Matrix", *Materiale Plastice*, vol. 55, nr. 2, pp. 161–166, 2018.

[192] Victorita Stefanescu, Marina Bunea, Adrian Cîrciumaru, „Impact Analysis of Fabric Reinforced Plates", *Materiale Plastice*, vol. 52, nr. 2, pp. 198–203, 2015.

[193] Victor Ungureanu, *Contribuţii teoretice şi experimentale la studiul proprietăţilor mecanice ale unor compozite polimerice (teză de doctorat)*. Universitatea „DUNĂREA DE JOS" din Galați, 2012.

[194] Laura Maftei, „Contribuţii la studiul comportării tribologice a compozitelor cu poliamidă şi microsfere de sticlă (teză de doctorat)", Universitatea „Dunărea de Jos" din Galaţi, 2010.

[195] Adrian Cîrciumaru, „Contribuţii la studiul proprietăţilor electrice şi mecanice ale compozitelor armate cu ţesături şi matrice din epoxi aditivat", Universitatea Dunărea de Jos din Galaţi, 2009.

[196] Vasile Bria, Contribuţii la Studiul Proprietăţilor Mecanice ale Materialelor Compozite armate cu Țesături și Matrice Epoxidică Aditivată cu Amidon (teză de doctorat), Universitatea Dunărea de Jos din Galaţi, 2011.

[197] Marina Schițanu (Bunea), „CONTRIBUȚII LA STUDIUL SOLICITĂRILOR LA IMPACT ALE COMPOZITELOR CU MATRICE EPOXIDICĂ ARMATE CU ȚESĂTURI (teza de doctorat)", Universitatea Dunărea de Jos din Galaţi, 2015.

[198] Georgel Mihu, „Studiul proprietăților sistemelor epoxidice modificate cu solvenți organici (teza de doctorat)". Universitatea Dunărea de Jos din Galaţi, 2016.

[199] Iulia GRAUR, „Studiul proprietăţilor mecanice ale materialelor epoxidice aditivate cu substanţe ionice prin strategii de dispersie bazate pe utilizarea ultrasunetelor (teza de doctorat)", Universitatea Dunărea de Jos din Galaţi, 2015.

[200] Ana Boboc (Căpățînă), „Contribuţii la studiul proprietăţilor materialelor compozite armate cu țesături și a efectului solicitărilor ciclice asupra acestor proprietăți (teza de doctorat)", Universitatea Dunărea de Jos din Galaţi, 2019.

[201] C. E. Estridge, "The effects of competitive primary and secondary amine reactivity on the structural evolution and properties of an epoxy thermoset resin during cure: A molecular dynamics study," Polymer, vol. 141, pp. 12–20, Apr. 2018, doi: 10.1016/j.polymer.2018.02.062.

[202] https://www.r-g.de/en/art/120305

[203] https://www.r-g.de/en/art/105100

[204] Radu Bosoancă, Vasile Bria, Claudiu Mereuță, Adrian Cîrciumaru, Iulian-Gabriel Bîrsan, "Tensile Analysis of Fabric Reinforced Materials." 2019, [Online]. Available: http:///www.revmaterialeplastice.ro.

[205] Cîrciumaru, A., Caracterizarea şi testarea materialelor compozite cu matrice polimerice (ghid pentru lucrări practice), Europlus, Galaţi, 2013, ISNB 978-606-628-058-7

Annexes

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