„POLITEHNICA" UNIVERSITY OF BUCHAREST
FACULTY OF APPLIED CHEMISTRY AND MATERIAL SCIENCES
DOCTORAL SCHOOL OF CHEMICAL ENGINEERING

MATERIALE COMPOZITE POLIMERICE ARMATE CU FIBRE AVÂND PROPRIETATEA DE AUTO-REPARARE

FIBRE REINFORCED POLYMER COMPOSITE MATERIALS WITH SELF-HEALING PROPERTIES

PHD THESIS SUMMARY

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CONTENTS

ABBREVIATIONS, NOTATIONS AND SYMBOLS

Abbreviations

ASTM	American Society for Testing and Materials
CFRP	Carbon Fibre Reinforced Polymer
CNT	Carbon Nanotubes
DA	Diels-Alder
DCPD	Dicyclopentadiene
DMA	Dynamic mechanical analysis
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
E	Elasticity Modulus
EDX	Energy Dispersive X-Ray Analysis
EMMA	Ethylene Methyl Methacrylate
ENB	Ethylidene Norbornene
F	Tensile load
FRP	Fibres Reinforced Polymer
FT-IR	Infrared Spectroscopy
GFRP	Glass Fibres Reinforced Polymer
INCD	National Research and Developed Institute
ISI	Institute for Scientific Information
ISO	International Standardization Organization
MUF	Melamine Urea Formaldehyde
CNT	Carbon Nanotubes
PAN	Polyacrylonitrile
PEEK	Polyether ether ketone
PMMA	Polymethyl methacrylate
PUF	Poly Urea Formaldehyde
PVA	Polyvinyl alcohol
ROMP	Ring Opening Metathesis Polymerization
SEM	Scanning Electron Microscopy
SLS	Sodium Lauryl Sulphate
TEM	Transmission Electron Microscopy
Tg	Glass Transition Temperature
TGA	Thermogravimetric Analysis
UF	Urea Formaldehyde

Notations and symbols

a	Crack length	ε	Elongation at break
d	Particle diameter	ν	Poisson coefficient
K	Stress concentration factor	ρ	Density
M	Mass	ρ_r	Curve radius in crack's plane
r, θ	Polar coordinates	σ_m	Ultimate flexural strength
t	Impact time	σ_u	Tensile strength
V	Speed	σ_x, σ_y	Strength expressed in cartesian coordinates
δ	Penetration distance	τ_x	Tangential strength

CHAPTER 1
DOCTORAL THESIS PURPOSE MOTIVATION AND OBJECTIVES

1.1. General considerations

The actual trend in the aerospace industry is to create structures having superior performances, using new materials with special and better performances compared to the traditional materials, which cannot fulfil the current requirements imposed by the high-end industries. Also, the development of the global market and quality of life was influenced by a series of factors which include the development of materials over time.

The aerospace industry is a domain in which minimum mass and improved strength are essential requirements (elements which are transposed in the design phase and the safety factor), all of these representing, since its beginnings, a top domain in the technology worldwide, which uses the newest results of the technological progress and the most performant materials. Also, in the frame of this industry, the development of materials having improved mechanical properties and low mass progresses along with a management control and a prevention of the possible defects which could occur during use, as a consequence of being subjected to mechanical loads. This concept is based on the idea that the deterioration of a material is not an issue, as long as this one is countered by an autonomous, "management" or "healing" process of the defects. The defects do not necessarily imply a total loss of the system functionality, but rather its degradation compared to the ideal desired level of functionality.

In order to avoid the process of material yielding/deterioration, the materials engineering domain focused on the development of solutions to avoid propagation of cracks, thus leading to the design of material having self-healing properties.

Thus, the current thesis approaches an actual theme, namely the study of the self-healing process of composite materials reinforced with fibres. The general objective of the thesis is to investigate systems having self-healing properties for the composite materials which could lead to the increasing of structures operational life, eliminating the defects at microscopic level and restoring (at least partially) the structural properties of the material, avoiding the degradation of the respective structure. The structures manufactured from materials having self-healing properties are characterized by high performances and durability during functioning, contributing to: reducing the use of raw materials and energy associated with the component replacing, maintenance costs optimization, increase of the safety by minimizing the risks of total failure in case of a unpredicted load occurrence etc.

1.2. Motivation and objectives

The doctoral thesis has as a general objective to contribute to the development and implementation of polymeric composite materials having self-healing properties which can easily being translated to the aerospace industry, targeting the increasing of the structures life. As the polymeric composite materials can find easily a use in domains of interest, the development of such systems is considered an important option in order to improve them and also to offer to the market more competitive products which account for the current environment requirements. The

implementation of such materials and structures is translated directly to the reducing of the maintenance times and implicitly of the economical factor. Thus, the current doctoral thesis has the purpose to develop self-healing systems which can be integrated in layered composite materials in order to manufacture primary and secondary structures for the aerospace industry and more.

In the following the specific objectives of the doctoral thesis are presented:

- Thorough analyses regarding the applicability of the self-healing polymeric materials and polymeric composites;
- The development and evaluation of synthesis processes for self-healing systems using microcapsules with different repairing agents;
- Development and evaluation of the self-healing systems as a microvascular network;
- Definition of the optimal process to integrate in the polymeric matrix and in the layered composite material the developed self-healing systems;
- Analyses concerning the thermal stability of the developed systems;
- Studies regarding the introduction of nano-reinforced elements in order to improve the healing process;
- Conducting numerical simulations in order to evaluate the behaviour of self-healing systems constitutive elements over the mechanical properties of the materials in which they are integrated;

Evaluation of the self-healing systems efficiency by specific mechanical tests and validation of the healing process.

1.3. Thesis structure

The doctoral thesis "***Fibres reinforced polymeric composite materials having self-healing properties***" is structured in 7 chapters, annexes and bibliography, as follows:

- **Chapter 1**, titled "***Doctoral thesis purpose motivation and objectives***", emphasizes the necessity of research regarding the introduction and applicability of the self-healing systems in the polymeric composite materials, especially in the aerospace domain, along with the proposed objectives in order to conduct the scientific research, respectively the associated work steps;
- **Chapter 2** titled „***Current state of the art research in the domain of materials having self-healing properties***" consists of the analysis of the current literature domain regarding methods for repairing of the polymeric composite materials, studies regarding the numerical analyses applied to the self-healing systems and applications of the composite materials having self-healing properties in high interest domains such as aerospace.
- **Chapter 3** titled „***Contributions regarding the synthesis methods and integration of self-healing systems in the form of microcapsules***", consists in the development of two self-healing systems. Also, investigations regarding the thermal stability of the developed self-healing systems were conducted in order to identify optimal conditions for integration in the fibres reinforced composite material. These analyses are the basis of evaluating the self-healing properties of the developed systems. Moreover, analyses regarding the most efficient method to integrate self-healing systems in the polymeric matrices, scanning electronic microscopy and

transmission electronic microscopy were conducted in order to emphasize the manufacturing of self-healing systems and thermomechanical analyses.

- **Chapter 4** titled „***Contributions regarding the synthesis and integration methods of the self-healing systems in the form of microvascular network***", follows the development and analysis of one of the least studied self-healing systems in the materials domain, namely the microvascular self-healing system. Using this microvascular system, microstructural analyses were conducted in order to emphasize the existence of "core-shell" fibres, respectively thermomechanical analyses. Also, test samples made of composite materials which integrate core-shell microvascular systems were manufactured, in order to conduct mechanical tests through which the mechanical properties of the self-healing system were evaluated.

- **Chapter 5** titled „***Contributions regarding the conducting of finite element numerical analyses over the tensioned state of the polymeric matrix***" emphasizes a series of authors own investigations over the effects of self-healing systems presence in the epoxydic matrix. More exactly, the finite element numerical analyses present the effects over the tensioned state and the effect of the self-healing systems based on microcapsules over the polymeric matrix yielding strength. Also, in this chapter numerical analyses regarding the delamination of the reinforced polymeric composite material which integrates self-healing systems were conducted.

- **Chapter 6** titled „***Contributions regarding the evaluation of the polymeric composite materials self-healing properties based on microcapsules***" presents an evaluation of the recovery of the mechanical properties for fibres reinforced composite material using the two developed self-healing systems based on microcapsules. More precisely, in this chapter are evaluated the influence of the volume of healing system integrated in the matrix over the mechanical properties of the composite material, but also the efficiency of the self-healing process by conducting three-point bending and impact tests.

- **Chapter 7** titled „***Contributions regarding the evaluation of the polymeric composite material self-healing properties using microvascular self-healing system***" presents an evaluation of the recovery of the mechanical properties for fibres reinforced composite material using core-shell self-healing systems. In this regard, specific sample were manufactured and subjected to three-point bending and impact tests. Thus, the efficiency of a new self-healing system was evaluated, system developed and analysed in the frame of this doctoral thesis.

- **Chapter 8** titled „***Final conclusions, original contributions and future perspectives***" presents the evaluation of the obtained materials having self-healing properties. Also, in this chapter future perspectives in order to continue the fundamental and applicative research in this domain of superior self-healing systems, which can be integrated in polymeric composite materials for high-end industries, but also the possibility to industrialize such systems.

ACKOWLEDGEMENTS

I would like to emphasize that all the work behind this research could not materialise in the present doctoral thesis without the support of other persons, from the closest ones to work colleagues, professors, respectively specialists with vast experience in this domain. There are many that I would wish to thank for, from the ones who encouraged me, and up to the ones which helped me to finish this thesis. Their contribution cannot be contested. I remain deeply grateful and I want to thank them for all they have done for me.

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Last but not least, I would like to thank and I am deeply grateful to my family, for all the moral support, understanding and patience offered during.

CHAPTER 2
STATE OF THE ART IN THE RESEARCH AND DEVELOPMENT OF SELF-HEALING MATERIALS

In time, structural components can lose their integrity, operating capacity or usage due to the degradation phenomenon which occur in functioning or due to the physical/mechanical loads to which they are subjected to. These degradations occur both at micro (microcracks, pores etc.) and macro (breaking, delamination, corrosion etc.) level. Mainly, the deterioration of the materials/structures is influenced by two factors [1]:

- Internal factors, disregarding the structures manufacturing parameters lead to defects inside the parts/semifinished parts;
- External factors, disregarding the technological parameters during mechanical machining of the parts/structures or destructive contact due to interaction with hard objects or chemical agents.

A timely detection of such defects is very important from safety factor point of view, but also economically, and, in this regard, different sensors were developed, depending on the application and domain of interest. Another prevention method is using self-healing systems, integrated in the material, or used as surface coatings, depending on the material's nature, which could extend the material's operational life and implicitly reduction of cost associated to the part replacing or conventional repairing. Such self-healing mechanism are reported in the form of microcapsules, shallow fibres and microvascular networks.

FRP composite materials are widely used for aircraft fuselage, and some of the biggest civil aircraft (Boeing 787 and Airbus A350) are developed more than 50% from polymeric composites. However, the polymeric composites are susceptible to deterioration due to impact at low speeds, which leads to the necessity of designing in more detail such structures, in order to ensure the safety requirements.

The self-healing process is one of the most promising approaches in order to reduce the vulnerability due to the impact phenomenon and to design fuselage structures from composite materials which have low mass and require less maintenance. The majority of the composite materials used in the aerospace domain are carbon fibres reinforced plastics, which lead to a high number of studies which focus on evaluating their mechanical properties, especially following integration of self-healing systems.

Most of the encapsulation systems reported until now do not offer stability at high temperatures and, due to this reason, they are limited to their use in polymers and polymeric composite materials having relatively low crosslink temperatures. The factors which influence the manufacturing of microcapsules are solubility, reactivity, viscosity, volatility and pH of the material which shall be encapsulated.

In order to increase the efficiency of these self-healing systems, the behaviour of different constituents and interaction between them shall be known. Although this aspect can be

experimentally analysed, a numerical analysis can be beneficial. From numeric point of view, three phases of the repair process can be analysed as follows:

- Formation and propagation of cracks due to external factors;
- The transport of the repairing liquid material in the cracks;
- Crack repairing by chemical reaction between the repairing agent and catalyst.

Although there are a number of experimental studies for such analyses, there are few numerical simulations that address to this type of experiment. In the performing of these numerical simulations, the calculus parameters consider that the polymer is a homogenous material, having uniform properties, as these simulations address directly to the crack propagation.

In the frame of the numerical analysis are introduced and propagated cracks along the microstructure, considering the microcapsules distribution, interaction between microcapsule and polymeric matrix and microcapsules thickness. The general properties can be estimated from the representative volume element. Starting from these results, the behaviour of the crack propagation and the properties of the polymeric material having self-healing systems based on microcapsules having different dimensions, volumetric ratios and thicknesses, can be analysed. The purpose of these simulations consisted in optimization of the design parameters, such as the radius and thickness of the microcapsules, but also of the volumetric ratios.

ORIGINAL CONTRIBUTIONS

CHAPTER 3
CONTRIBUTIONS REGARDING THE METHODS FOR SYNTHESIS AND INTEGRATION IN THE EPOXIDIC MATRIX OF THE SELF-HEALING SYSTEMS BASED ON MICROCAPSULES

In the frame of this chapter several development iterations for two innovative self-healing systems based on microcapsules were performed, the first using poly urea formaldehyde for the microcapsules shell and dicyclopentadiene as healing agent, and the second one consisting of melamine urea formaldehyde for the microcapsules shell and 5-ethylidene-2-norbornene as healing agent. After establishing the process and the development parameters of the two self-healing systems, and their manufacturing, these were subjected to thermo-mechanical analyses, based on which several optimisations were performed. These optimisations considered the thermal stability, in order to identify the mass loss depending on the polymerization temperature of the polymeric matrix. Also, two integration methods for the self-healing systems in the epoxydic matrix were investigated, and, based on a testing plan, these samples were microstructurally and mechanically analysed by performing three-point bending tests.

3.1. Development of the PUF-DCPD self-healing system

In a glass beaker with a capacity of 1000 ml were added 300 ml of distilled water, 7,0 gr. of urea, 0,5 gr. resorcinol and 0,5 gr. ammonium chloride. The solution was put on a magnetic plate at 400 rpm for mixing at room temperature. To the mixture 100 ml of copolymer solution

with 5% maleic anhydride were added, and, after mixing, the solution pH was adjusted to a value of 3,5 using NaOH and HCl. The mixture was mechanically mixed at the same speed of 400 rpm. The magnetic plate temperature was raised to 50°C, adding on the same plate a glass beaker of 250 ml capacity in which 60 gr. of DCPD were put.

The two solutions were heated in the same time on the plate in order to prevent the transformation of the DCPD from liquid (after melting), back to gel, when this one is introduced in the previously mentioned mixture. Due to the fact that the DCPD quantity was increased compared to the previous manufacturing processes, the necessary time to melt the DCPD was bigger, approximately 25 minutes. After the 25 minutes, the DCPD solution was added gradually over the first solution and let to mix for 1015 minutes in order to obtain droplets having a mean diameter of 200-300 μm, at a speed of 500 rpm. To the obtain emulsion 20 gr. of formaldehyde (37%) were added, while the temperatures was raised back to 60°C and maintained for 150 minutes. Then, 200 ml of distilled water were added and let for another 150 minutes at the same temperature. Finally, the mixture was cooled at room temperature and the microcapsules were separated. The suspension containing the microcapsules was diluted with 200 ml of distilled water, subsequently washing the microcapsules with water (3 washings, 500 ml of water each). The microcapsules were separated by means of a coarse filter and a Buchner funnel.

Following to the microcapsules synthesis process, after cooling, an non-capsulated quantity of DCPD monomer was observed, as it crystalized at surface. This aspect can be due to the difference in the mixing speeds used compared to the literature, which report speeds of 300 rpm. Following the drying of the filtered materials, a quantity of approx. 30 gr. of microcapsules were obtained, from which samples were taken for microstructural and thermomechanical analyses. The necessary materials were supplied through La Supplies (http://www.redox.ro) from Sigma-Aldrich (https://www.sigmaaldrich.com).

3.2. Development of the ENB self-healing system

The DCPD repairing agent was replaced with 5-ethylidene-2-norbornene (ENB), which is known for a stronger polymerization reaction and, due to this reason, it has a better reactivity compared to the dicyclopentadiene. The micro-encapsulation process was performed by in-situ polymerization of the melamine, urea and 37% wt. formaldehyde solution in order to obtain the MUF microcapsules in aqueous solution. Sodium lauryl sulphate was used as emulsifier and polyvinyl alcohol as stabilizing agent. The process consists of the following phases:

- Preparing the sodium lauryl sulphate and polyvinyl alcohol solutions;
- Preparing the melamine – urea – formaldehyde polymer;
- Dispersing of the repairing agent in the urea solution.

The first solution consisted in mixing 1 gr. of urea in 50 ml of distilled water under continuous mixing (400 rpm) at room temperature until the urea was dissolved and mixed, for approximately 15 minutes. The second solution, consisting of a mixture of melamine – formaldehyde, 100 ml of distilled water, 7 gr. of melamine and 10 gr of 37% wt. formaldehyde, was introduced in a 500 ml glass beaker and let for 25 minutes at 70°C to react and mix at a constant speed of 400 rpm. Following, this was let to cool at room temperature. The third solution

was based on sodium-lauryl-sulphate (0,5% mass), let for 20 minutes for mixing at 70°C at the same mixing speed. After the mixing process, the solution was let to cool at room temperature. The fourth solution was polyvinyl alcohol (6,3% mass), let for 2 hours in continuous mixing at room temperature.

After obtaining the urea solution, 50 ml of sodium-lauryl-sulphate solution was added along 50 ml of polyvinyl alcohol solution. In order for the solutions to be homogenous, the mixing speed was raised to 500 rpm. After this process (approx. 10-15 minutes) 50 ml of ENB was gradually added. As this is not miscible in water, spherulites were formed, under continuous mixing. The mixing speed was maintained for 15 minutes at room temperature, after which the temperature was raised to 90°C. The shelling process for the microcapsules obtained in the MUF polymeric solution takes place at a temperature of approx. 86°C, but in order to ensure the process suitability, the solution was let at 90°C for 6 hours. After the reaction was finalized, the plate was turned off and the solution was let to cool under continuous mixing. The obtained emulsion was filtered in vacuum and washed three times with 300 ml of distilled water, and then let to dry for 12 hours at room temperature. After drying, a congestion trend was observed for the microcapsules, these being easily separated by a smooth mixing. The fact that the microcapsules easily separate by mixing emphasizes the fact that the obtaining process was a success.

Following the microcapsules drying, a quantity of 28 gr. of microcapsules was obtained, from which samples for microstructural and thermo-mechanical analyses were taken. The necessary materials were supplied through La Supplies (http://www.redox.ro) from Sigma-Aldrich (https://www.sigmaaldrich.com).

3.3. Microstructural and thermomechanical analyses for the developed self-healing systems

3.3.1. Microstructural analysis

The microstructural analyses performed using a stereomicroscope, emphasized the formation of the microcapsules for the two self-healing systems, but also the presence of non-capsulated monomer on their surfaces, even after washing. It was observed that, when the microcapsules shell breaks, the repairing agent evaporates and the crack area darkens in colour. Analysing the size of the MUF-ENB microcapsules, compared to the PUF-DCPD ones, a major difference could be observed. Considering that a scale division represents 100 μm, one can observe that most of the microcapsules have sizes under 100 μm, which makes the MUF-ENB system easier to integrate, and the defects induced to the epoxy resin to be more reduced.

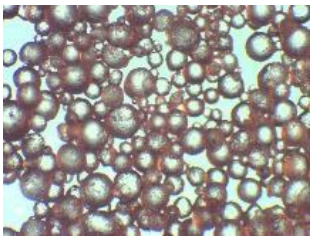
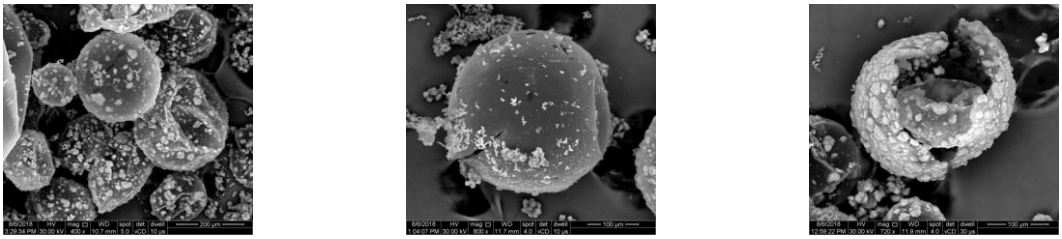


Figure 3.1**.** Images of the PUF-DCPD microcapsules using stereomicroscope (up to 25x magnification)

(a) (b)

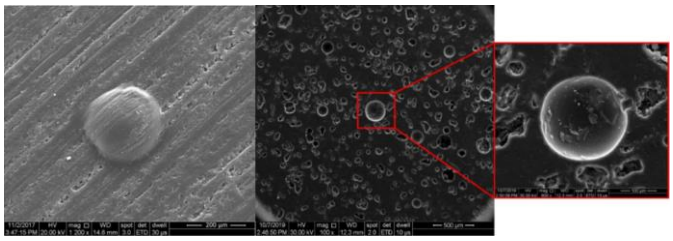
Figure 3.2**.** Stereomicroscope images of a) MUF-ENB microcapsules; b) images in reflection

The SEM investigations emphasize more clearly the traces of non-capsulated monomer which adhere to the PUF-DCPD surface, and also the size of the microcapsules. One can observe in Figure 3.3, Figure 3.4 and Figure 3.5 that the dimensions vary between 100-300 μm, with a majority of these ones not exceeding 250 μm.

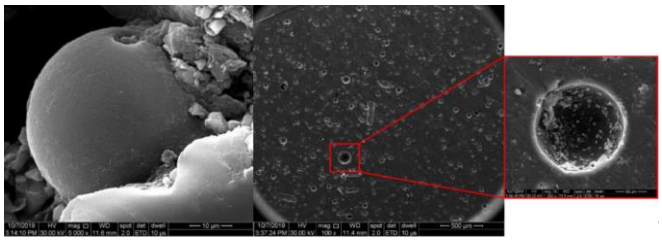


(a) (b) (c)

Figure 3.3**.** SEM images which emphasize a) microcapsules congestion; b) microcapsules larger than 250 μm; c) broken microcapsule



(a)



(b)

Figure 3.4. SEM images of a) microcapsule embedded in resin and several broken microcapsules for the PUF-DCPD microcapsules, respectively b) MUF-ENB system

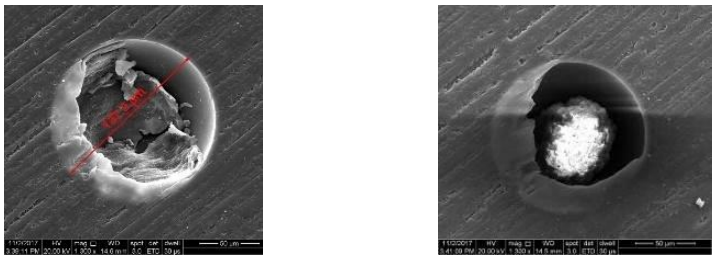
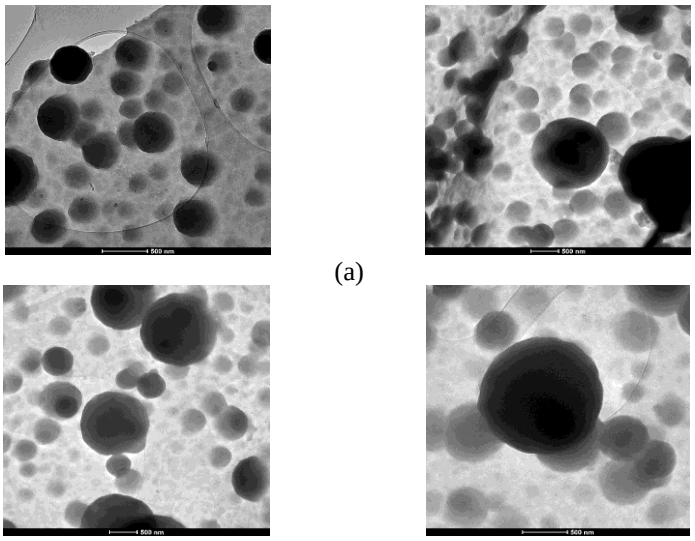


Figure 3.5**.** Microcapsules degraded during the embedding process in the polymeric system and the presence of some residues inside them.

The TEM analyses were performed to observe if the PUF-DCPD, respectively the MUF-ENB repairing agents are embedded in the microcapsules of the two developed self-healing systems. Following the analyses, the spherical shell of the microcapsules, the shell thickness (approx. 150 nm), and the presence of the two repairing agents were identified and evaluated.



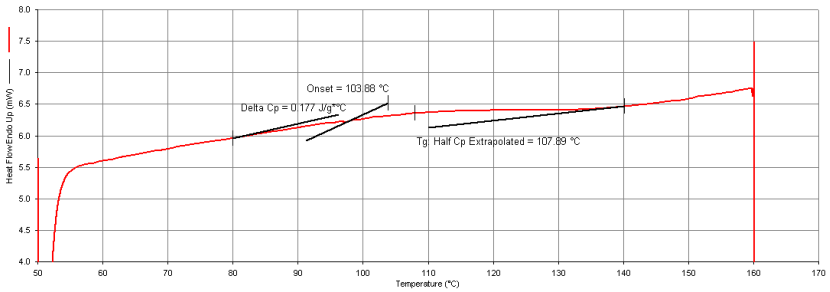
(a)

(b)

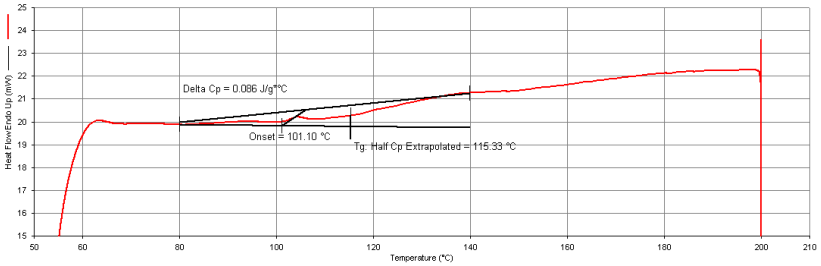
Figure 3.6. TEM images of the a) PUF-DCPD and b) MUF-ENB systems

3.3.2. Thermomechanical analyses of the developed self-healing systems

Following the DSC results obtained (Figure 3.7), the glass transition temperature for the PUF-DCPD is 107,8°C, while for the MUF-ENB system is 115°C. The difference between temperature is due to the components of the two systems, more exactly of the melamine which has a high melting point (345°C), and it could also favour the thermal stability of this system.



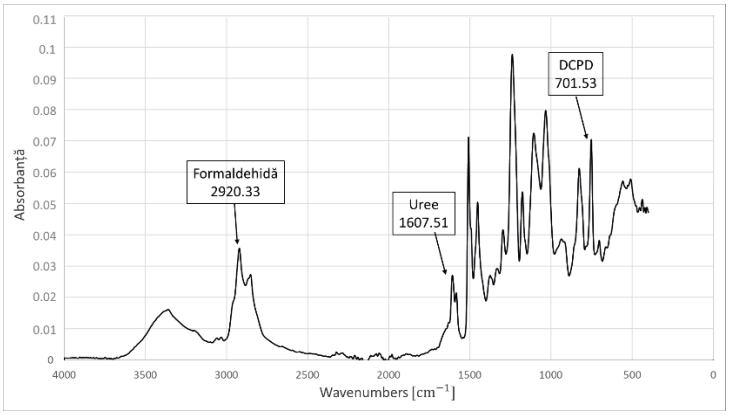
(a)



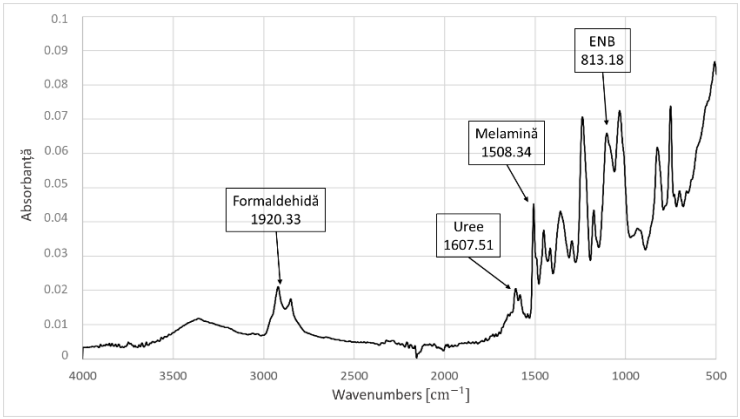
(b)

Figure 3.7. DSC analyses images for a) PUF-DCPD and b) MUF-ENB

The results of the FT-IR analyses are presented in Figure 3.8. and they confirm the presence of the specific shell materials of the two systems, as well as of the repairing agents.



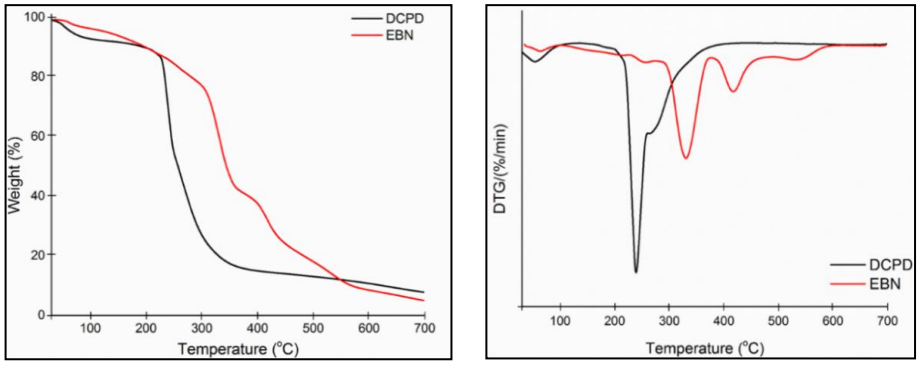
(a)



(b)

Figure 3.8**.** FT-IR analyses images for systems a) PUF-DCPD and b) MUF-ENB

Regarding the TGA/DTA analyses, a mass loss of 72.6% was identified for the PUF-DCPD analysis, and 74% for the MUF-ENB system, in the temperature domain of 30°÷600°C, as one can observe in Figure 3.9.



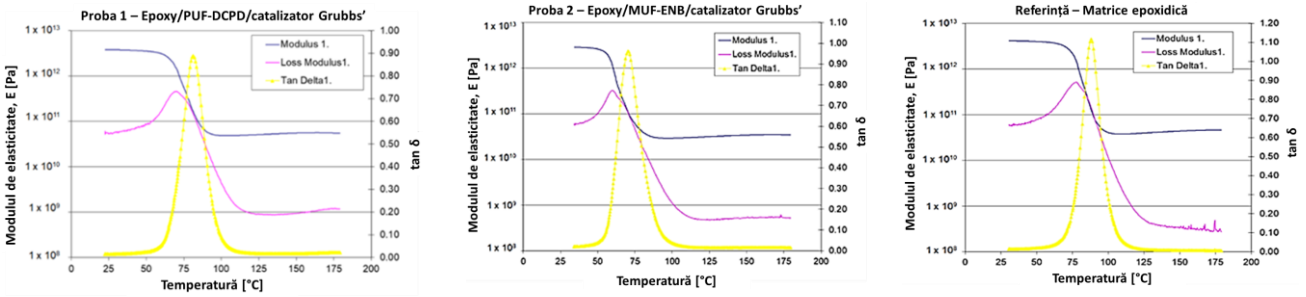
(a) (b)

Figure 3.9. Thermogravimetric analyses images for systems a) PUF-DCPD and b) MUF-ENB

Following the DMA analyses, the values of the crosslink densities, of the storage modulus and of the loss modulus for the realized samples are presented

Table 3.1. Crosslink densities for the two developed systems

Sample	Tg (°C)	Crosslink density (v_e)	Storage modulus, ε' (MPa)	Loss modulus, ε'' (MPa)
Reference	88.1	3098	3789.05	57.48
PUF-DCPD	80.5	5092	2892.66	59.29
MUF-ENB	70.2	3149	4130.25	59.61



(a) (b) (c)

Figure 3.10. Thermo-mechanical analyses images for the systems a) PUF-DCPD, b) MUF-ENB and c) epoxy matrix.

Moreover, one can observe that the crosslink density of the samples for the two self-healing systems grows compared to the one of the reference samples, mainly due to the participation of the DCPD and ENB monomers from the UF shell during the formation of the molecular chains, as observed in Figure 3.11.

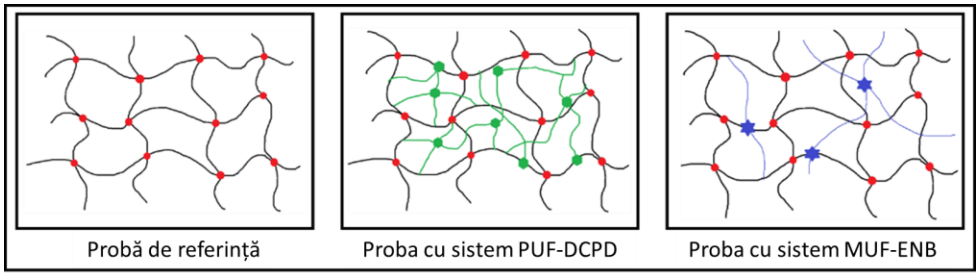
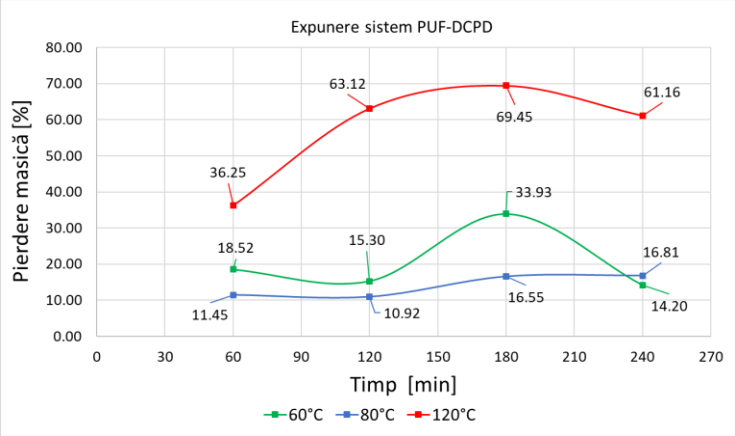


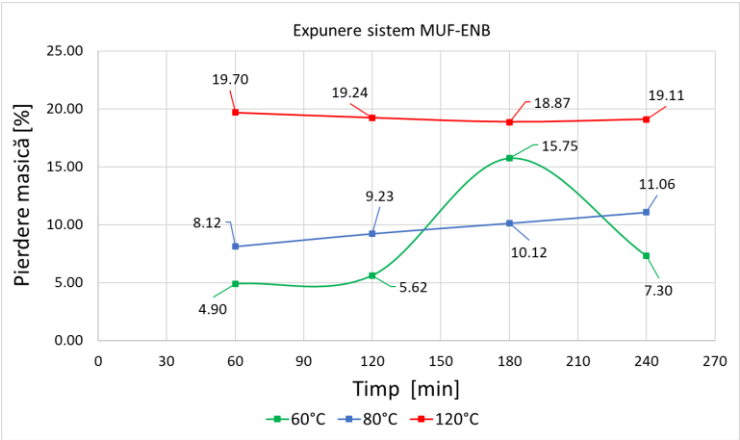
Figure 3.11. Schematic presentation of the crosslink density for the two self-healing systems

3.4. Thermal stability analyses of the self-healing systems developed

As the two self-healing systems developed (PUF-DCPD and MUF-ENB) will be included in the epoxy resin (Resoltech 1050/1058), in order to establish the optimal method for integration in the CFRP composite type (M49/42%/200T2X2/CHS-3K) and to evaluate their self-healing properties, it is necessary to conduct a preliminary thermal stability analysis for it. Considering the polymerization temperatures for the two materials, the thermal stability tests were conducted at 60°C, 80°C and 120°C for time intervals of 60, 120, 180 and 240 minutes. Thus, four recipients in which 0.2 grams of microcapsules were introduced, were weighted for each system. Each recipient was exposed on turn in the previously mentioned temperature domain. After exposure, the samples were weighted again and weight losses were identified depending on the thermal exposure. The results are highlighted in Figure 3.12 for the two self-healing systems



(a)



(b)

Figure 3.12**.** Qualitative analysis of the mass loss following the thermal exposure for a) PUF-DCPD system and b) MUF-ENB system

Following the weighting, each recipient with microcapsules was analysed by stereomicroscopy in order to observe if the microcapsules' structure was maintained. It was observed that the majority of the microcapsules was not affected due to thermal exposure, the mass loss being mainly due to the evaporation of the repairing agents through the microcapsules' shells.

3.5. Analyses regarding the integration methods of the developed self-healing systems

3.5.1. Homogenisation by magnetic dispersion

Following the polymerization program at 80°C for 120 minutes, a pre-polymerization step of the epoxy matrix was proposed during the integration of the microcapsules, mainly by pre-heating the epoxy resin at 60°C in order to reduce the viscosity and to homogenize the microcapsules by magnetic dispersion. The volume of a sample was calculated in order to obtain the necessary quantity of materials (resin, hardener, acetone, microcapsules, catalyst). In order to realize the samples, the following materials quantities were used for both the developed self-healing systems.

Resoltech 1058 resin	14,82 g
Resoltech 1058 hardener	5,18 g
Acetone	2 g
PUF-DCPD (7% wt.) microcapsules	1,4 g
Grubbs (2% wt.) catalyst	0,4 g

In order to reduce the viscosity, the epoxy resin was diluted with acetone (10% wt.). The hardener was added and let until the solution was homogenous, using a magnetic mixer which worked at a speed of 200 rpm. After this step, PUF-DCPD (7% wt.) microcapsules were gradually added along with the 2% wt. Grubbs catalyst, while the temperature was raised to 80°C in order for the acetone to evaporate. The mixture was poured in a metallic mould and introduced in the pre-heated oven in order to expose it to a polymerization cycle for 120 minutes at 80°C. Due to the fact that the MUF-ENB system has smaller dimensions than the PUF-DCPD system, the volumetric fraction is smaller, which made the integration in the epoxy resin easier to perform. The integration process by magnetic dispersion of the two systems is presented in Figure 3.13.

(a) (b)

(a) (b)

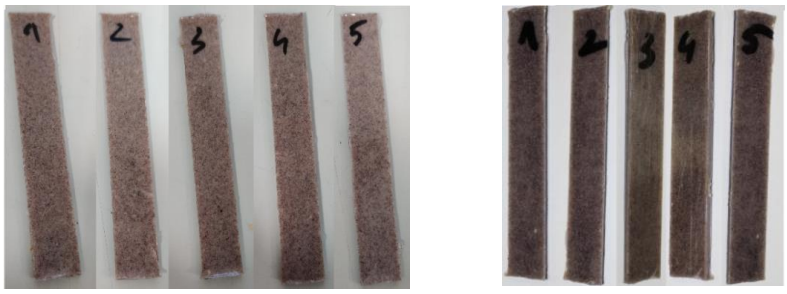
Figure 3.13**.** Realizing the mixture between Resoltech resin 1050/1058, with a) PUF-DCPD microcapsules and b) Grubbs catalyst by magnetic dispersion

3.5.2. Homogenisation by ultrasonication

Before integrating the self-healing system in the epoxy matrix, the working parameters of the sonicator, respectively the amplitude, pulsation and off time, and total ultrasonication time:

Amplitude	60 %
Pulsation time	10 s
Off time	2 s
Total time	600 s

Following the parameters mentioned above, two solutions containing resin and self-healing system were made, and then poured in moulds to obtain the samples which shall be tested to bending and respectively to establish the optimal dispersion method. The polymerization was conducted at 80°C for 120 minutes.



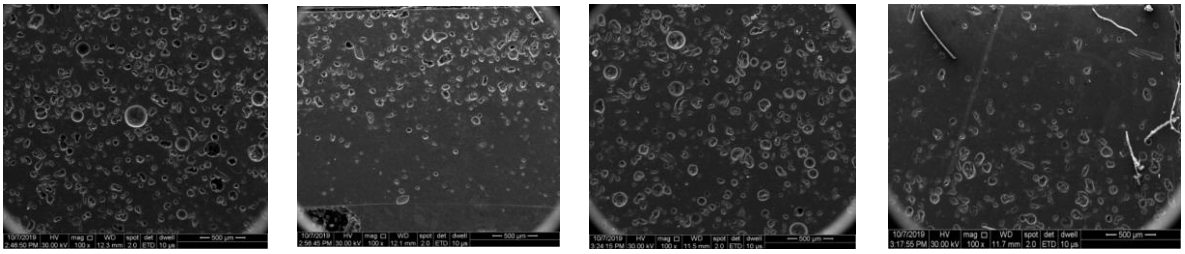
(a) (b)

Figure 3.14. Samples with epoxy resin and a) PUF-DCPD/Grubbs catalyst, respectively b) MUF-ENG/Grubbs catalyst.

3.6. Microstructural analyses of the dispersion methods

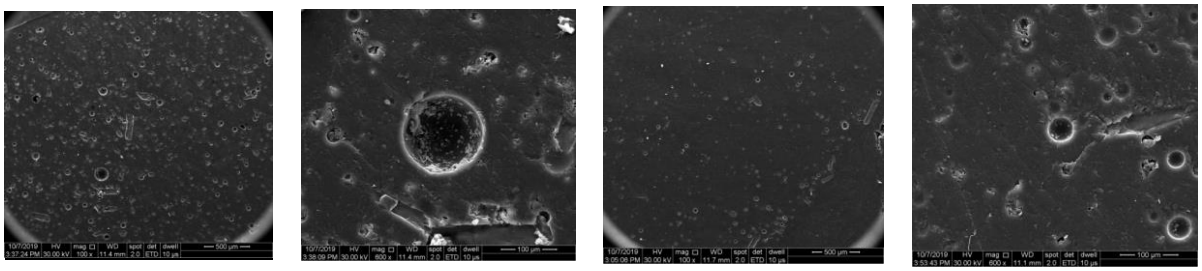
From the manufactured samples, smaller samples were cut to perform microstructural analyses, the results being presented in Figure 3.15 for the PUF-DCPD system and in Figure 3.16 for the MUF-ENB system. Following the SEM analyses, a better homogeneity was observed for

the integration of the PUF-DCPD system in the epoxy matrix by magnetic dispersion compared to the ultrasonic method. Also, several residues were emphasized due to solution dispersion process. The images from the samples' sections show the agglomeration of the microcapsules in the upper part of the sample. This agglomeration occurs during the polymerization process, due to the resin viscosity reduction which determines the microcapsules to migrate in the upper part of the sample. In the same way as the PUF-DCPD samples, the ones with the MUF-ENB system show a better homogeneity after using magnetic dispersion, while for the ultrasonic dispersion methods, most of the microcapsules were destroyed. Comparatively, in the case of the samples made by magnetic dispersion, whole microcapsules can be observed in section, embedded in the epoxy matrix.



(a) (b)

Figure 3.15. SEM images show overall and detailed view for the PUF-DCPD system embedded by a) magnetic dispersion and b) ultrasonic dispersion

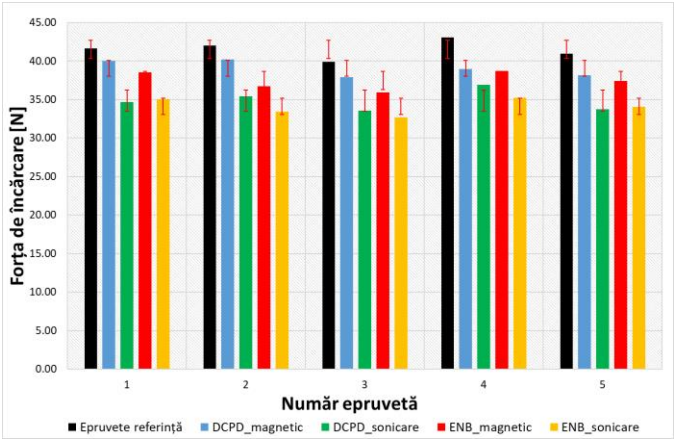


(a) (b)

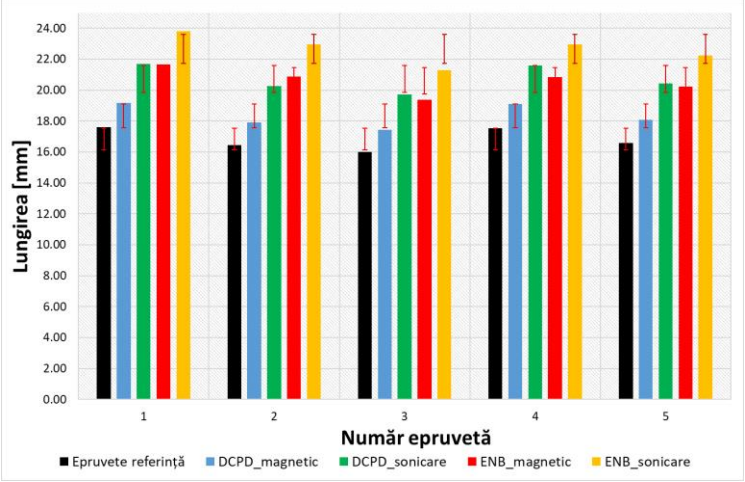
Figure 3.16. SEM images show overall and detailed view for the MUF-ENB system embedded by a) magnetic dispersion and b) ultrasonic dispersion

3.7. Evaluation of the dispersion methods by three point bending mechanical tests

In order to conduct the mechanical tests, the samples presented in Chapter 3.5.2 were used, either by magnetic dispersion or ultrasonic dispersion. The results of the bending tests are presented in Figure 3.17. Due to the large number of samples, the specific curves are presented in two separate plots.



(a)



(b)

Sample	Reference		DCPD Magnetic		DCPD Sonication		ENB Magnetic		ENB Sonication	
	E [MPa]	AE [J]	E [MPa]	AE [J]	E [MPa]	AE [J]	E [MPa]	AE [J]	E [MPa]	AE [J]
1	3325.72	4062.69	2447.37	3430.54	3513.05	2280.84	2416.34	3038.26	3039.09	2792.08
2	3704.74	3963.80	3569.16	2742.37	3575.05	2496.05	2978.9	3167.35	3549.13	2372.28
3	3309.20	3126.31	3002.83	2153.04	3864.28	2805.59	2731.06	3034.97	3196.19	2292.53
4	5679.64	4316.23	2364.42	3535.88	3350.56	2926.37	2694.80	3115.84	3037.63	2890.93
5	3835.18	3795.85	3034.49	2412.54	2757.11	2656.36	3278.13	2862.83	3275.54	2610.37

Figure 3.17. a) Tensile load and b) elongation (ε) for the samples of the two self-healing systems

Following the microstructural analyses and mechanical bending tests, it was found that the ultrasonic dispersion method destroys the microcapsules, which creates a disadvantage, as this can significantly reduce the mechanical properties of the matrix. This was observed in the case of the mechanical bending tests, were the bending strength is 10-12% lower for the samples obtained by ultrasonic dispersion compared to the ones made by magnetic dispersion.

CHAPTER 4
CONTRIBUTIONS REGARDING THE METHODS FOR SYNTHESIS AND INTEGRATION IN THE EPOXIDIC MATRIX OF THE SELF-HEALING SYSTEMS BASED ON MICROVASCULAR NETWORK

In order to cover larger areas and thus increase the possibility of multiple repairs or, repair of defects located near each other, the use of microvascular systems brings a great benefit to polymeric structures. To stimulate the microvascular self-healing system, the introduction of multiwalled carbon nanotubes in the epoxydic matrix were also investigated. Along with the increase in mechanical properties, embedding CNT along with the healing system within the composite material aims to increase the molecular level reactions (between the free radicals of healing agent-matrix-CNT), and thus, of the whole healing process. Also, this may lead to an increase in electrical conductivity that could be transformed in thermal conductivity which benefits the repair process by speeding up the reactions. At the same time, the UV radiations (from technical inspections/maintenance) can be converted into thermal energy, thus leading to an increase of molecular reaction speed and healing of the microcrack.

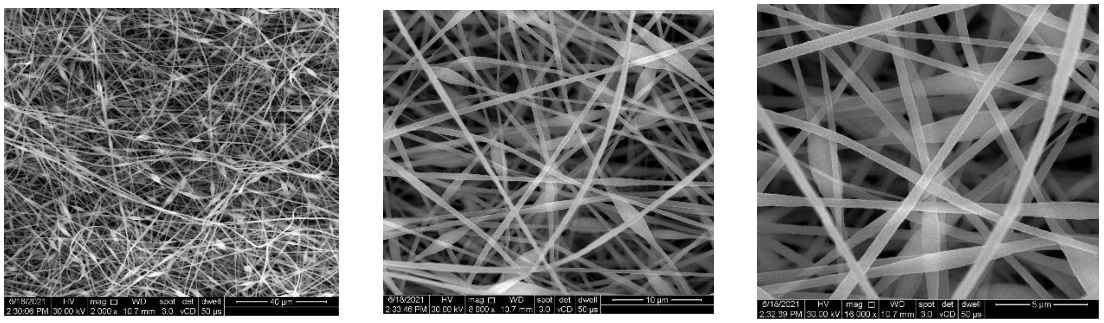
4.1. Development of self-healing system based microvascular network

For the manufacturing of the microvascular system, a PAN solution was used to create the shell and DCPD as healing agent. Two solutions were made using DMF as solvent, a solution of 10% PAN and a solution of 10% DCPD. For the preparation of PAN/DMF solution, 2g of polymer was dissolved in 18 ml solvent under magnetic stirring at 400 rot/min and 80°C for 6 hours. For the second solution, DCPD/DMF, 1g of monomer was dissolved in 9 ml solvent under the same conditions. The two solutions were placed within the injection system of the electrospinning machine and the parameters were set. Following the electrospinning process, the PAN/DCPD healing system was removed from the collector (Figure 4.1).

Figure 4.1 Image of the obtained microvascular network

4.2. Microstructural and thermomechanical analyses of the developed self-healing system

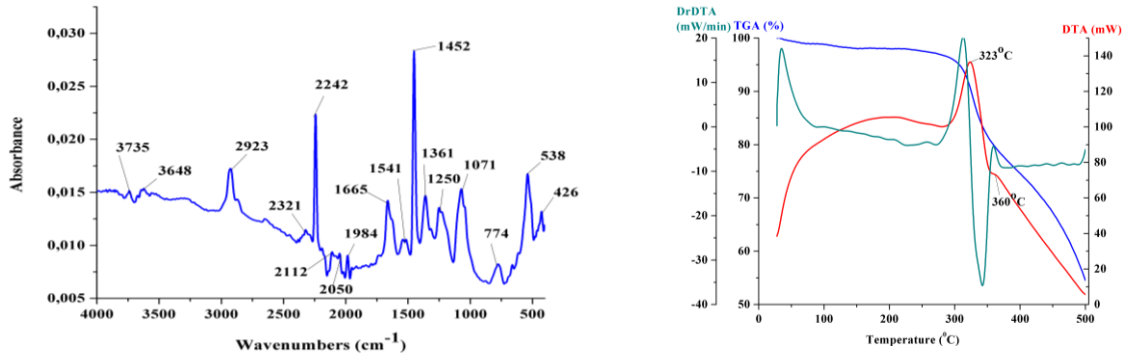
Following the SEM analysis, it could be observed that the morphology of the nanofibres is indeed similar to a microvascular network. Nanofibres dimensions were found between 200 nm and 800 nm.



x2000 x8000 x16000

Figure 4.1. SEM images of obtained microvascular network

FT-IR analysis confirms the presence of the two healing system constituents, namely DCDP healing agent and PAN shell. TGA/DTA analysis have identified a total mass loss of 45.50% in two steps, a rapid loss between 300-350°C associated to the melting of PAN shell, and a faster mass loss between 350-500°C.



(a) (b)

Figure 4.2. (a) FT-IR and (b) TGA/DTA spectrum for PAN/DCPD microvascular self-healing system

4.3. Evaluation of self-healing properties by means of three point bending mechanical tests

For the fabrication of samples with embedded microvascular network and Grubbs catalyst, the latter was initially homogenised with the resin and hardener. After the homogenisation, part of the mixture was poured into the mould, followed by three layers of the microvascular system and the remaining of the mixture. For the fabrication of samples with CNT and microvascular system and CNT, the nanotubes were initially mixed with the resin and hardener to assure a good homogenisation. It is to be mentioned that due to the matrix nature (thermoset), it passes very fast though a state of elastic deformation followed by a plastic deformation that leads to material failure. Thus, it was considered that the mechanical tests to be performed until a 10% decrease in flexural force was observed, to avoid sample rupture and consequently the impossibility to evaluate the healing ability.

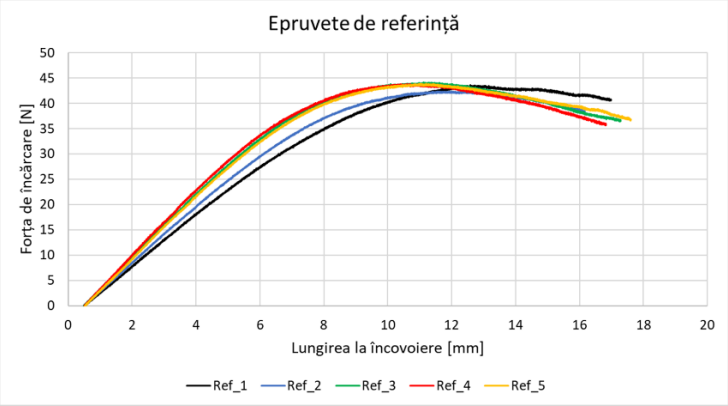


Figure 4.3. Three point bending mechanical test results for reference samples

For the samples containing 0.5% CNT, a 61% increase in flexural load was observed together with a 32% increase in flexural stress and a 20% flexural strain over the reference samples. Samples with 1% CNT have doubled the flexural load and further increased the flexural stress up to 57% over the reference samples. Maximum deformation for samples with 1% CNT has increased by 28% as compared to the reference samples. Thus, it can be said that, the CNT addition extends the deformation ability of the matrix. This presents an advantage in developing thermoset composite materials with self-healing properties, as it delays the material failure and thus allowing more time for the healing systems to activate. Following the flexural tests of the samples containing the microvascular network, it was found that adding the healing system increase the flexural properties of the material by 2-3%, as compared to the reference samples. After the first three point bending tests, all samples were conditioned at 40±1°C °C for 48 hours to allow the self-healing system to activate. Retesting the samples with embedded microvascular system led to a 74% recovering of flexural properties compared to the initial test, and 92% flexural properties recovering when compared to the reference samples. The maximum load values after the second testing were found to be in close range of the deformation values for the initial testing, which concludes that the healing process has taken place, otherwise, the sample failure would have occurred faster at much lower deformation. For samples containing 0.5% and 1% CNT, flexural load after the second testing is much closer to the one obtained after initial testing, which confirms that the CNT embedding presents an advantage. However, an increase in flexural strain was observed for the samples containing microvascular system and CNT as compared to the sample containing only the microvascular system, which can be interpreted as an increase in matrix stiffness and flexural strength. Also, failure points of the retested samples are in close range to the ones where the initial test was stopped, meaning that the healing process was successful.

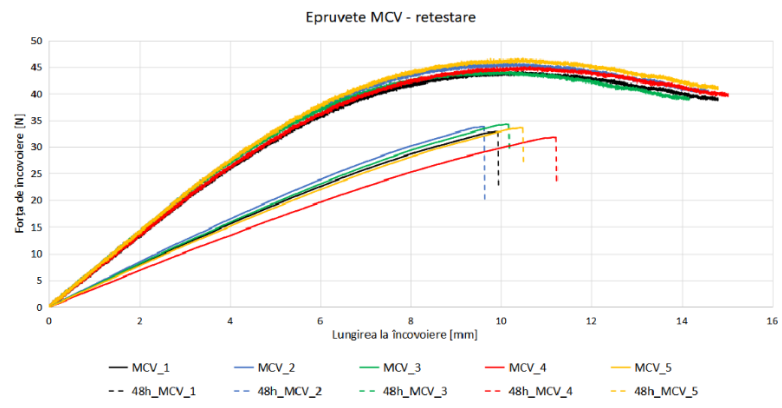
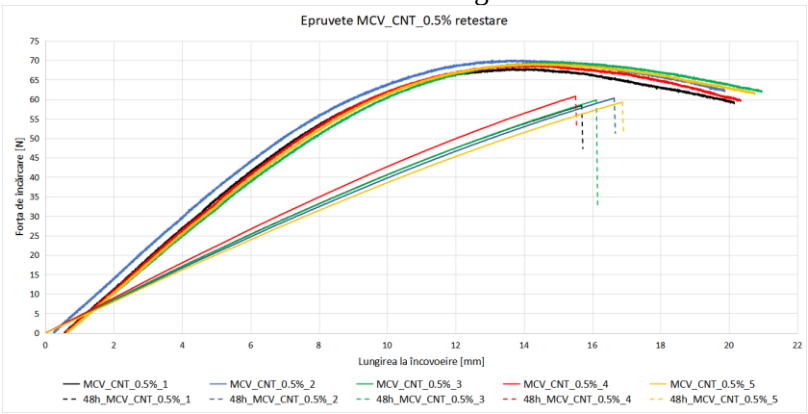
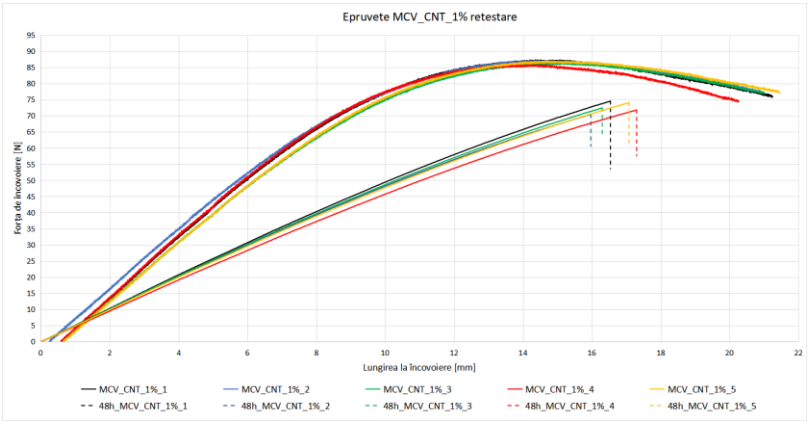


Figure 4.4. Three point bending test results for samples with embedded microvascular network after second testing



(a)



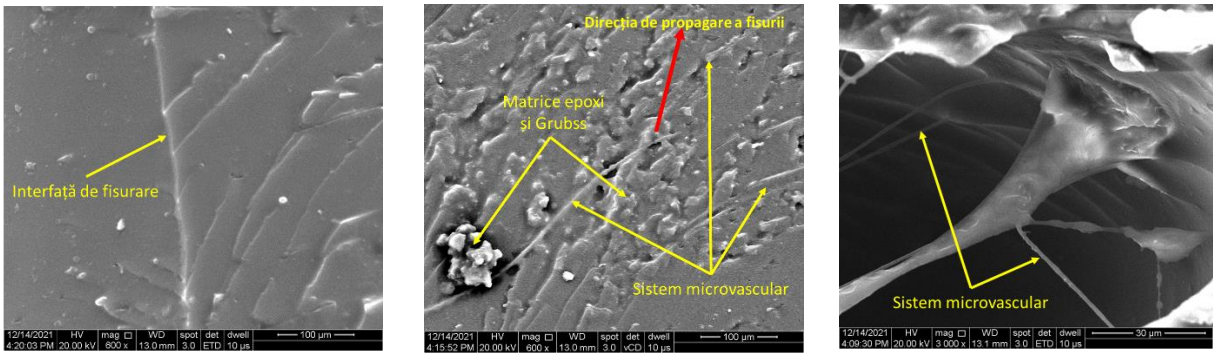
(b)

Figure 4.5. Three point bending test results for samples with microvascular network and a) 0.5% CNT, b) 1% CNT after second testing

4.4. Microstructural analysis

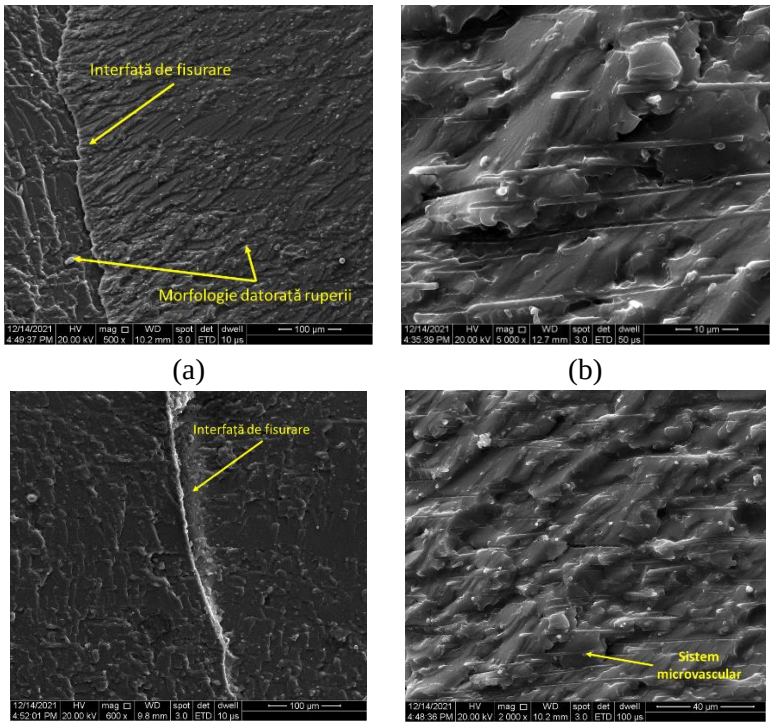
After performing the second three point bending tests, probes from each sample were cut for SEM analyses. In Figure 4.7 can be seen a representative image of an area containing a healed microcrack. It can also be seen the bridging between the crack interface and the remaining of the microvascular system that did not take part in the healing process. In Figure 4.8 are shown images

of the 0.5% and 1% CNT samples, from the two separating crack planes. The morphology of crack depth and of the two adjacent crack planes can be easily observed.



(a) (b) (c)

Figure 4.6. SEM images of microvascular sample illustrating a) microcrack, b) crack plane, c) bridge between two crack planes



(a) (b)

(c) (d)

Figure 4.7. SEM images of microvascular sample containing a,b) 0,5% CNT, and c.d) 1% CNT, illustrating the microcrack plane and morphology

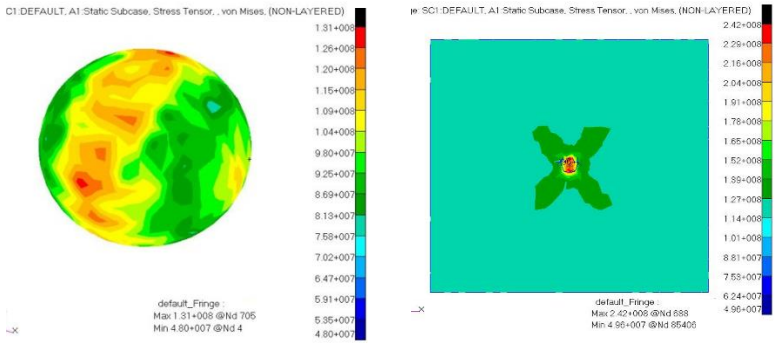
An advantage of the microvascular self-healing systems is that, by comparing it with microcapsule self-healing system, do not reduce the mechanical properties of the material, thus provides a greater opportunity in the development of thermoset polymer composite materials with self-healing properties. By the use of CNT, the flexural properties of the material have increased by 61% with a 28% increase in flexural strain. This is a positive factor in the development of thermoset polymer composites incorporating self-healing systems, as it delays the material failure, giving more time for the self-healing systems to act.

CHAPTER 5
CONTRIBUTIONS REGARDING THE FINITE ELEMENT NUMERICAL ANALYSES ON THE STRESS STATE OF THE POLYMERIC MATRIX

Finite element numerical analyses were performed to establish the numerical modelling criteria for composite materials with self-healing systems, something that is very little investigated in the specialized literature. Thus, a series of numerical analyses were carried out in order to understand the effects of the integration of microcapsules on the stress states of the epoxy matrix, thus making a contribution to the development of self-healing systems. At the same time, it was considered to study how the distribution of microcapsules influences the stress distribution and the concentration factor in the epoxy matrix, thus being able to decrease the breaking force and the crack extension.

5.1. The effect of self-healing systems presence on the stress state

The embedded microcapsules can be considered inclusions, and by releasing the healing agent it generates a void that constitutes a stress concentrator. For the stress analysis, a unit cell was considered for the epoxy matrix, defined by a cube that has a microcapsule filled with repair agent in the centre. The unit cell is subjected to tensile stress, the value of the applied force being set so as to cause a stress of 125 MPa, exceeding the tensile strength value of the epoxy resin. Modelling of the repair agent was performed by using an elastic material with a very low modulus of elasticity and a Poisson's ratio of 0.495 to simulate its incompressibility.

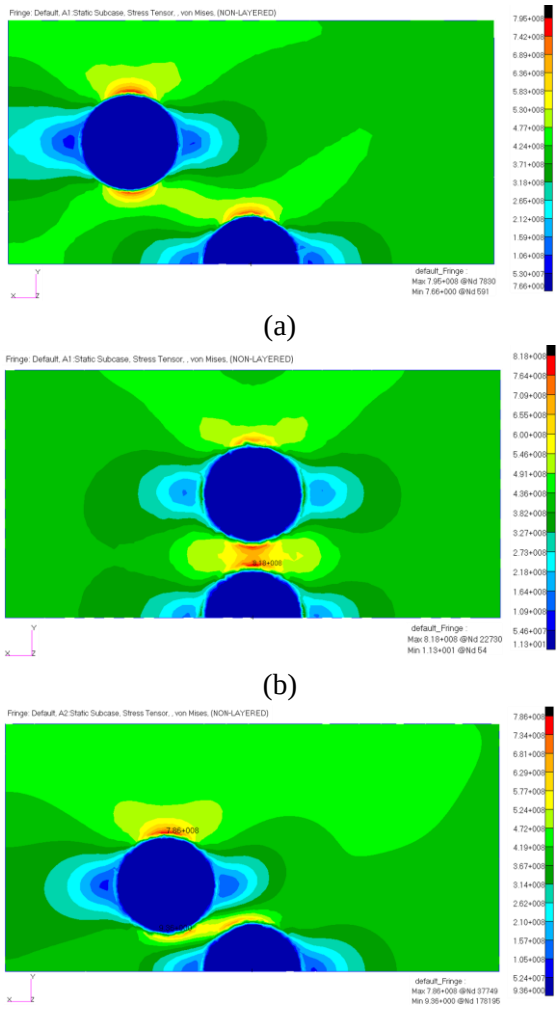


(a) (b)

Figure 5.1. Images of FEM analysis showing von Mises stress distribution for a a) microcapsule with healing agent, b) empty microcapsule

In the case of microcapsule with healing agent, the maximum stress is 150 MPa with a concentrator factor of $\mathbf{K_c}$ = 1.2, while in the case of an empty microcapsule (after microcapsule break), the maximum stress is 242 MPa with a concentration factor of $\mathbf{K_c}$ = 1.94. The stress concentrator effect has decreased the safety coefficient by 17%. Maximum stress caused by the existence of the microcapsule is 634 MPa, which leads to the increase of stress concentrator factor $\mathbf{K_c}$ from 1.2 to 1.49. Another aspect of interest was the study of the matrix stress state as a function of two microcapsules distribution in relation to their positioning. Thus, in the first case study, the two microcapsules were placed at a 45° angle at a distance of each other of 0.085 mm. The analysis showed a maximum stress of 795 MPa with a concentration factor of 1.87. In the second case

study, by placing the microcapsule in their median plane along the direction of the tensile load, at a distance of 0.05 mm between them. In this case, the maximum stress was found at 818 MPa with a concentration factor of 1.82. The third case study is characterised by placing the microcapsules in the perpendicular plane on the direction of tensile load. For this, the maximum stress was found at 786 MPa with a concentration factor of 1.85.



(a)

(b)

(c)

Figure 5.2. von Mises stress distribution for the two microcapsules as a function on their positioning at a) 0,085 mm and 45°; b) 0,05 mm in median plane; c) 0,05 mm in perpendicular plane

Following these analyses, it was concluded that the presence of the two microcapsules has caused the increase of concentration factor by 29%, Moreover, by doubling the microcapsule diameter, the concentration factor increases by 25%. This can be translated in a 25% decrease in breaking force. Considering the results, it can be concluded that from elasticity theory point of view, the microcapsules break can cause stress concentrations when embedded in the polymeric matrix. This happens also when the microcapsules are not broken, the concentration coefficient being 1.2. The releasing of healing agent increases the concentration factor by 62%, up to 1.94. Succeeding the healing process, the crack length is halved and thus, the stress intensity factor is reduced by 30% altogether with the material risk of failure due to crack propagation. At the same

time, the healing effect will be less efficient when the mechanical loads exceed the crack intensity factor, thus leading to a fast crack propagation and a rapid material failure.

CHAPTER 6
CONTRIBUTIONS REGARDING THE SELF-HEALING PROPERTIES EVALUATION OF POLYMER COMPOSITE MATERIALS WITH EMBEDDED MICROENCAPSULATED HEALING SYSTEMS

In order to analyse and evaluate both the mechanical and self-healing properties of fibre-reinforced polymer composite materials following the integration of the two aforementioned self-healing systems, static (three-point bending) and dynamic (low speed impact) mechanical tests were performed. Flexural and impact tests were proposed as a result of the fact that these mechanical loads are often encountered in the aeronautical industry. Some additional analyses were carried out investigating how both the mechanical and self-healing properties of the composite samples are influenced by exposure to temperature variations (thermal cycling) between -20°C and +100°C. Five sets of samples were manufactured for each mechanical test, containing 5%, 7%, 10%, 12% and 15% volume of microcapsules to observe the implication at both mechanical and healing properties.

6.1. Self-healing properties evaluation by means of three point bending tests

A glass fibre prepreg was used for the manufacturing process of the flexural samples due to the its opacity, and in order to visualize in more detail the defects arising from the mechanical loads. A mixture of resin-microcapsules-catalyst-hardener was formed and poured between the prepreg layers, using the configuration: PP/PP/AM/PP/AM/PP/AM/PP/AM/PP/PP, where PP-prepreg, AM-mixture of matrix and healing system. Following the lay-up process, the samples were cured for 51 minutes at 80°C.

Figure 6.1. Flexural sample manufacturing with embedded microencapsulated healing system

6.1.1. Three point bending tests

A set of samples were exposed to thermal cycling, having their mass weighted before and after the temperature exposure. The reference samples did not present mass loss higher than 0.2%, thus their values were not presented in Figure 6.2.

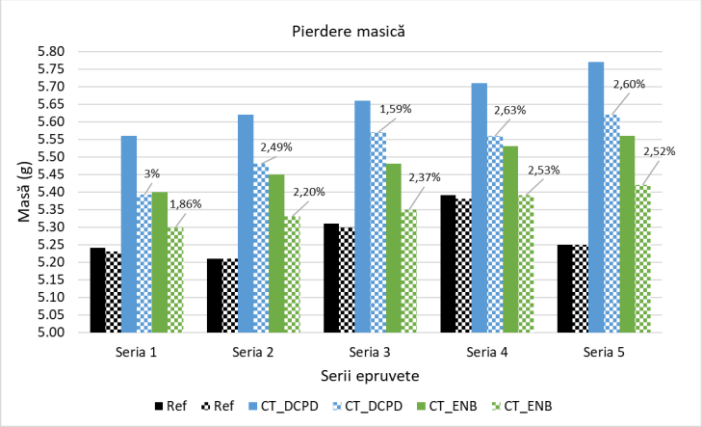
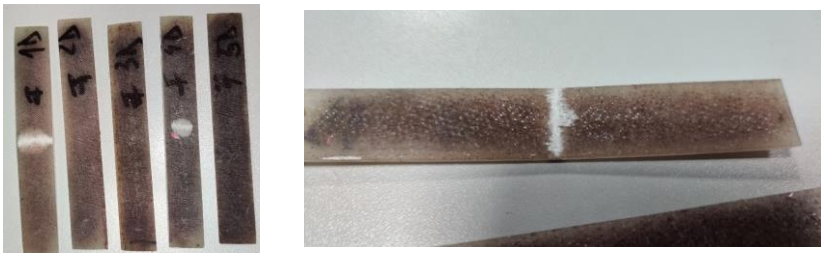


Figure 6.2. Mass loss of samples exposed to thermal cycling (-20°C ÷ +100°C)

Each sample was then subjected to three point bending tests until a drop in flexural load was observed, so that the sample would not be broken and the secondary test could be performed to evaluate the healing ability. The samples were conditioned at 40±1°C for 48 hours to activate the healing systems.

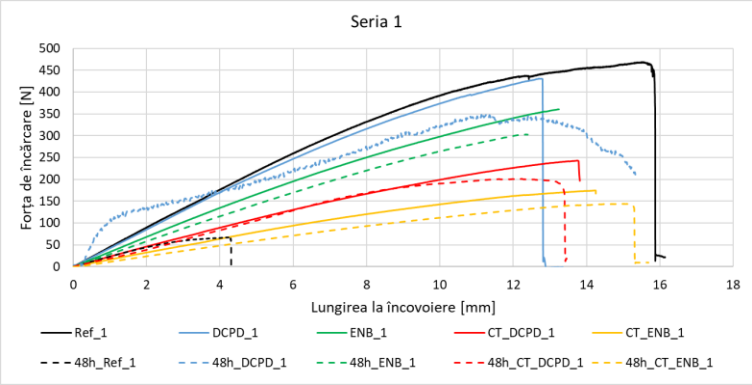


(a) (b)

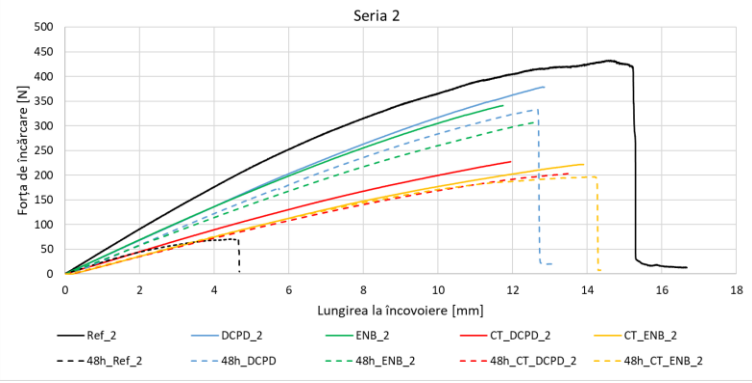
Figure 6.3. Images of (a) samples after first and (b) second flexural test

For the first set of samples (Figure 6.4a), it can be said that healing system reduces the flexural properties of the material by 10% for PUF-DCPD samples and by 12% for MUF-ENB samples. For samples subjected to thermal cycling, the flexural load was even more reduced, by 26% for PUF-DCPD samples and by 36% for MUF-ENB samples. After retesting, the flexural load for PUF-DCPD samples was found to be at 90% of the initial load and at 91% for the MUF-ENB samples. A major difference was found for the samples subjected to thermal cycling, namely the flexural load was found to be at 79% for PUF-DCPD samples of the initial load and at 71% for MUF-ENB samples, consequently. Thus, it can be said that the healing efficiency was more pronounced for the samples that were not subjected to thermal cycling. For the second set of samples (Figure 6.4b), the healing system reduced the flexural loads by 9% for the PUF-DCPD samples and by 12% for the MUF-ENB samples, as compared to the reference samples, meaning that it does not affect drastically the flexural properties of the material. The samples subjected to thermal cycling expressed decrease in flexural load by 27% and 25% for PUF-DCPD samples and MUF-ENB samples respectively, as compared to the reference samples. Retesting have concluded that PUF-DCPD and MUF-ENB samples obtained flexural load of 93-94% as compared to the initial tests, meaning that the healing systems have fulfilled their functional role. Resting the samples after thermal cycling have also determined an increase of flexural load compared to the

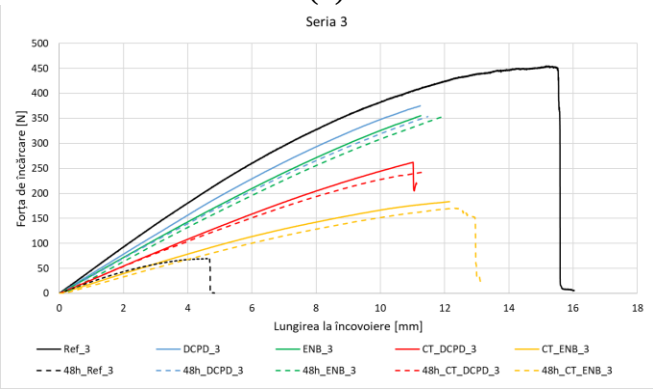
initial test, more precisely, up to 89% of the initial test for the PUF-DCPD samples and up to 87% for MUF-ENB samples. For the third set of samples (Figure 6.4c), a 10% decrease in flexural load was observed for PUF-DCPD samples and a 12% decrease for MUF-ENB samples. Although the microcapsule percentage was increased from 7% to 10%, there was no visible influence over the flexural properties of the material. The same decrease trend in flexural load was observed for samples subjected to thermal cycling, namely 25% for PUF-DCPD samples and 29% for MUF-ENB samples compared to reference samples. Following the second test, the flexural load for PUF-DCPD samples reached 99% and a 96% for MUF-ENB samples, from the initial tests. This indicates that even though the increasing of microcapsule volume tends to decrease the flexural properties of the material, the two healing systems fulfils their functional role in healing the material. The same tendency was observed for the sample subjected to thermal cycling, where flexural loads were found at 92% and 93% for PUF-DCPD and MUF-ENB samples respectively. Fourth series (Figure 6.4d) show a substantial decrease in flexural properties for both healing system samples, 18% and 15% respectively, meaning that further increasing the microcapsule volume have a tendency of affecting the overall mechanical properties of the material. Samples subjecting to thermal cycling present the same outcome with a 31% and 23% decrease in flexural loads, when compared to the reference samples. After 48 hours, the samples present only an 82% and 86% recovery in flexural properties. Samples that were subjected to thermal cycling show an even lower flexural properties, of 69% and 76% when compared to the initial tests. Same tendency was observed tot the fifth set of samples. Thus, it can be said that by increasing the microcapsule volume over a certain percentage, the microcapsules that do not take part in the healing process influence drastically the mechanical properties of the material.



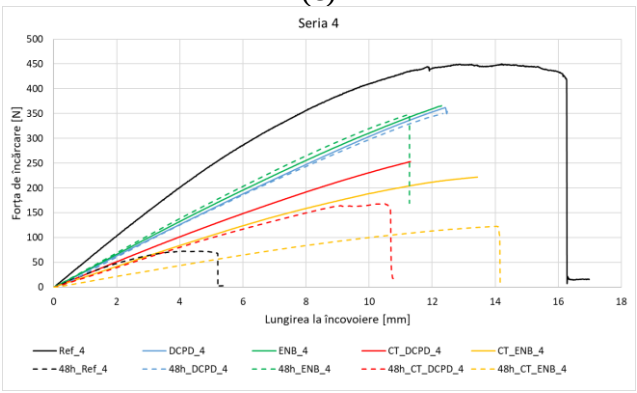
(a)



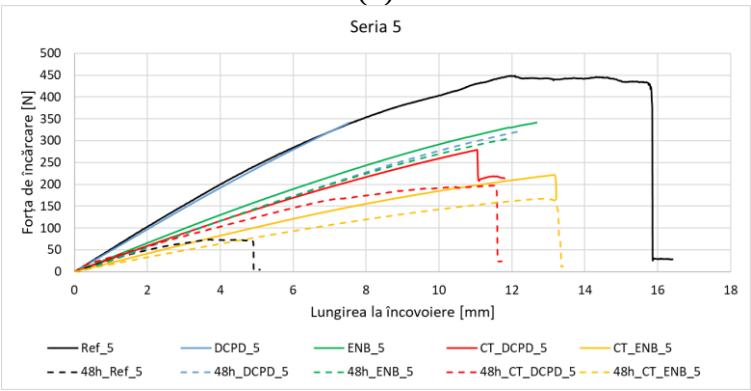
(b)



(c)



(d)



(e)

Figure 6.4. Stress strain curves for a) Set 1, b) Set 2, c) Set 3, d) Set 4, e) Set 5 of samples subjected to for the three point bending tests

6.2. Self-healing properties evaluation by means of low-speed impact tests

Samples for impact testing were manufactured out of the same composite material and using the same curing process (Figure 6.5). Impact tests were performed at a 4.13 m/s speed from a 0.7 m height.

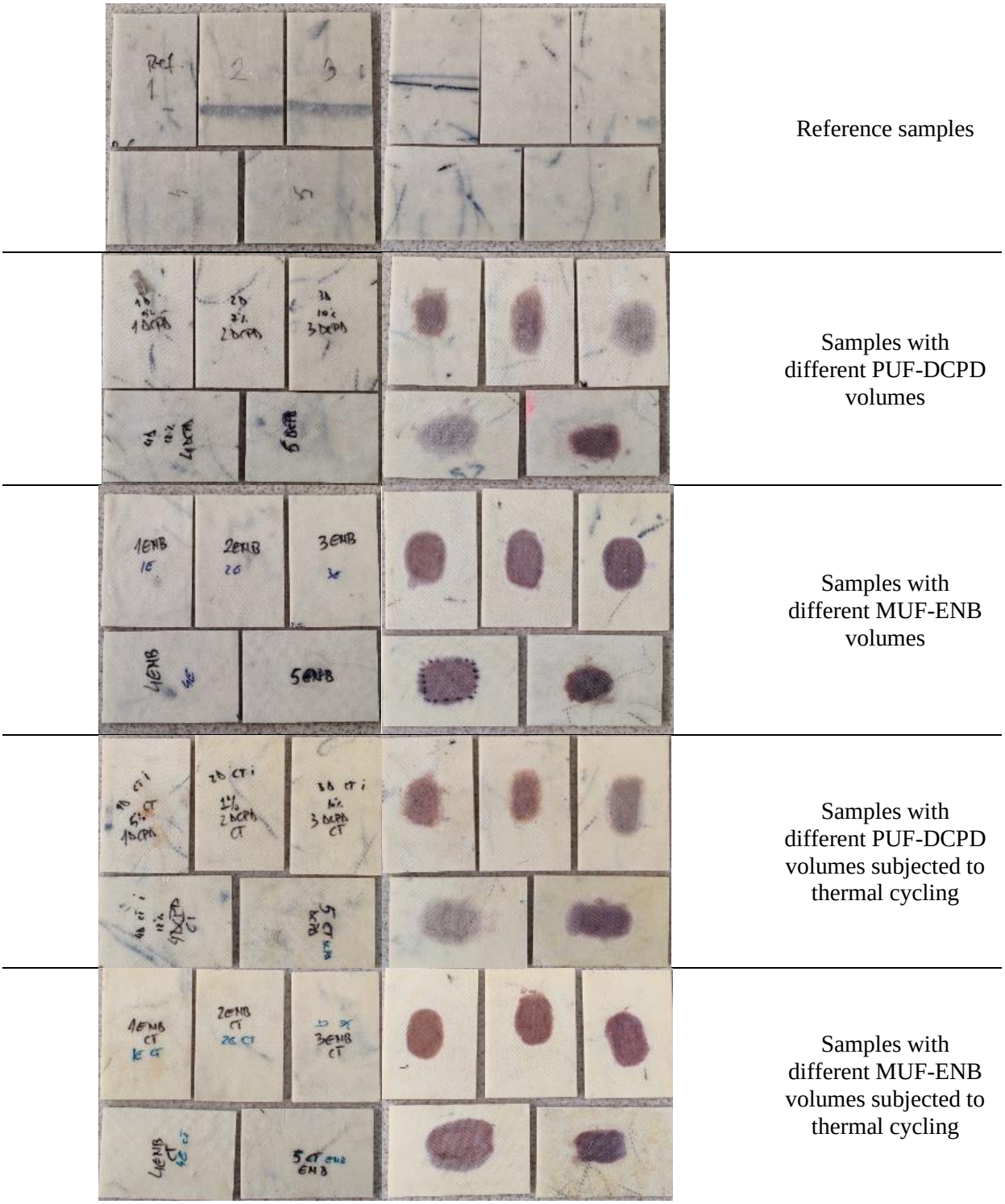


Figure 6.5. Impact samples showing the embedding of healing systems

Figure 6.6 shows the total mass loss of each sample. The reference samples did not show mass losses greater than 0.2%, so their values were not plotted in the graph.

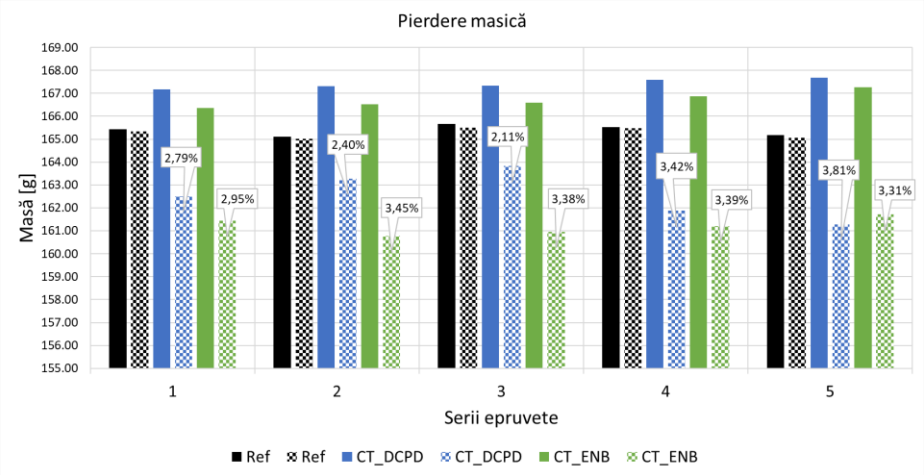
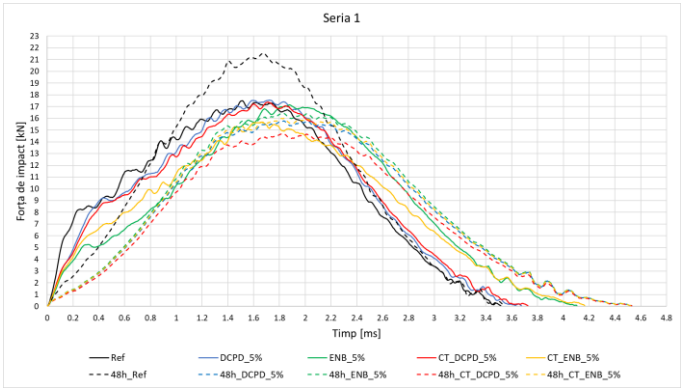


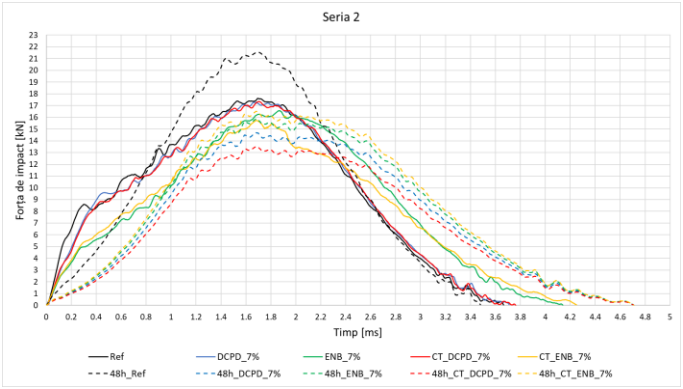
Figure 6.6. Total mass loss of samples subjected to thermal cycling (-20°C ÷ +100°C)

For samples containing PUF-DCPD system, using different microcapsule volumes have not shown any major difference in impact force, excepting the fifth set of samples (15% microcapsules) where a 5% decrease of impact force was observed when compared to the mean average of the other four sample sets. A similar behaviour was seen for the impact energy, where the increase in microcapsule volume led to an increase in contact time. The same behaviour was observed for MUF-ENB samples. However, a sudden decrease in impact force was observed for the 15% MUF-ENB sample which can be associated to a successive failure initiation event (microcracks, delamination) and the possible propagation of such events. Samples that were subjected to thermal cycling show that the 12% PUF-DCPD samples and 15% MUF-ENB samples impact behaviour is affected by the temperature variation, thus amplifying the already known defect caused by embedding the microcapsules in the composite material. The highest impact energy drop and penetration depth was found for the 15% MUF-ENB sample. After the first tests were performed, all the samples were conditioned at 40±1°C for 48 hours and retested. Retesting of sample did not lead to significant changes in the impact behaviour the reference samples. However, the 15% PUF-DPCD sample showed a 40% decrease in impact energy when compared to the initial test, meaning that cracks and possible delamination form the impact event (together with the high microcapsule percentage) did not affect only the material stiffness but also the matrix-fibre bonds. As a result of the impact event, a considerable decrease in the composite material mechanical properties was found, although these self-healing systems were placed only between the first three layers of materials. Also, a slight decrease in the impact force was noticed in the case of the sample with a volume of 7% microcapsules. Among the volumes of microcapsules used for the PUF-DCPD samples, the percentage of 12% can be considered ideal, its results presenting the most appropriate values in relation to those obtained in the first test. Similar to the PUF-DCPD samples, for the samples containing the MUF-ENB self-healing system, the volume of 12% microcapsules presents the highest impact force value, even slightly above the value in the first test. This may indicate a local repair of the epoxy matrix in the area of impact. As in the previous cases, the samples with 15% microcapsules shows a decrease in the impact force by 25%. The maximum impact force of the 15% microcapsule samples is correlated with the sudden drop in the impact force curve from the first test. The samples subjected to thermal cycles

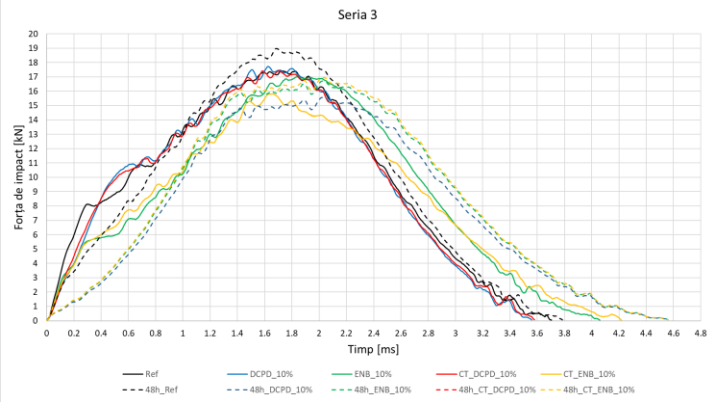
containing the MUF-ENB system have better impact behaviour compared to the samples with the PUF-DCPD system, this may be due to better thermal stability of this self-healing system. However, it was observed that for a 15% PUF-DCPD microcapsules volume the impact force is higher compared to a volume of 15% of MUF-ENB microcapsules. Of course, it should be taken into account that the 15% MUF-ENB microcapsules sample showed the largest impact area, due to the large volume of added microcapsules. To have an overview of the evolution of each microcapsule volume added and how it achieved its functional role, Figure 6.7 shows the impact test results by series.



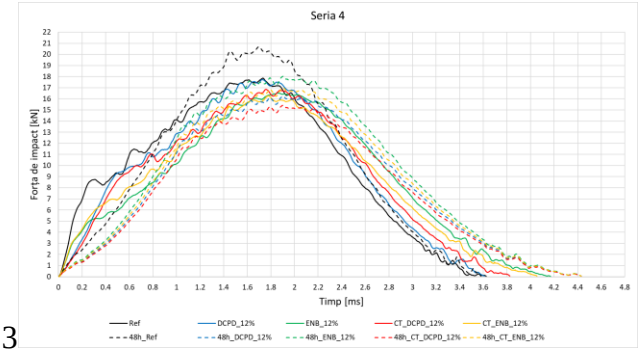
(a)



(b)

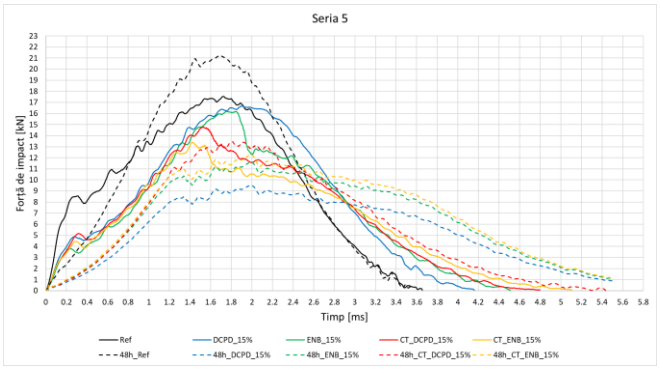


(c)



3

(d)

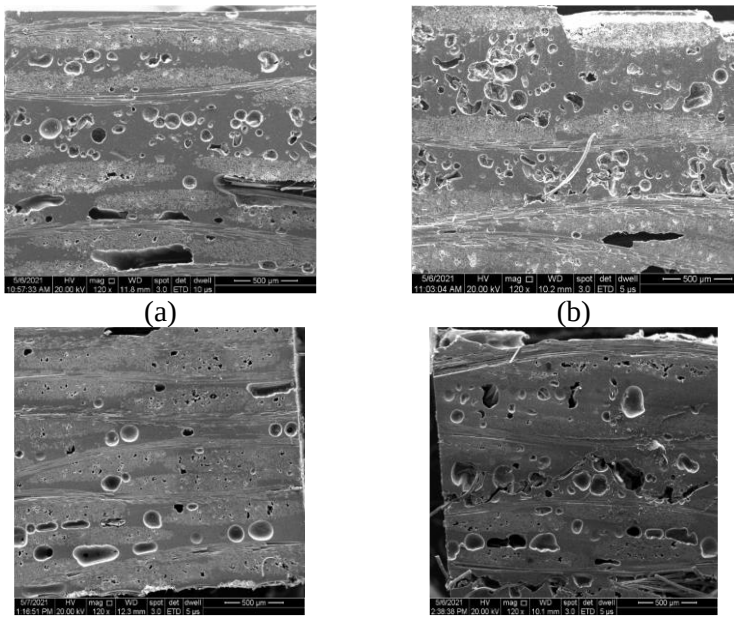


(e)

Figure 6.7. Impact test results with respect to the microcapsule volume addition for a) Set 1, b) Set 2, c) Set 3, d) Set 4, e) Set 5

Following the impact mechanical tests, it can be concluded that above a certain volume of microcapsules, the properties of the composite material are reduced, an aspect that is observed both in both impact force and impact energy. Favourable results were obtained for the samples containing a small volume of microcapsules, namely 5%, 7% and 10%, with a percentage of 80-88% of the impact force after retesting, compared to the initial value. In the case of the 12% volume addition, the results are the most favourable, in some cases these samples have better impact force values compared to the samples with a lower volume of microcapsules, showing 90-95% of the impact force compared to the initial values. For samples with a higher volume of microcapsules, respectively 15%, the values of the impact forces were reduced by 60% on average, which indicates a possible agglomeration of the microcapsules on a small surface. In the case of samples subjected to thermal cycles, the worst results were obtained for the samples with a large volume of microcapsules (15%) for both healing systems. The influence that the volume of microcapsules has on the mechanical properties of the composite material, more precisely on the low-speed impact properties, is thus confirmed. The difference between the reference samples and those with the PUF-DCPD system is only 2% for a volume of 5% and 1.5% for the volume of 12% considered ideal, while for the MUF-ENB system, a difference of 2.5% for a volume of 5% and 6% for a volume of 12% was identified. After retesting, the samples with 12% microcapsule volume showed the best performance, more precisely an impact force of 94% compared to the initial value for the PUF-DCPD system, and for the MUF-ENB system an impact value of 9 was obtained % above the initial one. The same trend was visible in the samples subjected to thermal cycles.

SEM analysis was performed on the samples after second testing. The samples showed a homogeneous dispersion of the two self-healing systems for volumes of 5%-12%. However, the volume of 15% microcapsules showed agglomeration for both systems, which also suggests the decrease in impact force, as presented previously. These agglomerations may be due to the use of a large volume of microcapsules on a relatively small surface area. Figure 6.8 shows the two systems, PUF-DCPD and MUF-ENB with 5% and 15% microcapsule volume. Also, the microcapsule volume density was analysed for both systems and is shown in Figure 6.9.



(a) (b) (c) (d)

Figure 6.8. SEM images of PUF-DCPD samples with (a) 5% and (b) 15% microcapsule volume and of MUF-ENB system with (c) 5% and (d) 15% microcapsule volume

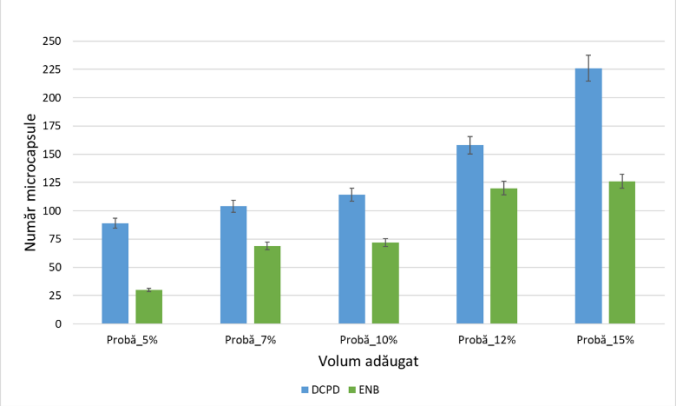


Figure 6.9. Microcapsule density with respect to added volume

6.3. Dimensional analysis of the impact area

After the impact tests were performed, the samples containing the two self-healing systems were dimensionally analysed in order to assess the impact area in detail. Only the impact area and how the percentages of self-healing systems influence the mechanical properties of the samples was analysed.

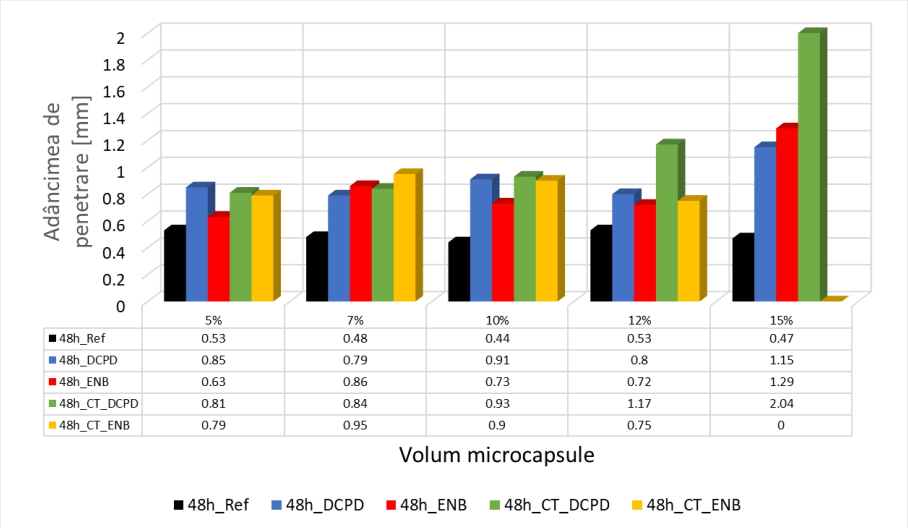
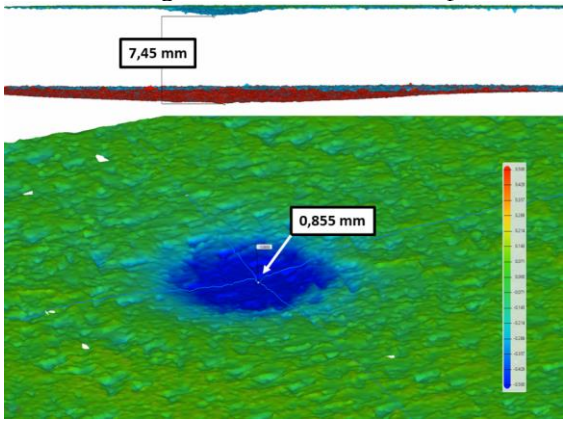
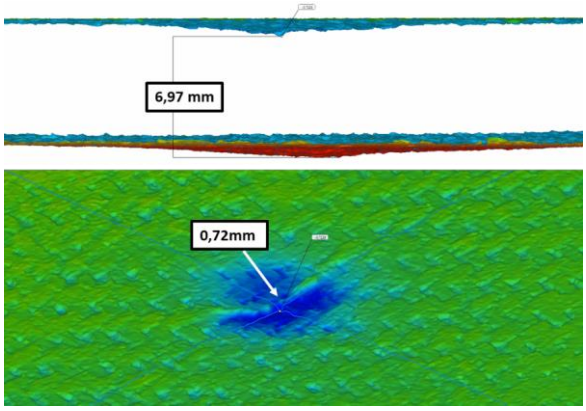


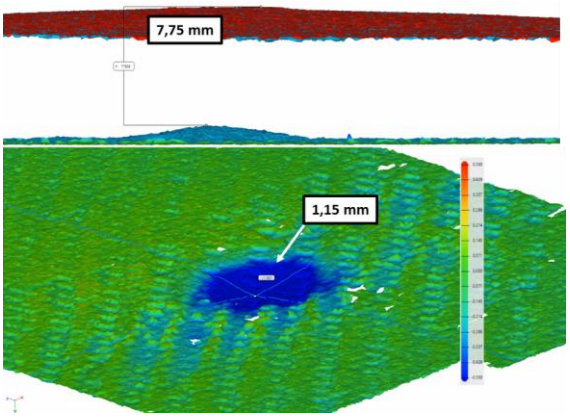
Figure 6.10 Penetration depth with respect to the microcapsule volume addition



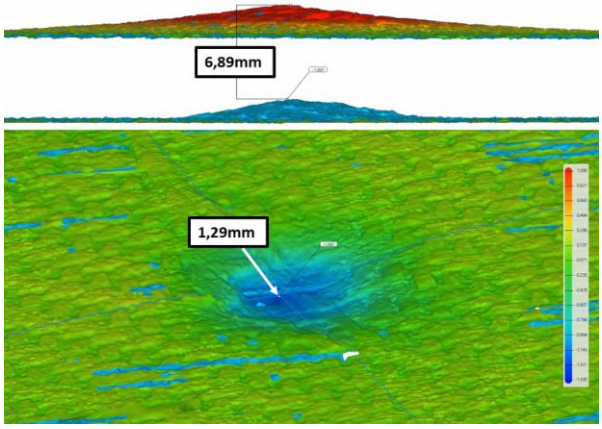
Sample 1 with 5% PUF-DCPD



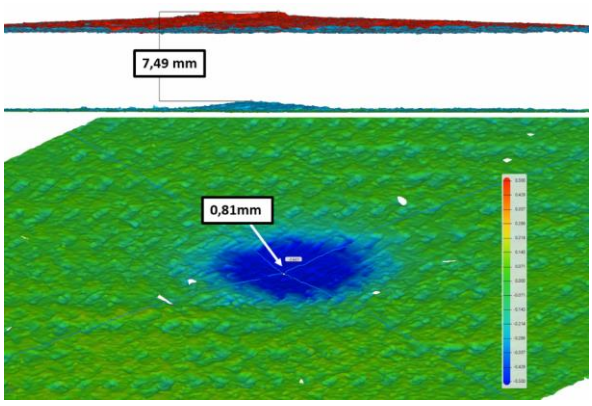
Sample 1 with 5% MUF-ENB



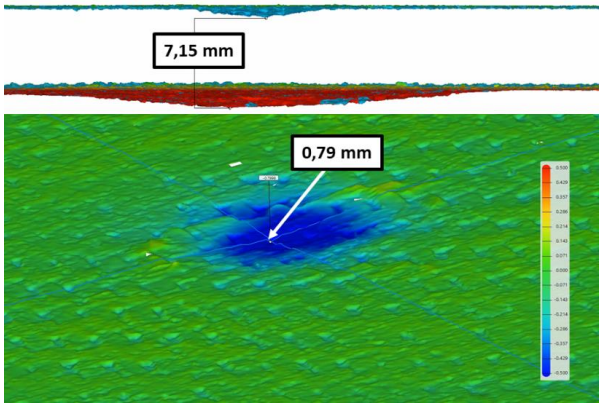
Sample 5 with 15% PUF-DCPD



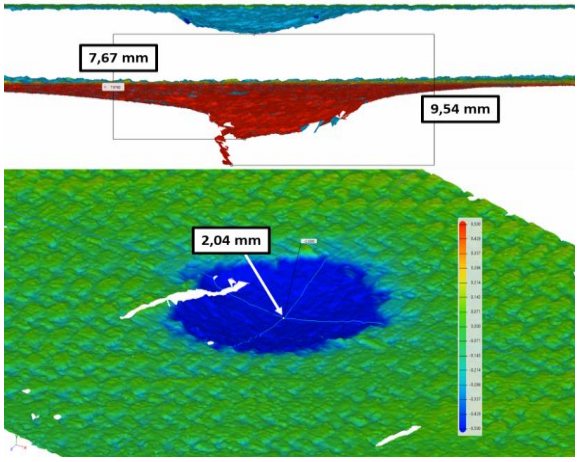
Sample 5 with 15% MUF-ENB



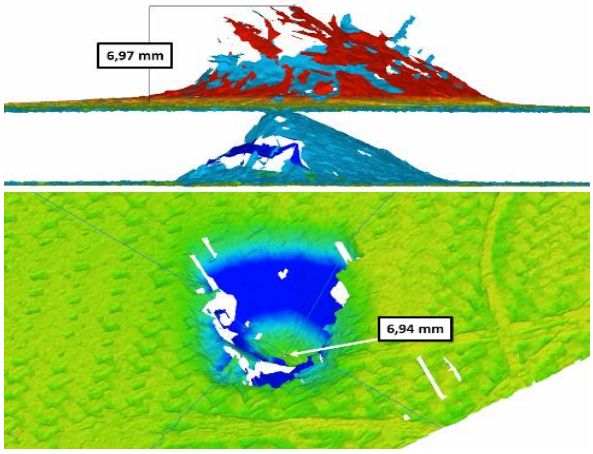
Sample 1 with 5% PUF-DCPD (thermal cycling)



Sample 1 with 5% MUF-ENB (thermal cycling)



Sample 5 with 5% PUF-DCPD (thermal cycling)



Sample 5 with 5% MUF-ENB (thermal cycling)

Figure 6.11. Dimensional analyses of the samples after retesting

CHAPTER 7
CONTRIBUTIONS REGARDING THE SELF-HEALING PROPERTIES EVALUATION OF POLYMER COMPOSITE MATERIALS WITH EMBEDDED MICROVASCULAR NETWORK SYSTEM

Given that there are currently not enough studies on polymer composite materials that deepen the phenomenon of self-healing through the integration of microvascular systems, in this chapter a series of analyses and investigations were carried out to evaluate the efficiency of the self-healing process that this innovative system can offer. Although, at first the microvascular systems integration in the composite material do not affect the mechanical properties, these systems can cause delaminations as a result of various mechanical stresses. At the same time, the small thickness of these microvascular systems allows them to be quickly impregnated by the excess resin released during the polymerization process.

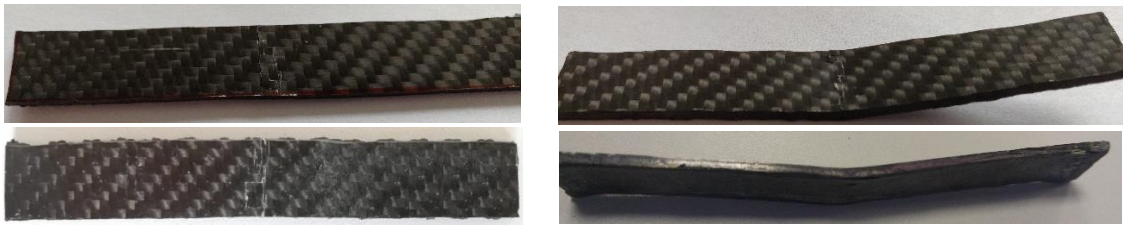
7.1. Three point bending sample fabrication

A pre-impregnated composite material (prepreg) M49/42%/200T2X2/CHS-3K was used to manufacture the samples. A total of 4 composite laminates were manufactured, each laminate

being assigned to a type of sample, respectively the reference samples, the samples with the microvascular system, the samples with CNT and the samples with the microvascular system and CNT. The laminates were cured at 140°C for 90 minutes.

7.2. Three point bending tests and evaluation of healing process

Samples were tested until the stress-strain curve no longer had a linear slope, more precisely until the first load drop. After the first test, all samples were conditioned at 40 ±1°C for 48 hours to activate the healing system.



(a) (b)

Figure 7.1. Representative images of samples after (a) first test and (b) second test

In the following, the specific curves of the mechanical bending tests for the tested samples are presented, together with the evaluation of the self-healing efficiencies.

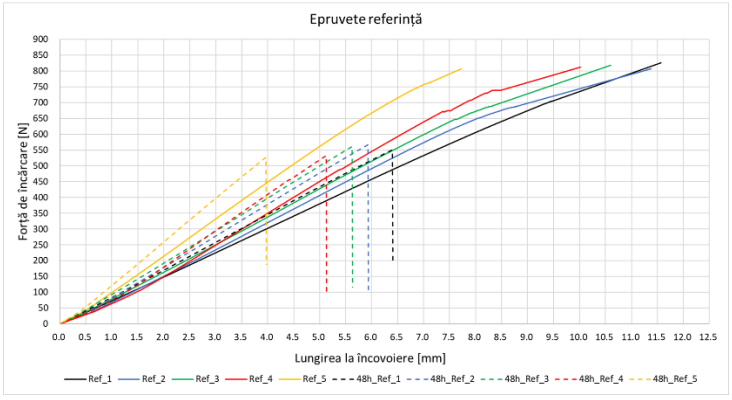


Figure 7.2. Stress-strain curves for reference samples after first and second test

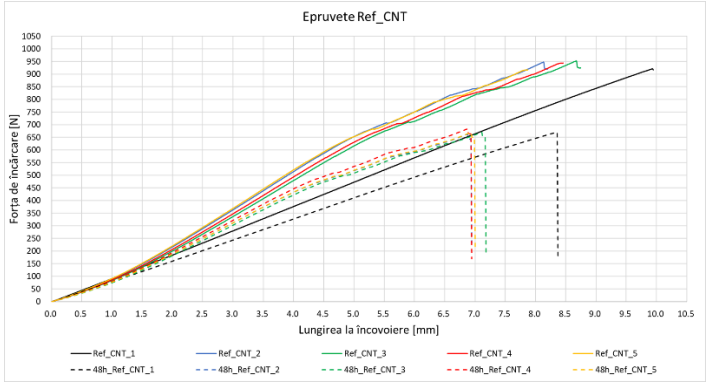


Figure 7.3. Stress-strain curves for samples with CNT after first and second test

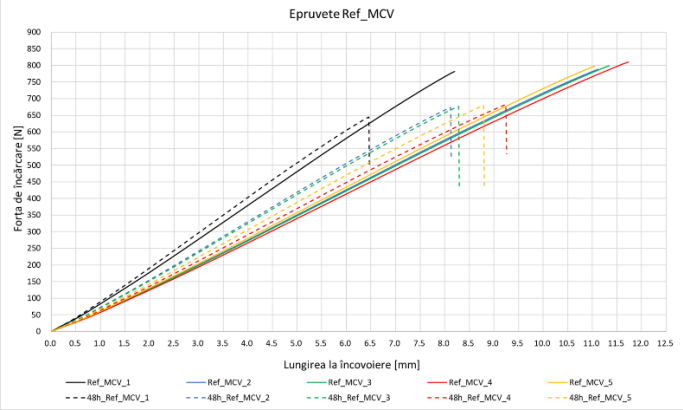


Figure 7.4. Stress-strain curves for samples with microvascular system after first and second test

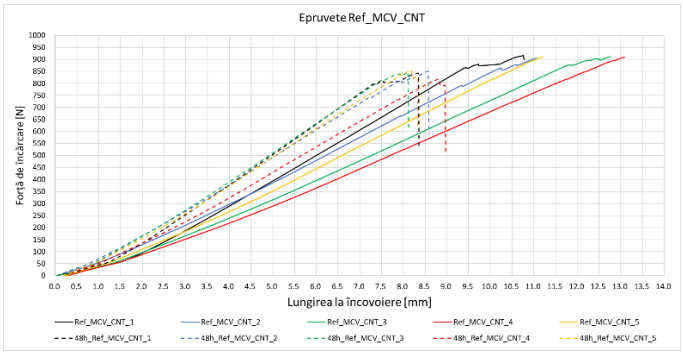


Figure 7.5. Stress-strain curves for samples with microvascular system and CNT after first and second test

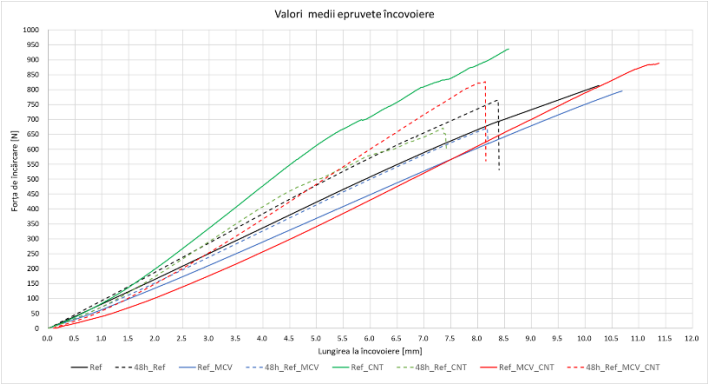
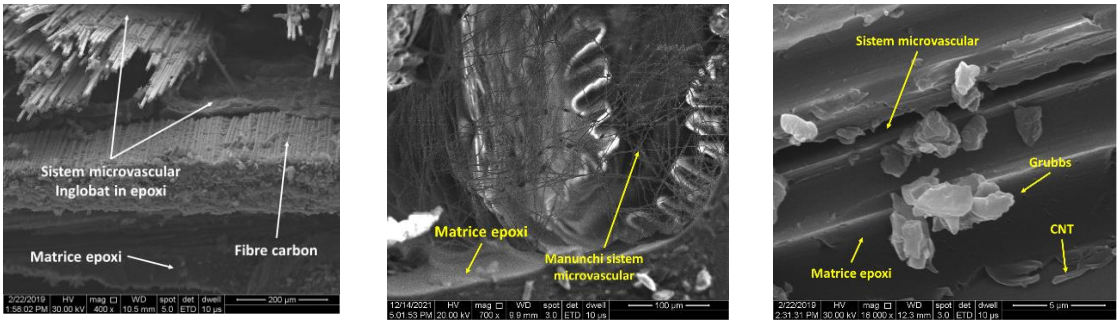


Figure 7.6. Average stress-strain results for the tested samples after first and second test

Regarding the reference samples, it is observed that the flexural load and stress are lower than those tested to failure, due to stopping the test when a 10% decrease in flexural load was observed. The CNT samples showed higher flexural strengths than the reference samples, as expected. Also, the CNT samples had a flexural load increase of 15% and a 14% increase in maximum stress. The results of flexural tests for the samples containing the microvascular system, respectively the microvascular system and CNT, show a slight decrease in mechanical properties (3%), however this can be neglected. As seen in Figure 7.2 and Figure 7.3 retesting the reference samples and those with CNTs showed much lower mechanical strengths. In the case of the reference samples, a flexural load of 547.29 N was found, representing 67% compared to the initial

values. A flexural load of 670.9 N was identified for the CNT samples, representing an 18% decrease from the reference ones and a 28% decrease from the originally tested CNT samples. The samples with the microvascular system without the addition of carbon nanotubes showed a flexural load of 83% compared to the reference samples and of 85% compared to the first test. Considering the percentage values obtained when retesting the reference samples and the samples with CNT, it can be said that these healing systems fulfil their functionality. The samples containing the microvascular self-healing system and CNT show higher mechanical test results compared to the samples only the microvascular system. This is precisely due to the use of nanotubes which, due to stronger reactions with the epoxy matrix and healing agents, provide a faster solidification of the system. Thus, the response of the flexural loads for the samples with microvascular system and CNT after retesting was only 8% lower than the first test (the best response compared to the rest of the samples), 3% above the value of the reference samples and 6% above the value of the samples with only microvascular system. Microstructural analysis probes were cut from the samples subjected to mechanical tests. The identification of microvascular systems was relatively difficult to achieve in scattered electrons field, therefore the visualization of the morphology/topology was set to secondary electrons field.



(a) (b) (c)

Figure 7.7. SEM images of samples containing both microvascular system and CNT

Microstructural analyses showed the presence of the self-healing system and carbon nanotubes, but due to the volume of the reinforcing material (carbon fibres) it was difficult to identify the matrix crack interfaces, as in the case of using only the polymer matrix. However, from the mechanical tests carried out it can be concluded that the repair and healing process has taken place. The use of a thin self-healing system such as the microvascular network can be extremely beneficial in the fabrication of thermoset polymer composite materials, as it does not influence the nominal properties of the material and can be applied between each layer of the laminate without causing delamination. The epoxy matrix of the composite material embraces the microvascular system during the curing process, which can even be attached to its reinforcing fibres.

CHAPTER 8
PERSONAL CONTRIBUTIONS AND FUTURE RESEARCH DIRECTIONS

8.1. General conclusions

The doctoral thesis entitled ***Fibre reinforced polymer composite materials with self-healing properties*** pursued the development of self-healing systems with potential applications in composite material structures used in the aerospace field, and not only. The development, analysis and evaluation of such self-healing systems can be considered an advantage in thermosetting polymer composite materials, due to the fact that this field is constantly developing, and large companies in the aerospace industry have begun to finance studies for the development of such materials on an industrial scale. Below are presented the general conclusions regarding the elaborated work:

- The development of the two self-healing systems based on microcapsules, taking into account the compatibility between the constituent materials of the healing systems and the polymer matrix;
- The thermo-mechanical analyses identified a decrease of the conservation modulus for the PUF-DCPD system suggesting a rigid behaviour, and for the MUF-ENB system an increase of the conservation modulus, representing an elastic behaviour;
- The cross-linking density of the samples with the two self-healing systems increases compared to that of the reference sample due to the participation of DCPD and ENB monomers in the UF coating in the formation of molecular chains;
- Considering the difference between the thermal stability of the healing agents and the catalyst, thermal stability tests were carried out, by exposure to temperatures up to 120°C, associated with the polymerization temperature of the epoxy matrix;
- It was found that the curing process can be carried out at a temperature of 80°C, for a longer period of time, with a relatively small loss of the microcapsule volume;
- The curing process of the epoxy matrix has been optimized according to the thermal stability of the self-healing systems;
- It was found that the process of integrating the self-healing systems into the epoxy matrix, respectively the composite material, through magnetic dispersion offers a better homogeneity;
- In the case of the MUF-ENB self-healing system, the ultrasonic integration process destroys a large percentage of microcapsules, due to their small size;
- Three-point bending test results confirm the low efficiency of the ultrasonic integration and homogenization method;
- By embedding the two microencapsulated self-healing systems in the reinforced composite material it was found that the flexural properties of the composite material decrease by approximately 12%, these systems acting as an induced defect;
- The PUF-DCPD system reduces the mechanical properties of the composite material more significantly compared to the MUF-ENB system, due to the 8-10 times larger dimensions

of the microcapsules in the PUF-DCPD system and implicitly the volume and space they occupy in the material;

- At the same time, increasing the volume of microcapsules has a tendency to reduce the mechanical properties of the composite material;
- Following the mechanical tests performed, it can be concluded that a volume of 7% of the two self-healing systems is ideal in terms of regaining the flexural mechanical properties of the epoxy matrix, by comparison with the other added volumes. Although the samples with 10% microcapsule volume showed better retest values, namely 97-98%, the increase in microcapsule volume leads to the reduction of the initial mechanical properties of the composite material;
- For the low-speed impact tests, it was found that the percentage of 12% is ideal for both self-healing systems, the results presenting the most appropriate values in relation to those obtained in the first test;
- In the case of the samples subjected to thermal cycles, the worst results were obtained for the samples with a large volume of microcapsules (15%);
- Increasing the microcapsules volume from 5% to 15% had a minor effect on the mechanical properties for the samples with the PUF-DCPD system compared to the reference ones, but a more thorough effect for the samples containing the MUF-ENB system;
- Following the microstructural analyses, the volume of 15% microcapsules presented an agglomeration for both systems, leading to reduced mechanical properties and the inability of the self-healing system to function;
- The mechanical loads to which the composite material and implicitly the self-healing system are subjected present an important factor that influences the effect of the self-healing systems. With the increase in the microcapsules volume, the efficiency of these systems is reduced, especially due to the change of damage modes starting from matrix cracking, to delamination and finally to fibre break;
- The agglomeration of microcapsules presents another phenomenon that determines the reduction of the mechanical properties of the composite material. A large volume of microcapsules may be deficient due to voids left as a result of damage to some of the microcapsules;
- Taking into account the agglomeration phenomena of microencapsulated self-healing systems, the effect that self-healing systems induce on the stress state of the polymer matrix was studied, which can lead to a failure of the material/structure in during operation;
- It was found that the inclusion of microcapsules causes the phenomenon of stress concentration in the polymer matrix (concentration factor 1.2), and its emptying causes the concentration factor to increase to a value of 1.94, an increase of almost 62%. Thus, the repair and healing effect will be less effective in the case of stresses that overcomes the crack intensity factor, because in this situation the crack usually propagates quickly leading to material failure;
- Although in reality it is almost impossible to control the positioning of the microcapsules, after performing the analyses on the stress state it was found that the presence of two

microcapsules in the immediate vicinity causes the concentration coefficient to increase by 29%. Therefore, increasing the stress value above the breaking limit can cause the appearance of a microcrack at the interface between the microcapsule and the matrix;

- The development of a microvascular system has been found to have greater benefits on the self-healing phenomenon. The introduction of the microvascular system into the epoxy matrix and the composite material did not influence their mechanical properties, in contrast to the microencapsulated self-healing systems. The microvascular system can be used in the development of self-healing composite materials that have higher curing temperatures of the epoxy matrix due to the PAN coating;
- The introduction of nanoreinforcing elements (CNTs) provided both an increase in the mechanical properties of the material and reactivity at the molecular level, speeding up the repair and healing process;
- The use of CNTs led to an increase in the elastic deformation of the epoxy matrix, which delays the failure of the material, giving more time for the self-healing systems to act;
- Microstructural analyses identified the healing interfaces of the cracks that occurred as a result of mechanical loads, both at epoxy matrix level and at reinforced composite material level. This confirms that the self-healing process and mechanism has worked;
- As a result of embedding the microvascular system in the epoxy matrix of the composite material, it attaches to the reinforced elements and can even increase the mechanical properties of the composite;
- The use of a thin self-healing system such as the microvascular one can be extremely beneficial in the fabrication of thermoset polymer composite materials because it can be applied between each layer of the laminate, without causing delamination or loss of mechanical properties.

Through the study, analyses and determinations made during the work, the process of manufacturing and evaluating the self-healing systems developed by implementing them in epoxy resin and composite material was validated. Thus, due to the research and results obtained, it can be stated that the thesis leads to the achievement of the main goal pursued, the development of fibre-reinforced polymer composite materials with self-healing properties.

The scientific impact consists in making contributions to possible solutions in a field of great interest, thus creating a solid basis for future activities or even research projects with even more ambitious objectives in a field in continuous expansion as well as growth the maturity of composite structures used in the aerospace industry or other terrestrial applications.

From an industrial point of view, the development of such systems is still questionable due to the economic and technical implications, but also the fact that these systems do not yet present a sufficiently high technological maturity to attract the necessary funds. However, the interest supported by large industries in the development of self-healing systems can be seen through the multitude of scientific studies in the field as well as through the financing of national and international studies and research programs.

From a social point of view, a possible technological transfer of the development process towards a possible industrialization of these systems can create new jobs, both through the

development of self-healing systems, their testing and validation, and through the research of new systems depending on the applicability, thus increasing the social impact.

From the environmental impact point of view, the use of these self-healing systems can only increase the life expectancy of the structures in which they are implemented, thus reaching the norms and directives on environmental protection and the reduction of polluting emissions.

8.2. Novelty degree

The novelty of the doctoral thesis generally consists in the development of self-healing systems applied to polymeric materials and thermoset composites used in the aerospace field and their validation through various experimental analyses and evaluations. In this sense, an extensive campaign of synthesis tests (by modifying and optimizing the development parameters), analyses and characterizations (microstructural and thermodynamic to validate the development process) and mechanical tests (three-point bending and impact) were carried out at matrix and composite material level. Thus, throughout the thesis, several new elements are found, such as:

- Development and optimization process of the self-healing systems in the form of microcapsules and in the form of a microvascular network by addressing different technological parameters (temperature, stirring speed, viscosity variation through dilution) in the manufacturing process;
- Determination of the optimal integration process in the matrix and the composite material, achieved by varying different technological parameters (temperature, stirring speed, viscosity variation through dilution) in order to define an optimum. At the same time, an analysis was carried out regarding the stability (chemical and thermal) of the self-healing systems, related to the curing temperatures of the epoxy matrix of the composite material;
- The use of CNT elements to increase the reactions and bonds between the healing agent and the polymer matrix. By introducing such elements in the composite material, the electrical conductivity generated by certain materials/components can be transformed into thermal conductivity which amplifies the repair process;
- Determination by numerical simulations of the behaviour of self-healing elements and how they affect the structural integrity of the material in which they are integrated.

8.3. Original contribution

The doctoral thesis contains an extensive study on the development and evaluation of some self-healing systems with applicability in polymeric materials and composites, marking own and original contributions, which bring new elements to the topic addressed. These elements are scored below:

- Development based on optimized parameters of self-healing systems in the form of microcapsules and microvascular type;
- The use of nanoreinforcing elements together with the self-healing system to increase the effectiveness of the repair process;

- Determining the optimal integration processes of self-healing systems and characterizing them in terms of chemical and thermal stability;
- Defining the input parameters and numerical analysis methodology and participating in the analysis interpretation, in order to identify the phenomena that they induce to the material in which the self-healing elements are inserted;
- Conceiving a plan and methodologies for evaluation and validation through mechanical tests the self-healing systems developed;
- Carrying out analyses on how the integration process of self-healing systems influences the mechanical properties of the material. It was also evaluated how the mechanical properties of the material are influenced by the volume of the healing elements inserted;
- The effect that self-healing systems have on composite materials by applying repeated thermal cycles. With the increase in the volume of healing elements, a substantial decrease in mechanical properties of the composite material was observed.

8.4. Perspectives for future development

The present doctoral thesis joins the studies in the field of research of polymer composite materials with self-healing properties through the development and evaluation of self-healing systems, but in order to increase the degree of technological maturity of these systems, the following directions for further development are identified:

- Identifying solutions to reduce the effect that the encapsulated self-healing system has on the mechanical properties of the material in which it is integrated;
- Analysis of other microvascular self-healing systems and the possibility to order the nanofibre network of the system;
- Testing the microvascular system within other functional tests in the aerospace field (vibrations, thermal cycles, etc.);
- Analyses regarding the transformation of electrical conductivity into thermal conductivity and verification of the healing process, thus simulating the repair and healing process during the operating regimes.

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I. Articles published in Web of Science journals in the field of doctoral thesis

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