NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY POLITEHNICA BUCHAREST

Doctoral School of Chemical Engineering and Biotechnologies

DOCTORAL THESIS

MATERIALS WITH RENEWABLE POLYMERS, COMPATIBLE WITH 3D PRINTING, FOR DURABLE APPLICATIONS

Summary

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1. Introduction

PhD thesis "Materials with renewable polymers compatible with 3D printing for durable applications"

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Below is a summary of the thesis in which the numbering of the figures, tables, equations and bibliographic indications used in it is preserved.

List of abbreviers: 2 pg. (pg.5 -6)
List of figures: 3 pg, 90 figures 90 of which 17 in the annexes (pg.7-9)
Lista de tables: 2 pg., 76 tables, of which 47 in the annexes (pg.10-11)

Chapter 1 Introduction (pg.12 – pg.14)

The doctoral thesis "Materials with polymers of renewable origin compatible with 3D printing for durable applications" studies the possibilities of physical modification of polylactic acid (PLA) by melting techniques in order to increase durability and transform, through 3D printing, into medium-life automotive components. in the perspective of 2050, including for the national industry as the manufacture of motor vehicles is continuously development. Along with other modernization features, the vehicles of the future will be lighter as larger quantities of polymer compounds will be used, among them an important role going to those with continuous polymers of renewable origin and/or recycled from post- and pre-consumer products (Annexes 1-3). PLA is a polymer of renewable origin as it is obtained by polymerizing a monomer obtained from polysaccharides (starch) by common synthesis methods in the case of conventional polymers. After the expiry of its lifespan, post-use waste made of PLA-based plastics is composted. The scientific interest of the topic results from the fact that we have tried to identify some possibilities of morpho-structural modification of this polymer by compounding in the melt and of tracking the behavior of the new compounds so that it is possible to select 3D printable variants in components for the automotive industry with medium life as those that do not present morpho-structural changes or alteration of mechanical behavior. The main challenges are related to the cancellation of the current drawbacks presented by PLA and the conferral of new structural characteristics that guarantee long-lasting functional properties. The practical realization of such compounds would mean moving from the use of PLA-based types only for short-lived applications, as at present, at least to those with a medium life.

Classification in the specific field of the doctorate. Main challenges

The theme is part of the specific field of the doctorate "Chemical Engineering" and is of scientific and applicative interest. The main challenges were related to: identifying the structural characteristics of PLA that make it possible to transform it into a finished product by 3D printing, choosing efficient methods of physical modification of PLA that can lead to thermodynamically stable compositional variants over time, studying the dependence between the lifespan of polymer compounds, their physical aging and long-term thermodynamic stability; experimental realization and tracking of behavior over time of the new compositions. Identifying the most effective methods of highlighting changes in chemical and morphological structure that have occurred over time. Primary selection criteria. Initial structural, morphological and functional characterization of the selected compounds. Detecting the variation over time of changes in chemical and morphological structure and when they are visible in the change in mechanical behavior. Identifying the moment when the first material breakages occur, eliminating the compositional variants that have deteriorated mechanically and considering the time elapsed from obtaining to breaking as a period of deepening the morpho-structural characterization in order to correlate with durability. Comparison of the chemical and morphological characteristics of compounds that have passed the durability test with the initial values. New material selections. Scale realization of selected compounds. Functional characterization and transformation into filaments for 3D printing. The behavior of these filaments in 3D printing. Future work related to the improvement of selected formulations, scaling and use of artificial intelligence in the realization of polymer compounds, AI-assisted modeling of compounding and physical aging outcomes in order to predict lifespan from physical aging tests.

Assumptions: The importance of long-term thermal stability in the design of compounds for medium-life applications and its control possibilities; Physical modification of PLA that can be 3D printed by compounding in the melt in order to control crystallization by hetero-nucleation and by racemic nucleation. Identification of the causes of morphological changes over time and elimination of working variants that lead to thermodynamically unstable compounds. Control of amorphous content to increase thermodynamic stability over time. The influence of crystal defects on long-term thermodynamic stability and finding methods to reduce crystal defects by conducting crystallization under controlled conditions. Method selection. Physical modification of PLA, which can be 3D printed by compounding in the melt with boosters (inorganic additives talc and CaCO3) and with a mixed-function agent, stress reduction at the inorganic filler matrix interface and flow agent in order to optimally disperse them in the PLA matrix. Thermodynamic miscibility studies through FTIR structural analysis and thermal behavior of new

compositional variants. Dependence of miscibility on the amount of additive with dual function of flow agent and control of interface phenomena. To study the synergistic effect of the combined use of a reinforcing agent (R) with a nucleating agent (AN) on the thermodynamic stability over time of modified PLA. Method selection. Physical modification by melt-compounding of 3D printable PLA with a shock modifier (MBS) for the purpose of transforming the break from brittle to ductile. Tracking behavior over time with identification of chemical and morphological changes. Comparative analysis of the initial structural and morphological characteristics with those after 2 years. Modification of 3D printable PLA with rupture character control agents (MBS) and lasting thermal stability (talc). Tracking thermodynamic stability over time. Characterization over time of the morphological structure and thermal behavior and comparison of the results with the initial ones. Variant selections of 3D printable PLA modification thermodynamically stable over time and scaling of the compounding and filament formation phases. Selection of compositional variants that lead to filaments that comply with dimensional standards (diameter and ovality). Evaluation of the 3D printability of new filaments. Functional characterization of compounds transposed to scale.

Research methodology

Considering the possible future industrial applications of the results of the thesis, the modification of PLA in order to increase the lasting thermodynamic stability was opted for compounding in the melt, as an easier technology to apply compared to those in solution. Methodology for characterizing the result from the specific behavior of polymers as a direct result of the relaxation of macromolecules over time. This behavior causes that, over time, the chemical and morphological structure of polymers and polymer compounds changes not as a result of the breaking of chemical bonds but of the relaxation of macromolecules that generate physical aging and variation of thermodynamic stability. In its early stages, these visible morpho-structural changes are not reflected by the mechanical, functional behavior. Therefore, the compounds that have been tracked over time to identify thermodynamic stability and highlight physical aging phenomena have been characterized from a structural point of view and thermal behavior that highlights these structural changes. The mechanical properties have been evaluated periodically over time, from a qualitative point of view, according to methods in principle similar to the quantitative ones, applied for automotive components made of polymeric materials at Renault Technologie Roumanie (RTR). The period of tracking thermodynamic stability was established according to the time after which the first material breaks occurred, in series of compounds with similar compositions. The selection of variants of scientific interest was made considering the compositions that have not broken at the time of expiry of the thermodynamic stability tracking period thus established. Only those compositional variants that in the analyzed period do not support changes in the chemical or morphological structure were transposed to scale. The scaled compounds were mechanically characterized, and the functional performance was established by comparison with the matrix polymer for the selected compound variants after scale experiments and transformation into filaments, 3D printability was verified. The thesis also presents the future works related to the correction of the current results in order to achieve all the functional properties of interest for the application. It also details the huge role of AI-assisted modeling, AI prediction of lifespan from current physical aging data, all in future TRL 5 – 6 papers, industrial experiments of corrected formulations with zero series industrial realization and eventual transition to manufacturing within TRL7 -9 papers.

Structure of the thesis. The content of the chapters contains 7 chapters, each with distinct reference to aspects related to the achievement of the general objective and those specific to the subject addressed. The pages in which the topic is theoretically documented represent 13% of the content of the thesis, and the original contributions 66% of it. The primary results subjected to a first selection process of the compositional variants studied from the point of view of sustainability are presented in annexes that have been included in the total pages related to the original contributions. In the annexes, important details related to the components of the components used in the studied compounding processes were also presented, details that conditioned the success of the studies and thus allowed clarifications related to the durability and thermodynamic stability of the new compounds.

The introduction presents the theme, importance, timeliness and justification of its approach. The way in which it fits into the specific field of the doctorate and what were the main challenges. The hypotheses and main research questions are then briefly described. The general object of the thesis, the specific ones and the experimental methodology used for each specific objective are then detailed. The structure of the thesis and the description of the content of the chapters are also briefly presented in the introductory chapter.

Chapter 2 presents the general and specific objectives of the thesis. Chapter 3 critically presents the literature data describing in 6 subchapters the up-to-date achievements related to the use of polymers in the automotive industry, 2050 trends related to the use of plastics in their composite, described quantitatively but also from the point of view of interest in new types, the national situation including from the point of view of future developments, technologies for transforming compounds designed and manufactured for this application into automotive parts with emphasis on future developments related to 3D printing. A dedicated sub-chapter details fundamental information related to the miscibility of polymer compounds, their stability over time, the possibilities of identifying changes in time and modeling these results. The following sub-chapter critically analyses the literature on the durability of plastics and lifetime estimation (Annex 4). Chapter 4 presents the original contributions made in the doctoral thesis. It is structured in 6 subchapters that describe the work done and the results obtained. The first sub-chapter presents both the processes used, the materials and the process of obtaining the mixtures, as well as the characterization methods used. The second subchapter presents the results obtained related to the first selection of compositions and the comparison between the initial values of the properties obtained with those after 2.2 years and 4 years, respectively. The next sub-chapter presents the scale-up and industrial production of the selected compounds and their viability in terms of thermodynamic stability for 3D printing. The causes of the thermodynamic instabilities that made the compositional variants not pass the suitability test for the field of interest or the durability test are identified and compositional variants of interest are selected for further work. The fourth sub-chapter highlights the multitude of thermodynamic instabilities that can occur when modifying PLA by compounding in the melt in order to achieve 3D printable compounds in medium-life components for the automotive industry. This diversity of factors that must be controlled in order to achieve the goal has prompted the idea of using artificial intelligence-assisted mathematical modeling of the thesis results in future TRL 5-6 papers in order to arrive at sustainable multi-component formulations with functional properties for 3D printed medium-life automotive components. Also in this sub-chapter, no.5 of chapter 4, the future works, TRL 7 -9, are described, which can lead to the transition to manufacturing of compositional variants based on PLA with functional properties of interest for the 3D printing of automotive components for the automotive industry. In the sixth and last sub-chapter, the results are summarized and the scientific conclusions of the paper are formulated. The last chapter describes the general conclusions on the doctoral internship, also presenting the author's contributions to the topic studied and the results obtained of the research. Chapter 5 focuses on the main general conclusions of the thesis and how to capitalize on its results regarding the published articles, their impact on the scientific world, and participation in international scientific events. Chapter 6 presents the 543 bibliographic references that were consulted for the conception and realization of the doctoral thesis. In the last chapter 7, there are the 18 annexes containing details about the polymeric compounds used in the automotive industry (annexes 1-4), the composition of the new experimentally made compounds (annex 5), the properties of the components used in experimental compounding with the explanation of the specific influence on the properties that describe their behavior over time (durability) (annexes 6-12), the methods of characterization of the new compounds, initially and after the durability test period (regulations, device name, manufacturer, working conditions) (Annex 13). Annex 14 presents both the attributions of each FTIR absorption of the new compounds analyzed, depending on its type, from a morphological point of view or of the miscibility of the components, the percentage variation, over time, after 2 or 4 years of each maximum and the comparison of the spectral characteristics of the new compounds with those of the components used to make them. Annex 15 presents the XRD diffractograms, initial and after 2 or 4 years, detailed analysis

by diffraction angles and intensities, crystallinity, for each mixture selected by the behavior in the time stability test that was performed. Annex 16 presents the SEM micrographs of the multi-component talc compounds, and Annex 17 presents the initial mechanical behavior and after 2-4 years of all the compositional variants studied from the point of view of long-term thermodynamic stability.

Chapter 2 Objectives of the thesis (pg.17-18)

The general objective of the thesis was the physical modification of PLA by melt compounding to increase durability so that it can be 3D printed in medium-life components intended for the automotive industry.

The specific objectives were: selection of the type of PLA that can be processed into a finished product by 3D printing (PLA_1); Identification of the thermodynamic stability of PLA processable in the finished product by 3D printing and PLA used for racemic nucleation; Hetero-nucleation of PLA and racemic crystallization of PLA, types obtained by compounding in melting; PLA_1 reinforcement with inorganic fillers (talcum, CaCO3). Modification of PLA_1 with reinforcing agent and nucleating agent (NA); Modification of PLA_1 with thermoplastic elastomer to obtain a compound with controlled fracture behavior (toughening); Tracking the qualitative mechanical behavior over time of the modified PLA; identification of the period after which the first mechanical damage of the new compounds occurs; periodic qualitative analysis of mechanical behavior; initial characterization and after the identified period and identification of changes in chemical and morphological structure produced over time; selection of compositional variants that have not physically aged after 2 and 4 years, respectively; scaling up variants that have passed the qualitative sustainability test; obtaining filaments from compounds made to scale. 3D printing; proposals for further research papers.

Chapter 3 Literature Data (pg.19-41)

Due to the advantages related to strength, durability, recyclability, etc., compounds based on fossil polymers, general purpose (PE, PP, PVC, PS), techno-polymers (PA, ABS, PC, PMMA, POM) or high performance (PPS, PEEK, PTFE) have been and are still intensively used in the manufacture of various components for industry. These components are found in all areas of vehicles, in the engine compartment, passenger compartment, exterior, and are mainly manufactured using classic melt processing technologies and only episodically, for prototyping by 3D printing. The rather numerous disadvantages of these manufactures related to environmental aggression, non-biodegradability, the large amount of waste that is difficult to recycle by mechanical methods have made this industry also turn to compounds with polymer content of renewable origin, currently those based on PLA, PE, PET, PA, PP are already used but which from the point of view of manufacture have not exceeded the TRL 4 level, that is, the level of demonstrations in the laboratory. The type of automotive applications specific to polymer compounds is conditioned by the automotive industry, traditionally known for the use of conventional materials such as steel and petroleum-derived plastic, is in a process of transformation. Advanced environmental awareness, along with strict emissions and waste management regulations, have led manufacturers to look for more sustainable manufacturing alternatives. This change represents a crucial step in reducing the carbon footprint of the automotive sector. By 2050, the automotive industry will complete a radical metamorphosis, transforming from a sector focused on the sale of metal products into an integrated provider of digital and green mobility services of functional performance. The challenges of the future automotive industry are related to the need to balance high-volume production with the costs of high-quality, recycled, and biodegradable materials. By 2050, automotive polymers will move towards: high-performance, sustainable, and smart materials to enable weight reduction, electrification, and circularity. Key trends include bio-composites, self-healing materials and recycled plastics. To reduce the carbon footprint, there is even a tendency to triple the amounts of plastic used in the automotive industry. The interest in PLA and PLA-based materials, from the perspective of 2040, including for the automotive sector, is growing. In Romania, there is no research based on estimating the lifespan of polymer compounds designed for the automotive industry based on the variation of thermodynamic balances over time and the physical aging controlled by them. The 3D printing of polymer compounds has to comply with rigors such as the following: ease of

feeding into the printer (obtaining filaments with a precise, constant diameter (1.75 mm / 2.85 mm) and perfectly round; Flow in the melt and especially through the nozzle to be light, to melt constantly but to solidify quickly and constantly for the formation of layers); the compound has thermal stability, which means that it melts and solidifies predictably, without degrading during the process); the melting must be uniform, monomodal, in a narrow temperature range, and the crystallization in a narrow and high range; low shrinkage to maintain part accuracy and prevent deformation as material cools) and under ambient conditions; the layers of compound successively deposited on top of each other to adhere well to each other and with the construction plate to preserve structural integrity); temporary structures are easily removed; uniform particle size for uniform spreading; low susceptibility to moisture; the appropriate quality of the final surface; durability and performance under operating conditions; minimal emissions of vapors / odors. Because *physical aging* alters the properties of the material (density, crystallinity, enthalpy, Tg, brittleness, stiffness, ductility, mechanical properties, brittleness), these polymeric materials often fail to meet the requirements for long-term applications. Moreover, physical aging can accelerate chemical degradation, leading to premature damage to plastic products before the end of their intended lifespan. Consequently, thermodynamic stability is governed by the energy state of macromolecular chains or crystals and their inherent tendency towards a minimum energy state. For the prediction of the lifespan based on physical aging data, the Struick model is used, which correlates the relaxation times with the stiffening of the material for periods specific to medium and long lifetimes. In this regard, many models are known (Master Curve, Bootstrapping statistically, temperature acceleration). *The durability* of polymeric materials is defined as the ability to withstand physical variations (weathering, extreme temperatures,) and/or chemical (chemical attacks) without morpho-structural changes (cracking, oxidation, wear, etc.) while maintaining functional performance, over the projected life (variable depending on the type of application, i.e. defines the quality of the material . It shall be assessed by appropriate methods. *The lifetime is the* time between the time the polymer material is placed on the market as a finished product and the time it is taken out of use. Beyond this range, the material is no longer able to fulfill its intended function. Polymer compounds used in the automotive industry must have the ability to maintain their structural, functional integrity and usability properties (mechanical, physical and chemical) for at least 1-2 years for short-lived components made of general-purpose polymer-based compounds, 2-15 years for medium-life compounds, and at least 15 years for long-lived compounds (Fig. 13) describes the main methods of increasing PLA properties.

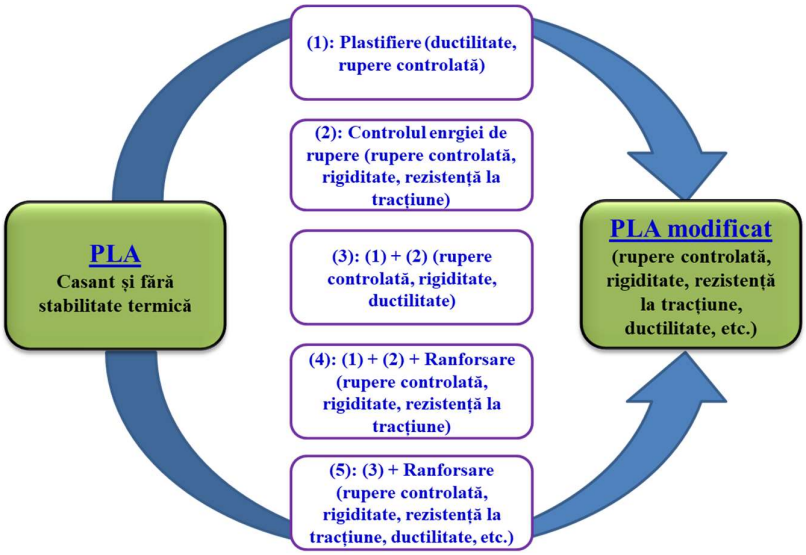


Fig. 13. Possibilities for upgrading the functional properties of PLA

Controlled nucleation - Controlled crystallization can follow a heterogeneous pathway, via an NA, or a "racemic" pathway, in which crystals are formed by stereo-complexing two enantiomers. Uninitiated crystallization typically produces 10^6 nuclei/cm³, resulting in spherulites of about 100 μm. In contrast, the initiated crystallization generates 10^{12} nuclei/cm³, resulting in spherulites of about 1 μm. Since

initiated nucleation forces the development of many more crystals in the same volume, their individual size is significantly smaller. Because these new spherulites are shorter than the wavelength of visible light, the light is no longer scattered and the polymer appears transparent. **Hetero-nucleation-** uses Nucleating Agents (**ANs)** which must be insoluble in the polymer matrix and remain solid at crystallization temperature. Using such agents in nucleated PLA to create 3D printable polymer biohybrids for automotive applications. **Racemic nucleation (Stereo-complexation):** coordinated by the selective interactions between two enantiomers, which have the same composition, but different three-dimensional configurations. The mechanism is governed by the hydrogen bonds established between the groups of macromolecules that generate high-velocity racemic nucleation and, therefore, the formation of a semicrystalline morphology with small crystallites, represented by homopolymer racemic mixtures, spread in an amorphous matrix. **Reinforcement** is the process of incorporating an inorganic or organic filler, which is called reinforcing and which constitutes the discontinuous phase in a polymer/polymer compound, called the matrix that makes up the continuous phase, the resulting compound being of the composite type. The purpose of reinforcement is to improve functional properties (e.g. thermal and/or mechanical, etc.) to increase durability. **Toughening** is the control of the ability of a polymer compound to absorb mechanical energy before breaking, it is defined as the area under the stress-deformation curve and axes and describes the resistance of the material to crack propagation due to the absorption of energy by plastic deformation. The consequences of toughening are the change in the behavior when breaking, which becomes ductile, and the behavior at the sudden action of some shock stresses. Toughening is a process in which the micro or nanoparticles of a resilient agent (toughener) are dispersed into a brittle polymer to promote energy absorption. **Mixed methods** Involve the combined use of the above agents together with the appropriate formulations related to small molecule additives. Currently the lifespan is estimated from chemical aging data

Chap.4. Original contributions (pg.42-115)

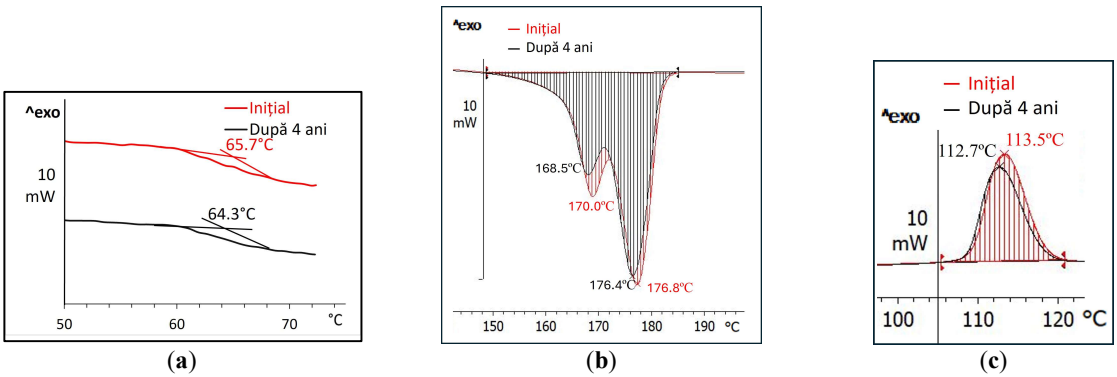
4.1 Experimental works (pg.42-46)

4.2 Results obtained (pg.47-89)

4.2.1 Physical aging of PLA (pg.47)

In addition to other properties that need to be corrected, PLA is affected by physical aging even at room temperature, which increases chemical degradation and makes it unsuitable for medium-life applications. Two types of PLA were used, namely PLA_1 and PLA_2

PLA_1 physically ages during the thermodynamic stability testing period (Fig. 21).



(**a**) (**b**) (**c**)

Fig. 21. Thermal behavior of PLA_1, initially and after 4 years (a) glass transition; b) melting; c) crystallization.

PLA_2 is much more thermodynamically unstable than PLA_1 (Fig. 22). This type of PLA initially has a Tg of 60.9 °C, cold crystallization with a maximum at 127 °C, and single-mode melting with a maximum at 153.2 °C. After 2.2 years, Tg increased to 66 °C (5.1 °C more), the maximum of cold crystallization moved to 113 °C (14 °C lower), and the enthalpy of crystallization increased by 29.9 J/g.

Melting becomes bimodal, between 148 °C and 188 °C, with two maximums at 156 °C and 169 °C and a melting enthalpy of 32.33 J/g. After 2.2 years, PLA has a polymorphic crystallinity, with large crystals coexisting with small ones, requiring an additional melting enthalpy of 1.98 J/g. These crystals occur practically over the entire temperature range from 200 °C to 66 °C. Therefore, several low crystallization maximums are recorded on the PLA cooling thermogram at 193 °C, 168 °C, 156 °C, 134 °C, 123 °C, 100 °C, 88 °C and 66 °C. If pure PLA had a crystallinity of 0.08%, after 2.2 years it increased to 2.7%, which represents an increase of 2.62%. The results demonstrate that even the PLA matrix changed over the course of the 2.2 years due to its tendency to reach thermodynamic equilibrium over time.

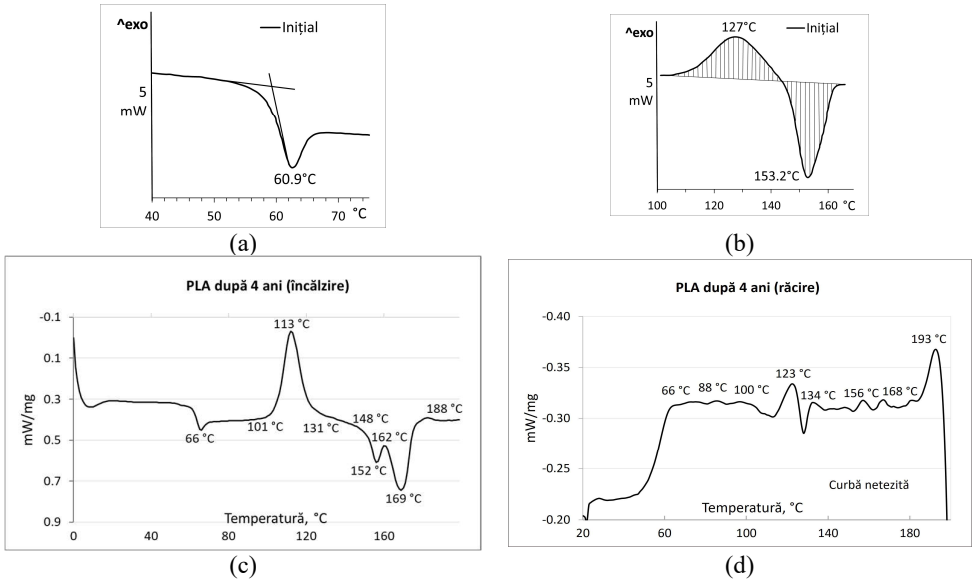


Fig. 22. Vitreous transition (**a**) and melting (**b**) of the initial PLA_2 and heating (**c**) and cooling (**d**) after 4 years of PLA_2

4.2.2 Nucleation (pg.48-62)

a) PLA_1 hetero-nucleation (pg.48-55) (*2 Q2 articles***)** Morphological analysis of the initial FTIR spectra and after 4 years showed that potassium 3,5bis(methoxycarbonyl)benzenesulfonate acts as a heterogeneous AN for PLA, inducing the growth of α and α' crystals that sometimes arrange radially inside the spherulites. The formation of α' crystals can be eliminated or reduced by ensuring that primary crystallization occurs at temperatures above 110 °C – 120 °C and/or by post-processing heat treatments. After four years, the intensity of the peaks increased by between 1% and 200%, suggesting a slight progression of nucleation. Future studies will aim to identify the specific causes of these spectral variations. The value of crystallinity after four years increased from 42.9% to 43.7% for unchanged PLA and from 65% to 67% for nucleated PLA. According to FTIR spectra, the resulting semi-crystalline morphology is relatively thermodynamically stable - Formation of mostly crystals α

Table 5. Spectral changes of the bi-component bio-hybrid obtained by hetero-nucleation, initially and after 4 years

Peak Change Type	**Comp.**	**Wavelength, cm^{-1} ; Height pic (H), a.u.**	**No. of peaks**
Disappearance	PLA1	2997 cm−1; 1453 cm−1; 1383 cm−1; 1358 cm−1; 1303 cm^{-1}; 1265 cm−1.	6
	AN	3071 cm−1; 2958 cm−1; 2905 cm−1; 2852 cm−1; 1722 cm−1; 1602 cm−1; 1442 cm−1; 1428 cm−1; 1323 cm−1; 1220 cm−1; 1117 cm−1; 1098 cm−1; 989 cm−1; 963 cm−1; 917 cm−1; 888 cm−1; 852 cm−1; 782 cm−1; 764 cm−1; 720 cm−1	20
Appearance		2884 cm−1; 802 cm−1; 645 cm−1	3
Shifted by more than 10 cm^{-1}	PLA1	-	0
	AN	1734 cm−114 cm−1, H <26%; 1197cm−1 16cm−1, H <59%; 933cm−1 22cm−1, H <93%	3

Identical or shifted less than 10 cm^{-1} and the variation in their height (H) compared to:	PLA1	2947 cm−1 2 cm−1, H < 48%; 2919 cm−1 6 cm−1, H < 48%; 2851 cm−1 7 cm−1, H < 64%; 1749 cm−1 1 cm−1, H < 58%; 1207 cm−1 2 cm−1, H < 48%; 1180 cm−1 1 cm−1, H < 52%; 1128 cm−1 4 cm−1, H < 55%; 1083 cm−1, H < 62%; 1042 cm−1 4 cm−1, H < 62%; 956 cm−1 1 cm−1, H < 75%; 920 cm−1, H < 50%; 870 cm−1 1 cm−1, H < 40%; 756 cm−1 1 cm−1, H < 33%; 694 cm−1 8 cm−1, H < 31%	14
	AN	1210 cm−1 1 cm−1, H < 71%; 1139 cm−1 7 cm−1, H < 55%; 1048 cm−1 2 cm−1, H < 58%; 875 cm−1 4 cm−1, H < 40%; 751 cm−1 4 cm−1, H < 75%; 676 cm−1 10 cm−1, H < 68%; 623 cm−1 4 cm−1, H < 95%	7

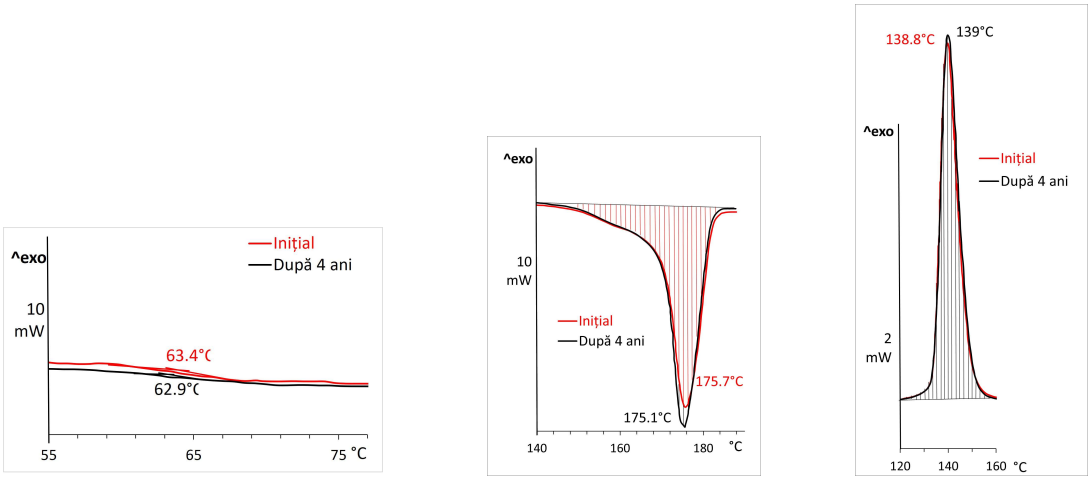


Fig. 24. Vitreous transition (a), melting (b) and crystallization (c) of the bi-component bio-hybrid obtained by hetero-nucleation, initially and after 4 years.

For heterogeneous nucleated polymer, the vitreous transition Tg occurs at 63.4 °C, which is lower than the 65.7 °C observed in unchanged PLA. The nucleated PLA exhibits a monomodal melting bit at 175.7 °C, with melting occurring over a range of 49 °C (137186 °C). This process requires an energy of 60.5 J/g, resulting in a crystallinity of 65%. These results indicate that nucleation significantly alters the thermal characteristics of unchanged PLA. PLA exhibits a bimodal melting between 149-185 °C, with two distinct peaks at 170 °C and 176.8 °C. Unchanged PLA requires only 39.9 J/g for melting, i.e. 20.6 J/g less than nucleated PLA, with a lower crystallinity of 42.9%. Heterogeneous nucleated PLA crystallization occurs between 157-115 °C, releasing 55 J/g. This represents a significant change in crystallization behavior compared to unchanged PLA, which crystallizes at a lower temperature (121-105 °C, peak at 113.5 °C) and releases only 36.2 J/g due to its lower total crystallinity. After 4 years, PLA shows a vitreous transition 1.4 °C lower than the initial state. However, its melting behavior remains bimodal and occurs in the same temperature range, with an almost identical enthalpy, while the crystallization characteristics remain unchanged. Heterogeneous nucleated PLA behaves similarly to the initial samples, showing only a minor 2% increase in crystallinity. This can be attributed to the unchanged behavior of the PLA, which itself showed a negligible increase of 0.8%. In addition, the Tg of the unchanged PLA decreases by 1.4% after 4 years. Considering the absence of significant displacements in the thermal behavior of both samples (heterogeneous nucleated PLA and unmodified PLA), it can be stated that the above results demonstrate that heterogeneous nucleated PLA remains thermodynamically stable over time. Nucleation initially increased crystallinity from 42.9% (unmodified PLA) to 65% (nucleated polymer), an increase of 22.1%. After four years, crystallinity in nucleated PLA increased slightly to 67%, this being driven not only by continuous crystallization, but also by the basic increase in crystallinity of PLA unchanged after 4 years, which rose from 42.9% to 43.7%.

The results regarding the analysis of the chemical structure by FTIR of thermal behavior by DSC and polarized light microscopy (POM) (Fig.26) of crystallized PLA by hetero-nucleation were presented in [8], [119], [356], [357].

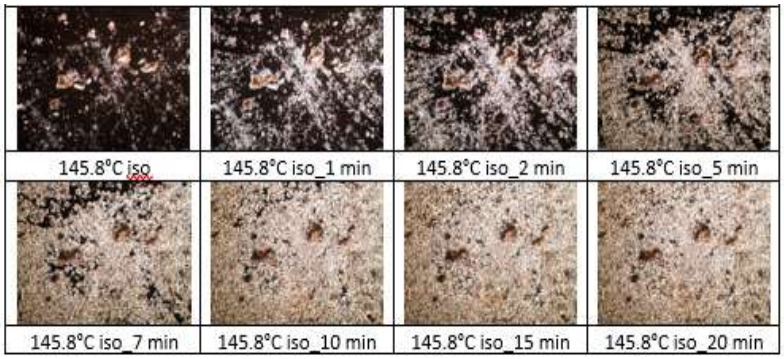


Fig. 26**.** Isothermal POM morphologies of the bi-component bio-hybrid obtained by hetero-nucleation

Compared to unmodified PLA, the new morphology of PLA significantly improves performance, increasing HDT (at 97 °C from 66 °C) and impact strength to 1.73 kJ/m² from 0.34 kJ/m² (Tab. 10).

Tab. 10**.** Functional properties of the bi-component bio-hybrid obtained by hetero-nucleation

Sample/Properties	**Functional property**	
	Resistance to Izod Impact, kJ/m²	**HDT, °C**
PLA	0,34	66
Heterogenic nucleated PLA	1,73	97

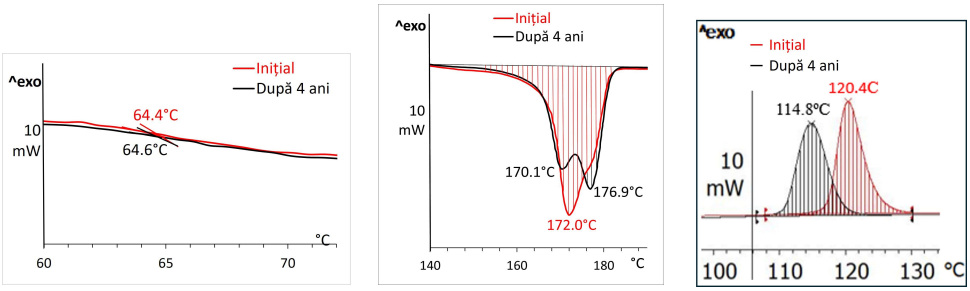
During the 4 years, this morphology does not change and, therefore, the thermal behavior differs insignificantly from the initial one. This means that crystal defects or those found in the amorphous phase did not induce sufficient energetic imbalances to generate structural changes during the transition to less energetically charged states, either through secondary recrystallization processes in the crystalline phase or by macromolecular relaxation in the amorphous phase. However, during the 4 years, there was a slight continuation of nucleation, as evidenced by the enthalpy variations of thermal transitions for heterogeneous nucleated PLA. Therefore, analysis and thermal behavior indicate the formation by hetero-nucleation of a relatively thermodynamically stable semi-crystalline morphology. The composition has proper mechanical behavior for 4 years.

Tab. 11. Spectral changes of the racemic nucleated bi-component biohybrid after 4 years compared to the initial

Peak Change Type	**PLA**	**Wavelength, cm^{-1} ; Height bit biohybrid (H), a.u.**	**No. of peaks**
Disappearance	SCXD	2997 cm^{-1}; 2947 cm^{-1}, 2919 cm^{-1}; 2851 cm^{-1}; 956 cm^{-1}; 920 cm^{-1}; 694 cm^{-1}	7
	SCXT	2995 cm^{-1}; 2945 cm^{-1}; 2928 cm^{-1}; 2900 cm^{-1}; 2880 cm^{-1}; 2851 cm^{-1}; 955 cm^{-1}; 700 cm^{-1}	8
Appearance		3508 cm^{-1}; 1293 cm^{-1}; 845 cm^{-1}; 801 cm^{-1}; 740 cm^{-1}	5
Shifted by more than 10 cm^{-1}	SCXD	-	0
	SCXT	-	0
Identical or shifted less than 10 cm^{-1} and the variation in their height (H) compared to:	SCXD	1749 cm^{-1} 2 cm^{-1}, H < 7%; 1453 cm^{-1} 1 cm^{-1}, H < 23%; 1383 cm^{-1}, H < 27%; 1358 cm^{-1}, H < 8%; 1303 cm^{-1}1 cm^{-1}, H < 56%; 1265 cm^{-1}, 1 cm^{-1}, H < 33%; 1207 cm^{-1} H < 4%; 1180 cm^{-1} 2 cm^{-1}, H < 57%; 1128 cm^{-1} 2 cm^{-1}, H < 13%; 1083 cm^{-1}, H < 15%; 1042 cm^{-1} 1 cm^{-1}, H < 22%; 870 cm^{-1} 1 cm^{-1}, H < 10%; 756 cm^{-1} 1 cm^{-1}, H < 8%.	13
	SCXT	1747 cm^{-1}, H < 28%; 1452 cm^{-1} 2 cm^{-1}, H < 29%; 1381 cm^{-1} 2 cm^{-1}, H < 38%; 1359 cm^{-1} 1 cm^{-1}, H < 8%; 1310 cm^{-1} 6 cm^{-1}, H < 50%; 1266 cm^{-1}; H < 67%; 1210 cm^{-1} 3 cm^{-1}, H < 11%; 1182 cm^{-1}, H < 65%; 1127 cm^{-1} 3 cm^{-1}, H < 18%; 1083 cm^{-1}, H < 35%; 1042 cm^{-1} 1 cm^{-1}, H < 28%; 867 cm^{-1} 4 cm^{-1}, H < 10%; 755 cm^{-1}, H ≈.	13

b. Racemic nucleated PLA (pg. 55-63)

PLA_1 was racemic nucleated with PLA_2. The FTIR results obtained and described in detail in the thesis (Table 11) reveal changes in all spectral ranges that indicate stereo-complexation, respectively in the areas that describe when the carbonyl and methyl groups, as well as the vibrations of the skeleton and the imprint region. These spectral changes persist over time, although the intensities of the peaks decrease by a percentage between 19% and 50%, indicating that the analyzed morphology is thermodynamically unstable. FTIR spectra demonstrated the resulting morphology: metastable semi-crystalline The efficiency of racemic nucleation depends on several factors: the molar ratio of PLLA to PDLA, the molecular weight of both types of PLA, the thickness of the analyzed sample, and post-processing treatments [259]. Racemic nucleated PLA exhibits monomodal melting and no cold crystallization, although it is formed by stereo-complexing a bimodal melting PLA with a monomodal melting and cold crystallizing PLA (Fig. 28). The Tg for racemic nucleated PLA is 64.4 °C, compared to 65.7 °C for PLA1 and 60.9 °C for PLA2. Although its melting profile is monomodal, it occurs in a wide temperature range of 54 °C (136 °C to 190 °C), with a bit at 172 °C and a melting enthalpy of 48.8 J/g. This intake is higher than that of stereo-complexed PLA (PLA_1 SCXD), which requires 39.9 J/g, or stereo-complexing PLA (PLA_2 SCXT), which requires 0.77 J/g. This is because, following stereo-complexation, crystallinity increased to 52.5%. Crystallization of racemic nucleated PLA occurs within a range of 17 °C, with a peak at 120.4 °C and a heat release of 43 J/g. The explanation lies in the higher crystallinity of racemic nucleated PLA, of 52.5%, compared to 42.9% for stereo-complexed PLA and 0.68% for stereo-complexing PLA. Racemic crystallization homogenized the thermal behavior of PLA_1 SCXD, a significant advantage for 3D printing. Moreover, this process converted the bimodal melting of the stereo-complexant into a bit monomodal. Unlike the stereo-complexant PLA_2, racemic crystallized PLA does not exhibit cold crystallization or multiple crystallization droplets between 193 °C and 66 °C. Although the wide melting and crystallization ranges of racemic nucleated PLA can be improved through stricter formulation control, it remains to be seen whether it will pass the durability test. After four years, mainly because the monomodal melt has turned into a bimodal one, accompanied by a 2.7% reduction and 2.5 J/g in the melting enthalpy. Because bimodal melting is incompatible with the requirements of 3D printing, these findings suggest that the racemic morphology exhibits internal stresses, likely caused by crystal defects, as confirmed by FTIR analysis. This evolution towards thermodynamic equilibrium triggered physical aging, eventually causing the transition from a monomodal to a bimodal melting profile.



a) b) c)

Fig.28. Thermal behavior of the bi-component bio-hybrid obtained by racemic nucleation: (a) Vitreous transition; (b) Smelting; (c) Crystallization.

As demonstrated by the values of the parameters describing the roughness of the measured surface (3D), racemic nucleated PLA has a smoother surface compared to stereo-complexed PLA and stereo-complexing PLA, because the roughness parameters have lower values (Fig. 31, Tab. 14) [260].

Tab. 15. Functional properties of the bi-component bio-hybrid obtained by racemic nucleation and its mechanical behavior after 4 years

Sample/Properties	Functional property	
	Resistance to Izod Impact	HDT
Racemic nucleated PLA	2,36 kJ/m2	95 °C
PLA_1	0,56 kJ/m2	78 °C
PLA_2	16 J/m	55 °C

The tests performed demonstrated that racemic nucleated PLA **is** thermodynamically unstable over time resulting from the FTIR analysis and thermal behavior. That is why it is unsuitable for processing by melting techniques and implicitly it is unsuitable for transformation into medium-life components for the automotive industry. It is possible that by reconsidering the factors that induce thermodynamic instabilities in racemic nucleation, the above results can be improved. *It is the first situation in which it is demonstrated that the mechanical properties change much later than the morpho-structural changes caused by physical aging due to macromolecular relaxation.*

The comparison between the durability of hetero-nucleated and racemic nucleated PLA and the analysis of the suitability of each of these methods for obtaining 3D printable variants in medium-life automotive parts was published in [400].

4.2.3 Reinforcement (pg.63-78)

a. Reinforcement with $CaCO_3$ and PCL

The comparative analysis of the FTIR spectra of the modified polymer and the modified polymer with inorganic filler and flow agent leads to the conclusion that the modification generated spectral changes described in Table A14.7. It is found that there are arguments that support thermodynamic miscibility but equally arguments that this miscibility is not impressive.

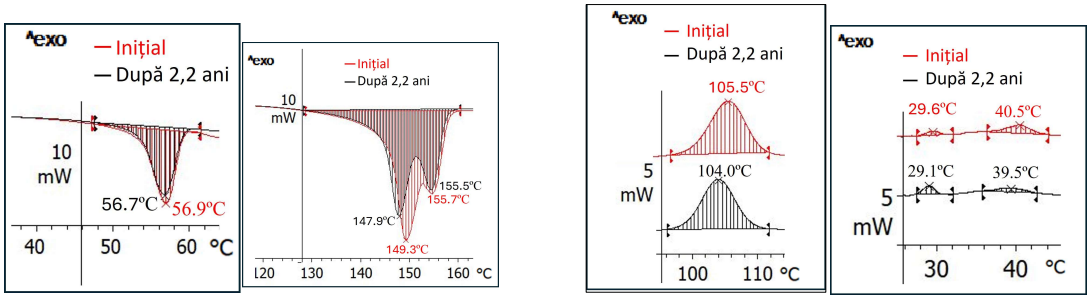
Table A14.7. FTIR absorptions of multi-component bio-hybrid with 19% $CaCO_3$ and 7% PCL

Peak Change Type	Comp.	Wavenumber, cm^{-1}	No. of peaks
Disappearance	PLA_2	2928 cm^{-1}; 2900 cm^{-1}; 2880 cm^{-1}; 2851 cm^{-1}; 1452 cm^{-1}; 1381 cm^{-1}; 1359 cm^{-1}; 1310 cm^{-1}; 955 cm^{-1}.	9
	$CaCO_3$	2513 cm^{-1}; 1796 cm^{-1}; 1387 cm^{-1}.	3
	PCL	2867 cm^{-1}; 1471 cm^{-1}; 1418 cm^{-1}; 1392 cm^{-1}; 1365 cm^{-1}; 1108 cm^{-1}; 961 cm^{-1}; 934 cm^{-1}; 783 cm^{-1}.	9
Appearance		3677 cm^{-1}; 1018 cm^{-1}; 822 cm^{-1}; 801 cm^{-1}; 689 cm^{-1}; 668 cm^{-1};	6
Displaced by more than 10 cm^{-1}	PLA_2	867 cm^{-1} 20 cm^{-1}, H < 40%; 700 cm^{-1} 12 cm^{-1}, H > 57%;	2
	$CaCO_3$	-	0
	PCL	1062 cm^{-1} 20 cm^{-1}, H > 417%.	1
Identical or displaced less than 10 cm^{-1}	PLA_2	2995 cm^{-1} 1 cm^{-1}, H < 23%; 2945 cm^{-1} 1 cm^{-1}, H > 10%; 1747 cm^{-1} 5 cm^{-1}, H < 31%; 1266 cm^{-1} 5 cm^{-1}, H < 8%; 1210 cm^{-1} 1 cm^{-1}, H < 22%; 1181 cm^{-1} 2 cm^{-1}, H < 6%; 1127 cm^{-1}, H < 6%; 1083 cm^{-1} 1 cm^{-1}, H < 9%; 1042 cm^{-1} 6 cm^{-1}, H > 13%; 755 cm^{-1} 1 cm^{-1}, H > 9%.	10
	$CaCO_3$	870 cm^{-1} 4 cm^{-1}, H < 78%; 848 cm^{-1} 1 cm^{-1}, H < 40%; 712 cm^{-1}, H < 73%;	3
	PCL	2943 cm^{-1} 3 cm^{-1}, H < 81%; 1721 cm^{-1} 4 cm^{-1}, H < 72%; 1294 cm^{-1} 1 cm^{-1}, H < 47%; 1240 cm^{-1} 3 cm^{-1}, H < 64%; 1171 cm^{-1} 8 cm^{-1}, H > 14%; 1047 cm^{-1} 1 cm^{-1}, H 137%; 840 cm^{-1} 7 cm^{-1}, H > 20%; 731 cm^{-1} 6 cm^{-1}, H < 66%; 709 cm^{-1} 3 cm^{-1}, H > 38%.	9

The passage of 2.2 years does not cause changes in the wavelengths at which the main absorptions occur, but only to a relatively small extent, their intensity. This behavior demonstrates a partial miscibility of the components of this compound, which is preserved over time. Pro-thermodynamic miscibility arguments: the appearance of new droplets, the existence of droplets composed of those of individual components, shifted more or less the one demonstrating more or less displaced changes, the non-appearance

on the spectrum of the compound of 2 drops from PLA, another 10 from PCL and 2 from $CaCO_3$. Arguments against thermodynamic miscibility: the occurrence in the spectrum of the compound of droplets identical in wavelengths, more or less intense. That is why it is considered that the studied mixture is partially thermodynamically compatible.

The comparative thermal analysis of the multi-component biohybrid with $CaCO_3$ versus the unmodified PLA (Fig.34) indicates changes that will be described below.



(a) (b)

Figure 34. Melting (a) and crystallization (b) of the multi-component bio-hybrid reinforced with 19% CaCO3 and 7% PCL

These changes are*:* the disappearance of the cold crystallization specific to the matrix polymer, melting in two temperature ranges, one specific to PCL with a maximum at 56.9°C and the other characteristic of PLA, but of the bimodal type with two maximums, one at 149.3°C and the second at 155.7°C; After 4 years, the melting takes place in two stages, one with a maximum somewhat similar to the initial value, 56.7°C compared to 56.9°C and the second bimodal with maximums at slightly lower temperatures, the first at 147.9°C (compared to 149.3°C initially) and the second at 155.5°C (compared to 155.7°C initially); crystallization in three temperature ranges, one above 100°C, with a maximum at 105.5°C, the second with a maximum at 40.5°C and the third at 29.6°C. After 2.2 the crystallinity decreases slightly from 5.7% to 5% after 2.2 years have passed. The change that occurs is the translation of the melting interval by 1,4 ºC-0,2 ºC lower temperatures but the increase in the total thermal requirement for melting from 3.6 J/g to 4.5 J/g and this is mainly due to the melting in the 127-162ºC range. The higher values of the heat required for melting, although the crystallinity is lower, can demonstrate that after the passage of the 2.2 years the crystals became more uniform and larger. Larger, more orderly crystals require more energy to break the strong intermolecular forces that hold the structure together. The change that occurs is the translation of the melting interval by 1,4 ºC-0,2 ºC lower temperatures but the increase in the total thermal requirement for melting from 3.6 J/g to 4.5 J/g and this is mainly due to the melting in the 127-162ºC range. The higher values of the heat required for melting, although the crystallinity is lower, can demonstrate that after the passage of the 2.2 years the crystals became more uniform and larger. Larger, more orderly crystals require more energy to break the strong intermolecular forces that hold the structure together.

XRD diffractograms (Fig. 35a) show demixing produced over time, illustrated by the small differences recorded between the HDT values and the Stress-Strain behavior over time.

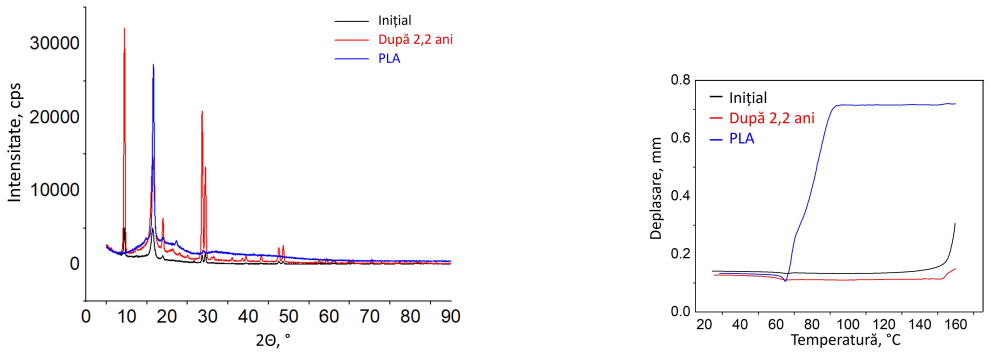


Figure 35. XRD (a) and HDT (b) diffractograms of PLA and reinforced multi-component bio-hybrid obtained by reinforcing PLA with 19% CaCO3 and 7% PCL

This compound has had a relatively convenient behavior over time. The composition was not very thermodynamically unstable, it had a good mechanical behavior during the 2 years. However, this wording is not suitable for 3D printing. Right after obtaining this compound melted in two temperature intervals, in the second process being even bimodal. Crystallization also took place in 3 temperature ranges, placed between 110°C and 20°C. This type of thermal behavior is not suitable for 3D printing, even if the mechanical properties were good and showed constancy over time. The mechanical properties do not reflect the reduced thermodynamic miscibility of the components. It is possible that in the case of this compound a level of technological compatibility has been achieved that has ensured the appropriate mechanical behavior for 4 years. The behavior of this compound, both initial and over time, demonstrates the appropriateness of primary material selections by morphology and primary chemical structure and their variation over time, not by mechanical properties. They may initially have the desired fracture profile and not vary over time, but the structural properties may indicate, even through initial values, the unsuitability for processing into the finished product by a certain technique or for a certain application.

b) Talc reinforcement

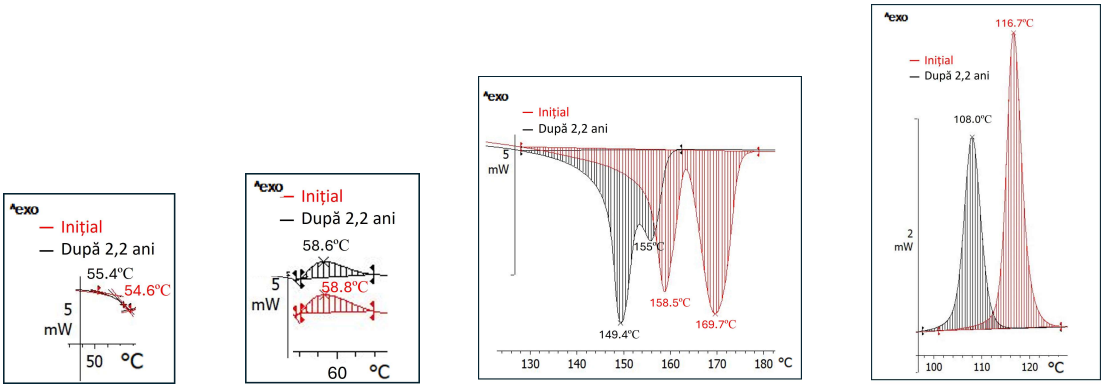
PLA was smelted compounded with PCL and talc in two variants, and with PCL, talc and an NA in the third variant. The biohybrids thus obtained were morpho-structurally characterized (FTIR, thermal analysis, XRD, SEM) and functional (HDT, density, hardness, mechanical properties qualitatively estimated), initially and after 2.2 years. The maintenance of properties over time was analyzed by examining physical aging, defined as the totality of transformations generated by the relaxation of macromolecules in the amorphous phase and/or by crystal defects (breakpoints of the ideal crystal structure). Physical aging alters morpho-structural and functional properties and occurs as a transition in time from a thermodynamically unstable energy state to a less energetic, thermodynamically stable state. Due to physical aging, the use of polymers as structural components in the automotive field, for example, or in electronics, is not possible.

In the case of semi-crystalline polymers, the intensity of FTIR peaks is directly related to the degree of crystallinity and the precision of the macromolecular arrangement inside the crystals. It is also known that strong interactions, which indicate a compatibility of the components, reduce the degree of order of crystallization, generating lower intensities of the drops. In the thesis, the two biohybrids are presented: one with a reduced amount of PCL, of 3.5%, and another with 16% PCL.

Compounds with 3.5 % PCL

The results described in the thesis demonstrate that the biohybrid with 3.5% PCL shows partial compatibility and a possible partial miscibility. During the 2.2 years, its macromolecules tend towards a state of thermodynamic equilibrium, i.e. the compound ages physically. And in this case, although the long-lasting mechanical behavior and HDT value were adequate, the compound is not suitable for 3D printing due to the almost bimodal melting of the initial compound, over a wide temperature range, from 130°C to 180°C (Fig. 40). The general conclusion related to this compound is that it is possible that the melt

compounding has achieved a technological compatibility that has ensured an appropriate mechanical behavior for 2 years.

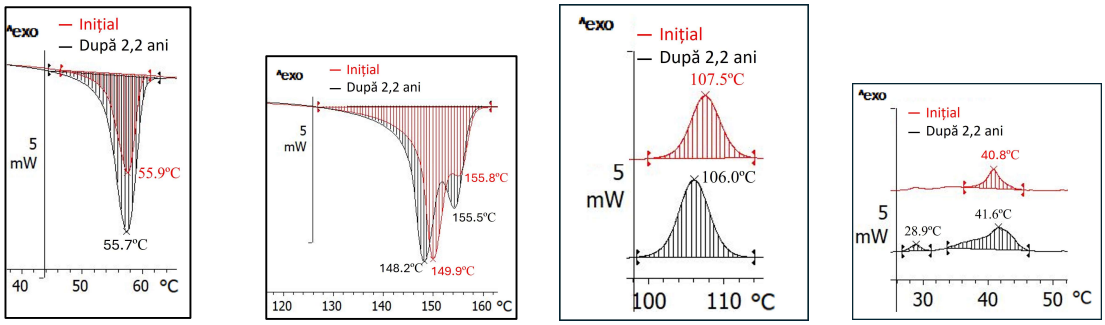


(a) (b) (c) (d)

Fig. 40. Vitreous transition (**a),** cold crystallization (**b**), melting (**c**) and cooling crystallization of the multi-component bio-hybrid with 3.5% PCL and 27.5% talcum.

Compound with 16 % PCL

In the thesis it is demonstrated that even in the compound with talc and 16 % PCL the components show a low thermodynamic miscibility. The melting is mono-mode with a shoulder that in time supports some splitting (Fig.44) Although the mechanical behavior over time is adequate, the compound showing a relatively adequate thermodynamic stability, however, it is not suitable for 3D printing due to the thermal behavior which, as a trend, has not changed during the period of stability of the mechanical behavior. It is possible that in the case of this compound, the technological compatibility of the components was achieved during the melt compounding, which ensured the appropriate mechanical behavior. And from these results it was concluded that estimating the lifespan from the mechanical behavior data is not the most inspired solution.



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

Fig. 44. Melting (a,b) and crystallization (c,d) of the multi-component biohybrid obtained by modifying PLA with 16% PCL and 20% talc.

Therefore, formulations with a low amount of PCL (0.6–0.8%), regardless of the amount of talc (13–42%), did not maintain their properties over time, while biohybrids with higher content (4–21%) did not lose their properties for at least 2.2 years.

Compound with 40% talc, 3.5% PCL, 3% nucleating agent (NA)

The analysis of the initial FTIR spectra and after 2 years (Table A14.15) demonstrated an important degree of miscibility as the ten drops of the biohybrid result mainly from the interactions between PLA (matrix) and the other three components, through combinations between two, one or two, three or all of the compound components. The only bit of the biohybrid that belongs to a component is the one at 3676 cm^{-1}, which probably comes from talc. The 1014 cm^{-1} peak is not found in any of the components. These results

seem to indicate improved compatibility and possibly miscibility between the components of this biohybrid. The same conclusion was drawn from the analysis of XRD diffractograms. Of the 35 different diffraction drops of the components, only 4 occur in the biohybrid, 3 at different angles from those of the components, and one of them identical to that of PLA at 2θ of 23°. This means that during the melt compounding process, the components lost their integrity and generated a new morphology with a crystallinity of 19%, containing polymorphic crystals.

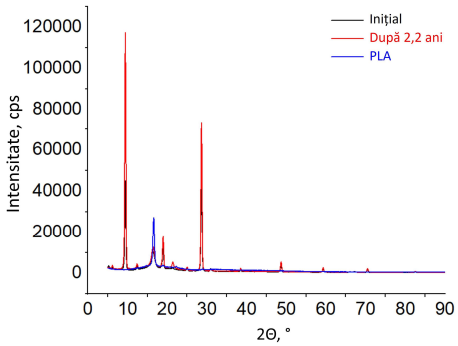


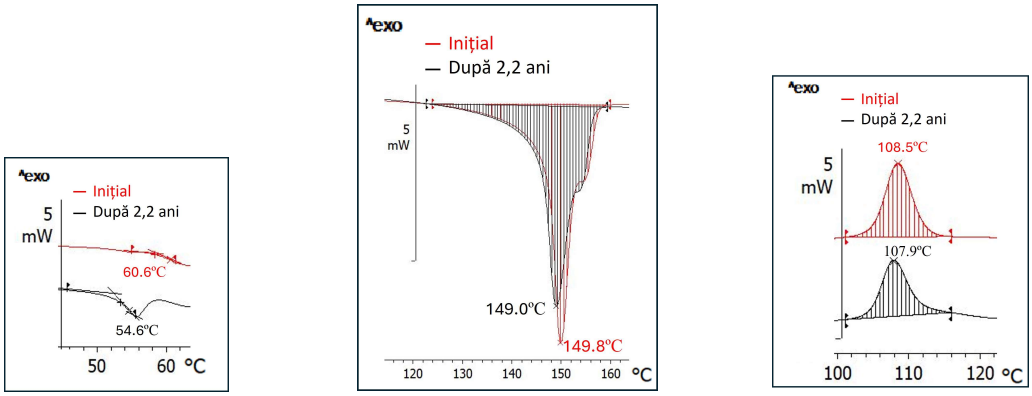
Fig. 39.c. XRD diffractogram of the multi-component bio-hybrid with 3.5% PCL, 40% talc and 3% AN

The thermal behavior (Fig.46) of this compound supports the conclusions of the chemical and morphological structure analysis. If the unmodified PLA has a Tg of 61,7 °C and a crystallinity of 0,8 %, the compound has a Tg of 54,6 °C and a crystal phase of 19,3 % that melts in a monomodal manner over a much narrower range from 130 °C to 159 °C, with a maximum at 149,8 °C and a small shoulder at 154 °C, requiring 17.9 J/g for melting. The small shoulder on the melting endotherm is easy to correct by adjusting the formulation Crystallization is also monomodal and occurs in a narrower range of 15 °C, between 116 °C and 101 °C, with a maximum at 108.5 °C and a release of 15.8 J/g. It is observed that the disappearance of the melting peaks of PCL and PLA is a proof of the advanced compatibility and even miscibility between the components of this biohybrid.

Table A14.15. FTIR absorptions of multi-component bio-hybrid with 3.5% PCL, 40% talc and 3% AN

Peak Change Type	**Comp.**	**Wavenumber, cm−1**	**No. of peaks**
Disappeared	PLA	2995 cm^{-1}; 2945 cm^{-1}; 2928 cm^{-1}; 2900 cm^{-1}; 2880 cm^{-1}; 2851 cm^{-1}; 1452 cm^{-1}; 1381 cm^{-1};1359 cm^{-1}; 1310 cm^{-1}; 1266 cm^{-1}; 1042 cm^{-1}; 955 cm^{-1}; 867 cm^{-1}; 755 cm^{-1}; 700 cm^{-1}	16
	PCL	2943 cm^{-1}; 2867cm^{-1}; 1471 cm^{-1}; 1418 cm^{-1}; 1392 cm^{-1}; 1365 cm^{-1}; 1294 cm^{-1}; 1240 cm^{-1}; 1062 cm^{-1}; 961 cm^{-1}; 934 cm^{-1}; 840 cm^{-1}; 783 cm^{-1}	13
	Talc	1671 cm^{-1}; 1448 $cm^{-1;}$ 940 cm^{-1}	3
	AN	3070 cm^{-1}; 2957 cm^{-1}; 1722; cm^{-1} 1601 cm^{-1}; 1441 cm^{-1}; 1428 cm^{-1}; 1322 cm^{-1}; 1219 cm^{-1}; 1196 cm^{-1}; 1098 cm^{-1}; 988 cm^{-1}; 963 cm^{-1}; 932 cm^{-1}; 917 cm^{-1}; 887 cm^{-1}; 875 cm^{-1}; 851 cm^{-1}; 782 cm^{-1}; 764 cm^{-1}; 623 cm^{-1}	20
Appeared		1014 cm^{-1}	
Displaced by more than 10 cm^{-1}	PLA	-	-
	PCL	1721 cm^{-1} 29 cm^{-1}, H < 60%; 1171 cm^{-1} 10 cm^{-1}, H < 40%; 1108 cm^{-1} 10 cm^{-1}, H > 13%; 1047 cm^{-1} 38 cm^{-1}, H > 53%; 731 cm^{-1} 25 cm^{-1}, H < 53%	5
	Talc	1067 cm^{-1} 18 cm^{-1}, H > 94%; 729 cm^{-1} 27 cm^{-1}, H < 10%; 664 cm^{-1} 21 cm^{-1}, H < 88%	3
	AN	1734 cm^{-1} 16 cm^{-1}, H identic; 1139 cm^{-1} 42cm^{-1}, H < 19%; 1117 cm^{-1} 11 cm^{-1}, H < 18%; 1048 cm^{-1} 37cm^{-1}, H < 12%;	4
Identical or displaced by less than 10 cm^{-1}	PLA	1747 cm^{-1} 3 cm^{-1}, H < 55%; 1210 cm^{-1} H < 44%; 1181 cm^{-1} H < 51%; 1127 cm^{-1} 1 cm^{-1}, H < 45%; 1083 cm^{-1} 2 cm^{-1}, H < 57%	5

	PCL	709 cm^{-1} 7 cm^{-1}, H <38%	1
	Talc	3674 cm^{-1} 2 cm^{-1}, H < 91%	1
	AN	1210 cm^{-1} H < 67%; 751 cm^{-1} 5 cm^{-1}, H < 72%; 720 cm^{-1} 4 cm^{-1}, H < 64%; 676 cm^{-1} 9 cm^{-1}, H < 29%	4



(a) (b) (c)

Fig. 46. Vitreous transition (**a**), melting (**b**), and crystallization (**c**), baseline and after 2.2 years values of the multi-component biohybrid obtained by modifying PLA with 3.5% PCL, 3% AN and 40% talc

HDT was 145 °C, compared to 65 °C for unmodified PLA (Fig. 41) density of 1,510 g/cm³ and hardness 95°Sh A and the compound has been mechanically resistant for 2.2 years (Tab. A17.3).

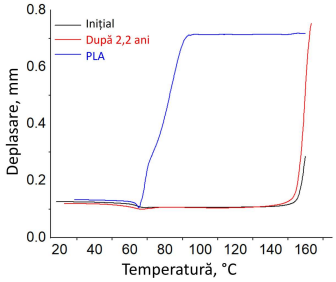


Fig. 41. HDT curve of multi-component bio-hybrid with 3.5% PCL, 40% talc and 3% AN

Table A17.3.Shipping: Mechanical behavior after 2.2 years of the biohybrid with 3.5 PCL, 40% talc and 3% AN

Estimated mechanical behavior after 2.2 years	
Test	**3,5 PCL 40% talcum 3% NA**
Flexural strength	YES
Shock resistance	YES

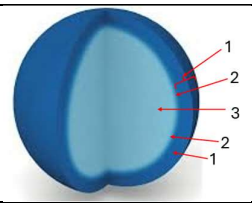
This composition has a high compatibility and even a certain degree of miscibility, which ensures thermodynamic stability over 2.2 years. Although the morphology of this biohybrid is still multiphasic, it is stable over time. It is possible that the crystallization, due to the nucleation of the PLA macromolecules, on the one hand, around the talc particles and, on the other hand, around the nucleating agent, diminished the surplus energy of the amorphous phase by forming new crystals and thus ensured a relatively constant behavior over time. This biohybrid is therefore compatible with medium-life 3D printed applications. There are many solutions to improve the long-term behavior of these biohybrids. Data on physical aging and thermodynamic stability help support the prediction of the lifespan of biohybrids based on molecular simulation models and advanced statistical methods, with the help of artificial intelligence. Through the reinforcement study carried out, it was identified the dependence between the physical aging of PLA-talc-PCL biohybrids, obtained by melt compounding of the degree of miscibility, and the identification of a formulation with a strain temperature under load (HDT) of practical interest, which would be thermodynamically stable for at least two years. . By melting PLA compounding with PCL and talc, partially miscible or very poorly miscible biohybrids with multiphasic, polymorphic morphology were obtained, which during the 2.2 years of testing proved to be extremely unstable thermodynamically. The physical aging of the biohybrid with 16% PCL was due to the relaxation of macromolecules in the amorphous areas (initial crystallinity 5% and 6.8% after 2.2 years), while for the biohybrid with 3.5% PCL, this was due to crystal defects (initial crystallinity 29.7% and 23.4% after 2.2 years). In both cases, physical

aging has a second cause, namely the thermodynamic instability of PLA. The thermodynamic instability of these two biohybrids makes them incompatible with 3D printed items intended for medium-life applications. The use of an NA in formulation with PLA, PCL and talc resulted in a single-bit biohybrid of monomodal melting in a narrow temperature range, which means good miscibility at the molecular level, thermodynamic stability over 2.2 years and even cancellation of PLA-induced instability. In this formulation, the positive compatibilization effect of PCL, which ensured good miscibility at the interface, was added to the nucleating role of talc, in conjunction with that of the sulfonate compound (AN), for additional crystallinity control. In this way, it was possible to remove the surplus energy contained in the amorphous phase and transform the defective crystals into homogeneous crystals of small size. The initial crystallinity of this biohybrid was 19% and remained 19% after 2.2 years. This morphology ensured a constant behavior of the biohybrid over time. The physical aging of biohybrids depended on formulation by the amount of PCL, the size distribution of talc particles, the presence or absence of the nuclear agent in the formulations, as well as the willingness of PLA macromolecules to relax over time. It is possible that, in addition to the nucleating effect of small talc particles, the larger particles exerted a reinforcing influence, which has not yet been investigated. Being reliable, even though they are complex and time-consuming to estimate, thermodynamic stability data help predict the lifetime of compounds using molecular simulation models and advanced statistical methods. Artificial intelligence helps to model, predict and understand the complex mechanisms involved in polymer-specific physical aging that exist in a thermodynamic equilibrium of minimum energy load. *The results of this chapter were published in* [182].

4.2.4 Toughening (pg. 79-84)

PLA was modified with the MBS elastomer with shell-core morphology and layers with a chemical structure designed in such a way as to ensure the resistance of these particles to dispersion in the molten matrix, compatible with it and to elastically take over the deforming force that can act on the resulting compound (Tab. 24)

Tab. 24. The shape of the MBS particles, the FTIR absorptions of each layer, and their dimensions [452], [453]

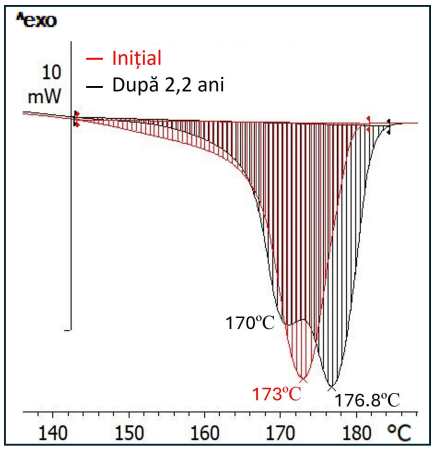
Shell : Methyl methacrylate or methyl methacrylate grafted copolymerized with a controlled fraction of styrene. Ensures particle strength, physical adhesion with matrix polymer, good dispersibility in it (*Layer 1)*	**Elastomeric interlayer made of PB or SBR (soft shell);** first shock absorption, prevents brittle breakage and determines superior flow resistance *(Layer 2)*	**Core (inner hard core): cross-linked PMMA or copolymer rich in styrene nuclei*** Styrene-methyl methacrylate copolymer. Sometimes methacrylate ethyl-allyl acrylate copolymer. Middle layer for adhesion and stress transfer between core and shell *(Layer 3)*
a) Particle shape		
		
b) Chemical structure (FTIR absorptions specific to each layer)		
2950 cm^{-1} – 2990 cm^{-1} Stretching vibration -CH_3	2800 cm^{-1} -2950 cm^{-1} Vibration C-H aliphatic	3025 cm^{-1}- 3060 cm^{-1} Stretch C-H aromatic
1725 cm^{-1} – 1730 cm^{-1} Stretching vibration C=O	1640 cm^{-1} Stretch C=C	1601 cm^{-1}, 1493 cm^{-1}, 1452 cm^{-1} Aromatic ring backbone (C=C)
1140 cm^{-1}-1250 cm^{-1} Stretching vibration C-O-C	966 cm^{-1} Def. Trans 1, 4 butadiene	699 cm^{-1} and 758 cm^{-1} Def. Outside the plane of the benzene ring
-	911 cm^{-1} Def. Vinil (1,2 - addition)	-
c) Layer Sizes		
10-50 nm	150-350 nm	-
10 -50%	50 – 90%	10 -20%

The data in Tab. A14.17 containing processed data of the interpretation of the initial FTIR spectra and after 2 years of this compound demonstrate that MBS is compatible with the PLA matrix and that the elastomer particles are relatively uniformly distributed in it.

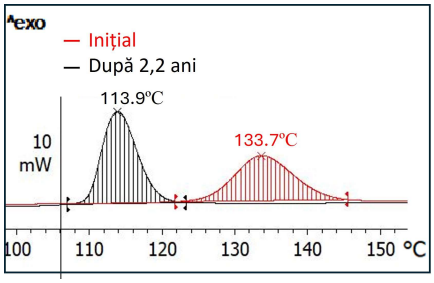
Tab. A14.17. Spectral changes of the two-component bio-hybrid by 23% MBS after 2.2 years

No.	Absorb., cm^{-1}	Assign	Intensity, a.u.		↑↓,% after 2.2 years	Displacement after 2.2 years, ←, →
			Initially	After 2.2 years		
1	3679	MBS Dispersion in PLA	0,006	Disappears	-	-
2	2997	Matrix crystallinity growth	0,026	0,015	↓42,30	←1 cm−1
3	2961	Interactions at the MBS-PLA interface	0,034	Disappears	-	-
4	2946	Change in the chemical environment of PLA chains due to MBS	0,033	Disappears	-	-
5	2922	It characterizes polybutadiene. Indicates the success of the compounding	0,030	0,040	↑33,33	←1 cm−1
6	2850	Interactions at the PLA-MBS interface	0,016	0,025	↑56,25	←3 cm−1
7	1752	MBS interface area with amorphous areas in PLA	0,480	0,120	↓75	←3 cm−1
8	1452	Relatively orderly arrangement of MBS in the matrix and slight increase in crystallinity.	0,130	0,080	↓38,46	-
9	1381	Increasing the order of macromolecular chains determined by MBS	0,105	0,060	↓42,86	-
10	1358	Ordering PLA chains around MBS particles	0,120	0,080	↓33,33	-
11	1261	Ordering PLA chains around MBS particles	0,120	Disappears	-	-
12	1211	Demonstrates miscibility between PLA chains and the outer layer of MBS particles	0,250	0,070	↓72	←1 cm−1
13	1180	Physical interactions between PLA and MBS. Crystallinity.	0,440	0,180	↓59,09	-
14	1127	Interactions between the array and modifier	0,350	0,140	↓60	-
t	1083	Interactions between the array and modifier	0,740	0,240	↓67,57	1 cm−1→
16	1042	PLA to MBS compatibility	0,490	0,150	↓69,39	1 cm−1→
17	967	MBS dispersion in matrix	0,100	Disappears	-	-
18	912	The matrix ordered by MDS favors the crystallization α	0,065	0,040	↓93,85	←10 cm−1
19	870	Crystals α formed under the action of MBS	0,125	0,070	↓44	-
20	845	Crystalline ordering under	0,065	Disappears	-	-
21	802	Formation of α crystals due to the presence of MBS	0,140	Disappears	-	-
22	756	MBS-induced PLA macromolecule ordering	0,150	0,080	↓46,67	1 cm−1→
23	699	The presence of styrene. Indicates the dispersion of MBS in the matrix	0,165	0,075	↓54,55	-
24	670		0,110	Disappears	-	-

The initial thermal behavior and the 2-year thermal behavior is shown in fig.49. The modification with MBS led to the increase of the crystallization maximum from 113.5°C for PLA to 133.7°C, which is due to the formation of larger crystals, not a high crystallinity, as indicated by the crystallization enthalpy values, lower than for unchanged PLA. After 2.2 years the maximum crystallization decreases by 22.2°C, it was recorded at 113.9 °C almost like in the matrix polymer. This behavior may suggest the formation over time of a crystalline structure close to PLA due to the transition of meta-stable crystals into stable variants, but without generating important variations in total crystallinity. These conclusions are supported by MBS-modified PLA diffractograms, initially recorded and after 2.2 years. After 2.2 years the main diffraction occurred at 2θ of 22° as in the case of the matrix polymer (Fig.50). The density of this compound is 1.21 g/cm3 initially and 1.22 g/cm3 after 2.2 years, it is mechanically resistant after 4 years (Table A.17.4).



(a)



(b)

Fig. 49. Melting (a) and Crystallization (b) of the two-component biohybrid obtained by modifying PLA by 23% MBS, initially and after 2.2 years

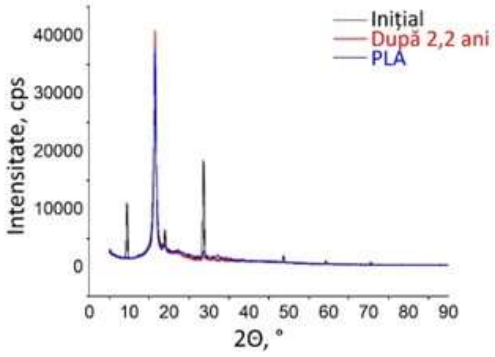


Fig. 50. XRD diffractogram of MBS-modified PLA initially and after 2.2 years

Table A17.4. Mechanical behavior after 4 years of the two-component bio-hybrid with 23% MBS

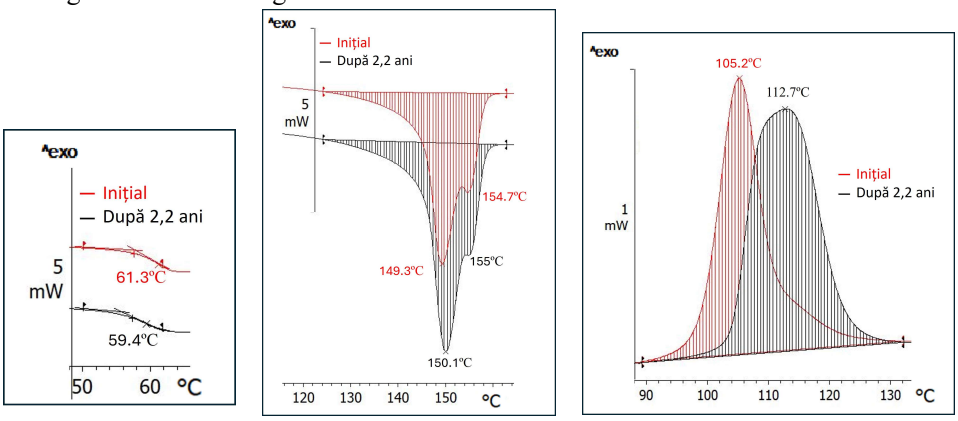
Estimated mechanical behavior after 4 years	
Test	**4 years**
Flexural strength	YES
Shock resistance	YES

The results obtained demonstrate that MBS is a good modifier for the control of breakdown energy. This modifier has sufficient miscibility with PLA to ensure a single-mode melt, both initially and after 2.2 years, of interest for 3D printing medium-life landmarks. However, the formulation requires improvements to narrow the melting interval and to decrease the percentage of meta-stable crystals that over time pass into stable crystals.

4.2.5 Multi-component formulation for tear control and thermal stability

The FTIR spectra and their interpretation in terms of miscibility, matrix dispersibility and the time behaviour of this mixture indicate good thermodynamic miscibility of the components and good thermodynamic stability over time (Tab. A14.19). The formulation used totally changes the thermal behavior of PLA (Fig.53). If it, initially, in addition to the monomodal melting, with a maximum at 153.2°, also has a cold crystallization due to the multi-component modification, it is also monomodal, with a main maximum at 149.3°C and a small shoulder at 154.7°C, but it loses cold crystallization. The cold crystallization of PLA indicates the transition of the polymer from a disordered amorphous state to an orderly crystalline state by reheating to a temperature higher than the glass transition temperature but lower than the melting temperature. After 4 years the matrix polymer retains cold crystallization, but with a maximum at 113°C and melts bimodally with a maximum at 156°C and another at 169°C. After 2.2 years, the multi-functional mixture retains the single-mode melt which has its maximum at 150.1°C but the initial shoulder has become smaller and occurs at 155°C. This means that, unlike the matrix polymer, this multi-functional mixture is thermodynamically stable over time. If the matrix polymer has a low crystalline phase content of 0.8% due to the physical change, this content increases to 27%, initially and to 31.1% after 2.2

years, which means that during the 2.2 years the crystallization process continued, as demonstrated by the crystallization enthalpy values. The further crystallization may also be due to the matrix polymer, since over time its crystallinity has increased. Unlike the latter, which crystallizes continuously between 168°C and 66°C with numerous low maximums, the multi-component compound shows a single crystallization maximum at 112°C, in a fairly wide range, which means crystals of quite different sizes. Over time, the XRD morphology changes slightly, with the preservation of the characteristics of the initial compound, but with the decrease in intensity of diffractions and the appearance of new diffractions that indicate the ordering of the amorphous phase (Fig. A15.1). The compound had an initial HDT of 140°C and after 2.2 years of 135°C. In future work the formulation of this compound will be improved to narrow the temperature range in which melting occurs and removal of the melt shoulder from 154.7°C.



(a) (b) (c)

Fig. 53. Vitreous Transition (a), Melting (b) and Crystallization (c) of the multi-component bio-hybrid obtained by modifying PLA with 12% talc, 4% AN and 4% MBS, initially and after 2.2 years

The initial compound had an initial HDT of 135^0C which was approximately constant over time (Fig.54) and good mechanical behavior (Tab.A17.5).

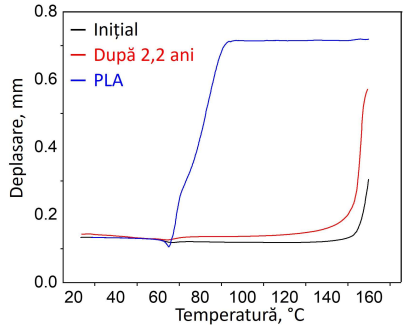


Fig. 54. HDT curve for modified PLA with 12% talc, 4% NA and 4% MBS

Tab. A17.5. Mechanical behavior after 2.2 years of the multi-component bio-hybrid with 12% talc, 4% NA and 4% MBS

Estimated mechanical behavior after 4 years	
Test	**4 years**
Flexural strength	YES
Shock resistance	YES

Therefore, this compound demonstrated a good miscibility of the components, was relatively thermodynamically stable over time and had a thermal behavior of interest for 3D printing. That is why it was selected for scale experimentation.

4.3 Realization at the scale of the selected compounds. Obtaining filaments. 3D printing. Characterize filaments (pg. 89-95)

The results of scaling-up the compounding (Fig. 55), transforming them into filaments (Fig. 56) and testing the 3D printability of industrially made filaments were very good. The filaments had Fig. 60) functional performance (comparable to similar compounds, currently marketed.

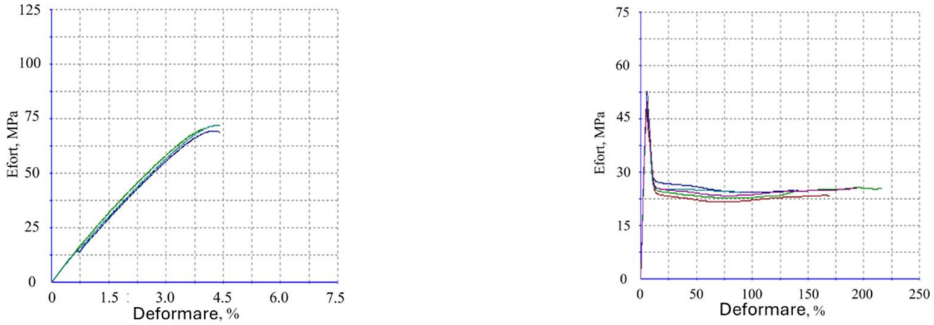


a) b) c)

Fig.55 PLA primary granules (a) and modified according to the selected formulations (with thermal resistance (b) and with shock resistance (c) made by scale-up



Figure 56. Filaments obtained from industrially made granules



a) PLA_1(witness) b) PLA_1 modified (controlled Tear)

Figure 60. Comparison of the shape of strain stress curves for unmodified PLA (a) and modified with industrially made MBS

4.4 Control of thermodynamic instabilities induced by PLA modification (pg.95-108)

The work carried out demonstrated that the long-lasting applications of polymer compounds depend on the specific thermodynamic stability. The chapter details the possibilities of reducing them with reference to each technique for controlling the functional properties of PLA.

4.5 Modeling of experimental results. Lifespan. Artificial intelligence. Future works (pg.109-111)

The role of artificial intelligence in the processes of physical modification of polymers is related to the prediction of properties of functional interest, the optimization of formulations, the modeling of crystallization processes and physical aging processes (over time), the prediction of behavior in 3D printing. In other words, AI is that it designs from a brittle PLA a type of 3D printable PLA, in medium-life components intended for the automotive industry. The use of AI is a multi-layered technology that uses artificial neural systems with multiple perception (the most appropriate Multilayer Perception) and that combines machine learning, with experimental results and human skill using multiple "decision trees", AI will know how to model very well the nonlinear interactions between components that require a very high computing power[530]. Artificial neural networks (ANNs) are used for advanced optimizations. These can be combined with genetic algorithms (GAs). RNA learns the composition properties and AG creates millions of possible combinations between the component. In this way, the optimal formulation with functional properties, apparently impossible to obtain through concrete experiment, can be identified. As a reliable, yet complex and time-consuming estimate, thermodynamic stability data helps predict the lifetime of compounds based on molecular simulation models and advanced statistical methods. AI helps to model,

predict and understand the complex mechanisms involved in physical aging due to the tendency of polymers to reach the thermodynamic equilibrium of minimum energy charge. For the analysis of the intrinsic mechanisms involved, at the molecular level in the physical aging of polymers, molecular simulation methods simulated with the help of AI are used. Otherwise, traditional methods are completely insufficient. With the help of predictive AI models, it is possible to identify the complex links between possible processes to develop during ageing, structural changes and the evolution of properties. Also with the help of AI, complex experimental results can be processed and, in this way to identify the mechanisms of recovery of thermodynamic equilibrium, etc., and thus understand the influence of thermodynamic factors on physical aging. In short, physical aging is the material's attempt to achieve thermodynamic stability, and artificial intelligence is a tool to model and predict this complex phenomenon.

They will focus on improving the durability of multi-component bio-hybrids, estimating the lifespan from accumulated physical aging data, followed by going through the experimental phases specific to the manufacture of durable, 3D printable compounds in order to obtain components for the automotive industry. Increasing the durability of multi-component bio-hybrids can be done through empirical experimentation or AI-assisted modeling of the results obtained in the physical aging study conducted. Overall, the workflow that still needs to be completed until the industrial manufacture of a PLA with increased durability for 3D printing automotive components with a medium lifespan.

5. Conclusions (pg.111 – pg.114)

i. *The topicality, scientific relevance of the thesis and the impact of its results;* The subject of the thesis is part of a very current theme and of both scientific and practical perspective, as it is related to the increase of the durability of polylactic acid (PLA) for the purpose of using parts used in the automotive industry in 3D printing. The field is very topical because the 2050 perspective for the production of vehicles is to decrease their weight by increasing the quantities of embedded plastics, and among these, priority is given to those containing polymers of renewable origin, including, explicitly, PLA and those recycled from post-consumer products. The scientific interest is related to the methods of increasing the thermodynamic stability of PLA, of achieving the thermodynamic equilibrium over long durations, which opens the possibility of estimating the lifespan based on physical aging data, not only those of chemical degradation as is currently done. Moreover, in future papers the results of physical aging will be mathematically modeled and used to estimate lifespan with the help of artificial intelligence.

ii. *The presentation of the content of the doctoral thesis;*

iii. The doctoral thesis contributes to the development of the field of engineering sciences through contributions related to the methods of increasing the thermodynamic stability of PLA, changing the fracture character of this polymer from brittle to ductile and increasing the deformation temperature under load with 60°C-70°C. The variants transposed to scale had a shock resistance of 5-7 J/cm^3 and elongation at break from 5-7% to 400% depending on the formulation and applicability. Through thermodynamic stability studies, the results of the thesis open the way to estimate lifespan, with the help of mathematical modeling and the use of artificial intelligence, from physical aging data, not chemical aging as they are most often the case in the field. Last but not least, the results of the thesis contribute to the development of the automotive industry through three novelties, the first related to the use of 3D printed parts, the second that these parts are made of a polymer of renewable origin and the third that these parts can be from the category of those with a medium life.

iv. *Independent critical approach of the doctoral student in presenting research hypotheses/questions and specific research objectives;*

v. The thesis has an innovative applicative character as it primarily aims to make materials for the automotive industry that, in the perspective of 2050, are expected to be used in increased quantities of materials based on polymers of renewable origin. Secondly, the innovative applicative character is proven by the concentration of research on the modification of a polymer of renewable origin of interest for the automotive sector in the perspective of 2050, namely polylactic acid (PLA), mentioned in most forecasting works. The third proof that the works have an innovative applicative character is that the

PLA variants modified according to the solutions developed in the thesis will be able to be 3D printed in medium-life components, with industrial manufacturing, after going through a detailed program of future works, in phases, in the work.

vi. *How to use the research methodologies formulated in the thesis and their reflection in the research results;*

vii. The ability to rigorously analyze, to problematize and justify each choice made in the design of the research, has been demonstrated since the substantiation stage of the doctoral thesis. The formulation of hypotheses and research questions was based on a solid theoretical foundation, based on the ability to conceptualize and honesty in interpreting the results obtained. By demonstrating the deep understanding of the studied phenomena, it was possible to distinguish the relevance and novelty of the results, all in perfect coherence and logical dependence.

viii. *Critical analysis of the existing solutions on the research direction of the doctoral thesis and the degree of presentation of the way of advancing the research, in relation to the relevant results in the field;*
During the research, the doctoral student demonstrated intellectual independence and her own analytical perspective on them. She thus proved a great ability to pass through his own rational filter, the complexity of the subject and thus the ability to support his opinions on the advancement of research and the identification of relevant results. She continuously had critical approaches, identified gaps, chose relevant results and solutions that eliminate dangerous limitations, validated comparative results, added value to knowledge and therefore was able to solve a topic of innovative application interest. She demonstrated all this first in the research reports he has prepared (references [8], [26], [52]) and then in the published articles and scientific communications presented. She has published as first author aspects on increasing the durability of PLA by hetero-nucleation (reference [119]) and by stereo-complexation (reference [261]), aspects also detailed in references [225] and [325]. She was the second author in publications related to miscibility and the influence on sustainability of modified PLA (references [181], [260]) and to the deepening of mechanisms related to controlled nucleation (references [356], [357]). It achieved a cumulative impact factor of 14.36 considering the year of publication and 13,7 considering the last available impact factor of the journals

ix. *Evaluation of the doctoral student's publications related to the topic of the thesis and its impact.*

a) Citations:

S. Mathe, D. Dimonie, and M. Cristea, „Thermal analysis and polarized light microscopy as methods to study the increasing of the durability of PLA designed for 3D printing", *International Journal of Polymer Analysis and Characterization*, vol. 26, nr. 3, pp. 253-264, apr. 2021[119]:

a) D. Dimonie, S. Mathe, M. M. Iftime, D. Ionita, R. Trusca, and S. Iftimie, „Modulation of the PLLA Morphology through Racemic Nucleation to Reach Functional Properties Required by 3D Printed Durable Applications", Materials, vol. 14, nr. 21, p. 6650, nov. 2021;

b) T. Raj, A. Jain, A. Raj, B. Tyagi, A. Sahai, and R. Swarup Sharma, „Infill strategies for improving the impact behavior of polymer composites utilizing statistical and thermal analysis", International Journal of Polymer Analysis and Characterization, vol. 29, nr. 2, pp. 109-126, feb. 2024

c) D. Dimonie et al., „The Influence of Miscibility of Some PLA-Based Bio-Hybrids Designed for 3D Printing and Medium-Life Applications on Their Physical Aging and Thermodynamic Stability", Polymers, vol. 18, nr. 1, p. 61, dec. 2025.

D. Dimonie, S. Mathe, M. M. Iftime, D. Ionita, R. Trusca, and S. Iftimie, „Modulation of the PLLA Morphology through Racemic Nucleation to Reach Functional Properties Required by 3D Printed Durable Applications", *Materials*, vol. 14, nr. 21, p. 6650, nov. 2021[260]:

a) P. Koczon et al., „Chemical Structures, Properties, and Applications of Selected Crude Oil-Based and Bio-Based Polymers", POLYMERS, vol. 14, nr. 24, dec. 2022;

b) S. Mathe and D. Dimonie, „The Dependence of the Racemic Crystallization of PLLA on the Molecular Weight of the Stereo-Complexer Macromolecules", UPB Sci. Bull. Series B, vol. 85, nr. 1, pp. 139-152, 2023;

c) J. Wan, Z. Liu, J. Luo, X. He, J. Yuan, and Q. Lu, „Post-Baking-Induced Self-Locking Interpenetrating Networks Strengthen 3D-Printed Polyimide Architectures With Enhanced Thermal and Mechanical Properties", ADVANCED FUNCTIONAL MATERIALS, oct. 2025;

d) I. Trofin, M. Boruvka, and S. Hild, „Characterization of poly(lactic acid) enhancement via poly(L-lactic acid)/ poly(D-lactic acid) stereocomplexation and its influence on material crystallinity and morphology", POLYMER TESTING, vol. 152, nov. 2025;

e) M. Sun et al., „From design to Deployment: The innovative role of nanomicelles in targeted ophthalmic therapeutics", MATERIALS TODAY BIO, vol. 35, dec. 2025;

S. Mathe and D. Dimonie, „The Dependence of the Racemic Crystallization of PLLA on the Molecular Weight of the Stereo-Complexer Macromolecules", *UPB Sci. Bull. Series B*, vol. 85, nr. 1, pp. 139-152, 2023[261]:

a) C. Babiș, A. Dimitrescu, S. A. Fica, O. Antonescu, D. Vlăsceanu, and C. Stochioiu, „Determination of the Mechanical Tensile Characteristics of Some 3D-Printed Specimens from NYLON 12 CARBON Fiber Material", Technologies, vol. 13, nr. 10, p. 456, oct. 2025.

Recommendations: The article "*The Influence of Miscibility of Some PLABased BioHybrids Designed for 3D Printing and MediumLife Applications on Their Physical Aging and Thermodynamic Stability*" was recommended on ReasearchGate.net (Fig. A18.1) by Dr. Prof. Dragoș Gabriel Zisopol, from the Faculty of Mechanical and Electrical Engineering, Department of Mechanical Engineering, Petroleum-Gas University of Ploiesti (Fig. A18.2).

5.1 General conclusions

i. The research carried out is original, having an obvious contribution to knowledge in particular by opening up the possibilities of evaluating the lifespan from thermodynamic stability data over time of a polymer of renewable origin designed for medium-life applications in the automotive industry made by 3D printing.

ii. During the research evaluation, 5 articles were published, 4 papers were presented at prestigious scientific events, and 2 papers were published as proceedings. The PhD student is the main author of two articles and co-author of the other 3 with the main author being the doctoral supervisor. The cumulative impact factor considering the year of publication is 14,36 and 13,7 for 2026. Therefore, all the CNATDCU and the additional criteria of the UPB were met.

5.2 List of published articles

1. Mathe, S.; Dimonie, D.; Cristea, M. „Thermal analysis and polarized light microscopy as methods to study the increasing of the durability of PLA deșigned for 3D printing", International Journal of Polymer Analysis and Characterization, Taylor&Francis, Volume 26 - Issue 3, 253-264, 2021, https://doi.org/10.1080/1023666X.2021.1880111. (F.I. 2021 → 1.837; 2024 → 1.6)

2. Dimonie D., Mathe S., Iftime M., Ionita D., Trusca R., Iftimie S., "Modulation of the PLLA Morphology through Racemic Nucleation to Reach Functional Properties Required by 3D Printed Durable Applications", Materials 2021, 14, 6650. https://doi.org/10.3390/ma14216650 (F.I. 2021 → 3.623; 2025 → 3.2)

3. Mathe, S. and Dimonie, D., „The Dependence of the Racemic Crystallization of PLLA on the Molecular Weight of the Stereo-Complexer Macromolecules", UPB Sci. Bull. Series B, vol. 85, nr. 1, pp. 139-152, 2023. (F.I. 2023 → 0.3)

4. Dimonie, D.; Mathe, S.; Truscă, S.D.; Damian, C.M.; Râpă, M.; Dima, S.-O.; Dumitru S.; Oancea, F. The Influence of Miscibility of Some PLA-Based Bio-Hybrids Designed for 3D Printing and Medium-Life Applications on Their Physical Aging and Thermodynamic Stability, Polymers. 2026, vol. 18, p. 61. (F.I. 2024 → 4.9)

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5.3 Extended Abstracts

1. **Mathe, S.;** Gîrbaciu, B.; Dimonie, D. DSC Study of Cold Crystallization Process Characterizing the Stereocomplexed PLA Compounds. Proceedings 2019, 29, 16. https://doi.org/10.3390/proceedings2019029016

2. Girbaciu, B.; Cristea, M.; Ionita, D.; **Mathe, S.**; Dimonie, D. Physical Modification of PLA for Increasing Its Durability (Polarizing Light Microscopy Study). Proceedings 2019, 29, 18. https://doi.org/10.3390/proceedings2019029018

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1. **Mathe, S.**, and Dimonie, D., "DSC study of cold crystallization process characterizing the stereocomplexed PLA compounds", PRIOCHEM, 15th Edition, 2019, Bucharest

2. Gîrbaciu, B., Cristea, M., Ioniță, D., **Mathe, S.** and Dimonie, D., "Physical modification of PLA for increasing its durability (Polarizing Light Microscopy Study)", PRIOCHEM, 15th Edition, 2019, Bucharest

3. Gîrbaciu, B., Cristea, M., **Mathe, S.** and Dimonie, D., "Study of increasing durability of PLA designed for 3D printing through nucleation with sulphonic ester derivate as nucleating agent", Next Chem, 2020, Bucharest

4. **Mathe, S.**, Ciuca, M., and Dimonie, D., "The dependence of the racemic nucleation efficiency on the chemical characteristics of the PDLA macromolecules", 5th International Conference of the Doctoral School, Gheorghe Asachi "Technical University of Iasi", 2022, Iași, Romania

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7. Annexes - 18 annexes