Biodegradable Polymeric Materials with Agricultural and Industrial Applications
Abstract

The habilitation Thesis entitled *"Biodegradable Polymeric Materials with Agricultural and Industrial Applications"* presents the results obtained in the main research activities carried out after the award of the PhD degree in Chemical Engineering (October 23, 2008) and confirmed by the Ministry of Education, Research and Youth, based on the Order of the Minister no. 3030 of 13.01.2009 and also the main directions aimed at further development of my academic career. The work is organized in two parts: *The main scientific, professional and academic achievements* (I) and *The evolution and development plan of the scientific, academic and professional career* (II) and contains 359 bibliographical references attributed to both parts.

Part I of the habilitation Thesis starts with the presentation of some relevant aspects of the professional activity, in teaching and scientific research, by highlighting *some Relevant scientific papers for the field of Chemical Engineering, elaborated after the defense of the PhD Thesis that is the basis of the habilitation Thesis* (I.1.) and on the *Experience in dealing with the topic "Biodegradable Polymeric Materials with Agricultural and Industrial Applications*" (I.2.). In terms of scientific balance, after the defense of the PhD thesis, on the topic of the habilitation thesis, I am first author/corresponding author or coordinator/co-author of a number of: 29 scientific articles published in ISI journals indexed Web of Science, 25 scientific articles published in journals indexed in international databases BDI, over 20 participations in international/national conferences/congresses, 2 books and director of 1 research project (I.2.).

The thesis continues with the presentation of the most significant experimental results, directed towards: *Development and mechanical, physico-chemical and structural characterization of polyfunctional materials based on polymers susceptible to biodegradation* (I.3.), namely: cellulose, lignin, chitosan and polycaprolactone.

Thus under subchapter I.3.1. *Polyfunctional cellulose-based materials, the research aimed at the efficient valorization of cellulose*, given its presence and fundamental role, both in the natural and manufactured environment, and focused on the extraction and characterization of cellulose from agricultural vegetable waste (rape stalks), in situ and partially in situ synthesis of cellulose and modification of native resinous cellulose in order to increase and diversify its polyfunctionality (addition of additives to obtain paper materials with superior properties, ultrasonication to increase crystallinity and use in ferromagnetic composites, hydrogelation to optimize active ingredient delivery agents). The study on the elucidation of the structure of native cellulose from oilseed rape stalks suggests that these agricultural wastes, with their high cellulose and hemicellulose content, plus their unique structural and mineral composition, represent a highly promising source for the development of a dynamic clean technology, which requires the development of new strategies for optimizing material quality and production yield (I.3.1.1). With regard to the modification of raw resinous pulp by the addition of additives, by the experimental conclusions obtained, it can be stated that the experimental procedure developed and the experimental conditions proposed, contribute substantially to the improvement of the quality of the fibrous pulp and implicitly to the optimization of the properties of the paper, in ecological and economically profitable terms (I.3.1.2). The study on the modification of pulp by ultrasonication also aimed to increase the crystallinity region of the pulp, which was also achieved under the experimental conditions of sonication (I.3.1.3). Subsequently, research continued with the

development of cellulose/magnetite/maghemite based composite materials under precisely designed experimental conditions, resulting in end products with ferromagnetic properties of real interest for biomedical applications (I.3.1.4).

Subchapter I.3.2. *Polyfunctional lignin-based materials*, presents research on the possibilities of valorization of lignin separated from annual plants (Sarkanda grass) and agricultural vegetable waste (wheat straw) and lignin derivatives (Protobind commercial products), given the availability of this bioresource, which is insufficiently exploited. Structurally and functionally characterized lignins and lignin derivatives (I.3.2.1.) were subjected to chemical modification by hydroxymethylation and epoxidation reactions in order to broaden their applicability, resulting in new products, which were also further characterized (I.3.2.2.; I.3.2.3.). The research continued with the development of systems with potential biocidal action for cellulosic materials (fir and beech wood and birch veneer), using lignins and lignin derivatives in unmodified and modified form, uncombined or combined with copper ions (I.3.2.4.). The conclusion drawn from the experimental analyses carried out recommends the formulated biocide systems both in terms of efficiency and on the basis of the fact that they are derived from renewable sources, so that they could represent new opportunities for effective biostabilization treatments, especially if we take into account the advantages related to their ability to increase resistance to destructive factors (physical-mechanical, chemical and biological), their relatively low cost price or their good biocompatibility. Subsequently, a method was developed which proved to be useful in the formulation of lignin/furfuryl alcohol/furanic resin based adhesive systems that could be evaluated relatively completely, imparting superior mechanical properties to the cellulose fibers in the paper structure, opening the field of possible applications in various fields (I.3.2.5.). The results of the study on the utilization of lignin as a possible biosorbent for heavy metal ions from contaminated media, namely: (Pb(II), Zn(II), As(III), Cu(II), Cu(II), Co(II), Cd(II), Cr(VI), Ni(II), Fe(II)), recommend the bioresource as a feasible solution in the context of sustainability (I.3.2.6.). Also, the conclusion of research directed towards testing the stimulatory effect of lignin and lignin products on the evolutionary process of plants, proposes to explore lignin for its potential as a biofertilizer mainly due to its function as a precursor of humic substances (I.3.2.7.).

Within subchapter I.3.3. *Polyfunctional chitosan-based materials*, a series of researches focused on the valorization of chitosan are presented. A number of investigations have focused on the design of urea and salicylaldehyde based hydrogels capable of soil conditioning (I.3.3.1.), while another series of investigations focused on the formulation of hybrid materials based on carboxymethylation modified chitosan and precipitated calcium carbonate, in order to obtain papetare products with improved mechanical and optical properties (I.3.3.2.). The experimental findings highlight the benefits of the use of formulated hydrogels in terms of soil amelioration and also reflect the efficiency of the created hybrid material which is considered a processable and economically and environmentally advantageous technological alternative to conventional practices.

In subchapter I.3.4. *Polyfunctional caprolactone-based materials*, the studies were focused on the development of polyfunctional and sustainable hybrid materials. Thus, the formulation and characterization of three hybrid materials based on polycaprolactone and polydimethylsiloxane with terminal aminopropyl group, synthetically modified as three molecularly differentiable derivatives and subsequently chemically and spectrally characterized (I.3.4.1.), was achieved. Due to the superior performance compared to the individual materials and the possibilities of domain-

dependent modeling of properties, the formulated hybrids may be an option for potential applications in advanced industries.

The subjet of the Thesis continues with possible, *Applications in agriculture and industry of the studied polymeric materials* (I.4.) and is based on my own theoretical and practical research, supported with arguments from the literature. Therefore, cellulose hydrogels can function as potential agents for the controlled release of agrochemicals into soil and soil-free independent substrates for plant cultivation (I.4.1.1.), but also as ingredients for the formulation of biodegradable agro-food packaging (I.4.1.2.), and lignin can be considered as a green source of pesticides and a retention agent for heavy metals (I.4.1.3.), a functional agent of active agri-food matrices and packaging (I.4.1.4.) or serve as an organic biofertilizer, agrochemical delivery and soil bioremediation agent (I.4.1.5.). Chitosan-based hydrogels may also serve as soil amendments or function as food additive systems (I.4.1.6.), and polycaprolactone-based hybrid materials may be useful for sustainable packaging and microencapsulation applications in the agri-food industry (I.4.1.7.). Cellulosic hydrogels can act as biomaterials with conductive and magnetic properties in advanced industries (I.4.2.1.), and lignin can be a useful biosource for the formulation of sustainable composite materials (I.4.2.2.), while chitosan hydrogels are viable alternatives for electronic sensors, for example (I.4.2.3.), and polycaprolactone may be useful in the development of sustainable adhesive systems (I.4.2.4.).

Part II of the habilitation Thesis contains the plan for the evolution and development of my academic career, the key objective being to develop my own professional competences and to ensure a synergism between teaching and research activity, while pursuing the fulfillment of the fundamental mission of the Iasi University for Life Sciences ,,Ion Ionescu de la Brad". As far as the teaching activity is concerned, the permanent concern is aimed at a continuous process of training and self-improvement, which provides the possibility to access the optimal ways of knowledge transmission. Also, the integration of research results within the specialized disciplines taught and the development of collaborative activities in teaching and research by creating links with disciplines from other universities in the country and abroad, is a priority segment. Several research directions are proposed for the scientific and research activity, aligned with current European and national policies on the valorization of biomaterials and their scalability to ensure sustainability. These proposed research directions are accompanied by a summarized explanation regarding their development and viability. In the context of the above, I can also state that among the ongoing concerns is also the dissemination and valorification of research results through publication in reputed journals and participation in prestigious national/international conferences and last but not least, to capture the interest of the younger generation in the field of Chemical Engineering.

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