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HABILITATION THESIS SUMMARY

Design of High Performing Materials with Increased Thermal Stability: Structure-Property Relationship and Degradation Mechanism

Dedicated to Professor Dr. Natalia Hurduc
on the occasion of her 85th birth anniversary

The habilitation thesis synthetically presents some of the original and relevant results obtained (after defending my doctoral thesis in 2000) within the main direction of research of my activity, *i.e.* in the science of materials and nanomaterials, the physicochemical characterization of new high-performance materials, respectively.

The thesis is structured into three chapters and a bibliography section. The first chapter comprises some of my own contributions regarding the analysis of the relationship between structure – thermal stability – degradation mechanism for small molecular compounds (**51** - ferrocene derivatives, phenyl derivatives analogues, respectively and **13** - [1,3,4] oxadiazole derivatives) with liquid crystal properties, a topic on which the literature did not provide any complete studies that would include both the analysis of the thermal stability limit, as well as the elucidation of important issues regarding the degradation mechanism and non-isothermal kinetic studies. Following the studies conducted, the thermal decomposition of ferrocene derivatives and of phenyl derivatives analogues has been noticed to take place in two or more stages of degradation, the initial temperature at which degradation begins (T_i) being above 200°C, with the sole exception of symmetric diferrocene derivatives with a marginal flexible part. The increased number of aromatic cycles leads to a lower thermostability. This behaviour can be attributed to the increased number of bonding groups that bind the aromatic rings and determine an increase in thermal stability, which can easily release small molecules such as N_2, CO_2, CO or CH_2O by breaking azo, amine or ester-type connections. Moreover, the azo junction has been noticed to induce a more reduced stability than the ester one. The results presented in subchapter 1.2 indicate a much better stability for Schiff [1,3,4] oxadiazole bases with terminal alkyloxy chain in comparison with those with a terminal acyloxy chain, an increase in initial temperature, respectively, at which the degradation (T_i) begins up to approximately 40°C. The characterization through thermal methods of the Schiff [1,3,4] oxadiazole bases with a terminal acyloxy chain has highlighted the dependence between structure – thermostability and influence of the length and type of terminal chain. The application of the TG/MS/FTIR coupled technique for this class of compounds has revealed the fact that the initiation of thermal decomposition takes place in the azo groups and continues with the cleavage of the aromatic units and of the terminal aliphatic chains.

The analysis of thermal degradation of the various types of polymers presented in chapter two is extremely important for the development of high-performance technologies for processing them, for verifying the possibility of using them at elevated temperatures, but also for understanding their decomposition mechanism. The **35** polymers contain a series of structural units that are part of the structure of the small molecular compounds analysed in the previous chapter: ferrocene, [1,3,4] oxadiazole, azobenzene, phenyl, etc. Magnetic, optical, electrical and electrochemical properties of polymers containing ferrocene make them ideal for a wide variety of applications. However, the analysis of thermal degradation of such polymers provides a guideline for their optimal processing and also information on the degradation mechanism. Understanding the mechanism of degradation of such polymers opens the door to the improvement of thermo-stability and also discovery of their new applications considering that ferrocene is a good precursor for the production of iron oxide nanostructures through thermal decomposition. The introduction of [1,3,4] oxadiazole in the structural unit of the macromolecular chains led to the obtaining of polymers with very good thermal and chemical resistance, low dielectric constant, good mechanical resistance, high radiation resistance, etc. These properties allowed the use of this type of polymers in the aerospace industry, in the car industry, in the microelectronic industry or in the electricity generation industry (photovoltaic cells, nuclear reactor wall construction). The studies presented in subchapter 2.2. of my habilitation thesis have analysed the influence of introducing into the polymer chain, alongside cycle [1,3,4] oxadiazole, the following structural units: isopropylidene, hexafluoroisopropylidene, cyclohexylidene, fluorene, phthalide, bisphenol A or phenylquinoxaline on thermal stability and on the degradation mechanism. By applying the TG/MS/FTIR coupled technique on a series of polymers containing [1,3,4] oxadiazole, it has been shown that, in the case of some aromatic polyetherimides, the initiation of thermal decomposition takes place in the oxadiazole group regardless of the work atmosphere and of its position in the structure of the polymer (in the main or in the lateral chain). The polymers containing azobenzene in their molecule have different applications in optoelectronics, in the industry of lacquers and paints, in obtaining data storage media, in medicine, in order to obtain artificial muscles, to obtain materials with controlled release of medicines etc. Given that a large part of the applications of the polymeric materials containing azobenzene involve their interaction with sources of laser irradiation, the determination of the thermal stability limits of this type of polymers becomes a compulsory requirement, even if the material does not have properties of liquid crystals. Moreover, understanding the mechanism of decomposition for this type of polymers can also contribute to the development of new materials with improved properties which can contribute to the enlargement of the fields with potential applications of them. In subchapter 2.3, the analysis of thermal stability for a series of azopolysiloxanes modified with nucleobases falling into the category of materials with potential application in medicine was presented. The potential applications of these materials entail the presence of a good thermal stability in isothermal conditions as well, in view of subjecting them to sterilization processes without affecting their structure and properties. The studies carried out have highlighted the fact that the thermal stability of these polymers is good until reaching a temperature around 300°C under dynamic temperature conditions, and that they do not change their structure and properties for 40 minutes in isothermal conditions at 180°C. The study regarding the thermal stability of polystyrene and of some substituted benzene ring compounds: chloromethyl polystyrene, poly(dimethyl 2-hydroxyethyl p-vinylbenzyl ammonium chloride) and poly(p-vinylbenzyl triethylammonium chloride) is presented at the end of the chapter two. The thermal and kinetic characteristics obtained for the chemically-modified polymers have revealed a complex mechanism of degradation, as a result of reticulation during thermal degradation.

The last chapter presents the prospects opened by the habilitation thesis and the evolution and independent development plan of my professional career. The main objective of my professional career development will be to analyse thermal stability and the degradation mechanism for a wide range of small molecular compounds and polymers, based on the constant collaboration with researchers from Romania and abroad. Furthermore, a second objective aims at setting up homogeneous databases containing a sufficiently large number of examples in order to allow the modelling of the various interactions between the basic structural units both for predicting thermal stability, as well as other properties.

Direction of research: the study of thermodynamic properties of liquid - liquid binary and ternary systems will also be developed in the coming years by determining the thermodynamic properties for systems about which there are no data in the literature. The main objective of this line of research is to obtain new high-quality thermodynamic data able to provide a reliable support in verifying new theoretical and empirical models of fluids and in formulating relevant theories. These data can constitute an important basis for designing plants for separation through distillation, fractionation, solvent extraction, as well as for determining the risk factors for the separation processes.

The activity which I have constantly undertaken, ever since the beginning of my academic career, in leading scientific papers for student circles and training students for professional competitions, as well as coordinating dissertation papers over the past 5 years have contributed to the development of my communication skills, as well as of those related to coordinating young researchers. I have been and still am a member of PhD mentoring committees within the Doctoral School of the Faculty of Chemical Engineering and Environmental Protection, “Gheorghe Asachi” Technical University of Iaşi, and I was part of three PhD Thesis Analysis Committees. Furthermore, in the 4 research projects that have been won in competitions, which I have coordinated as Project Director, I have involved students from all three levels of studies: Bachelor’s Degree, Master’s Degree and Doctoral level.

Given the above-mentioned aspects, the evolution and independent development plan of my professional career has the following main objectives:

- Constantly improving my teaching activity by updating courses, creating support materials for students and equipping laboratories with modern equipment.
- Continuing to exploit research results by publishing scientific papers in ISI-indexed journals and other types of specialized journals, by participating in national and international scientific congresses and publishing books/book chapters with renowned international publishers.
- Continuing to participate in project competitions and national and international research programmes by forwarding proposals in my capacity as project director or responsible partner.
- Involving students from the two levels of studies: Bachelor’s Degree and Master’s Degree levels in research activities and guiding them towards PhD programmes.
- Active involvement in all actions aimed at increasing the visibility of the department, faculty, university, research centre and doctoral school of which I am part, at national and international level.
- Continuing the active involvement in every aspect related to the activity in the academic community.

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