“Petru Poni” Institute
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HABILITATION THESIS

Thermal degradation of polymers. From fundamental aspects to treatment / valorisation of polymeric waste

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ABSTRACT

The habilitation thesis entitled **"Thermal degradation of polymers. From fundamental aspects to treatment / valorisation of polymeric waste"** presents the results of research performed by the author in the domain of the thesis after receiving the PhD title (after 2002). The thesis is structured in three main parts, as following:

I. Overview of professional and scientific career

This section started with the presentation of professional career, including the positions in "Petru Poni" Institute of Macromolecular Chemistry, where my activity started in 1995, as well as the research stages in various universities from abroad. The PhD thesis and the post-doctoral positions are also introduced.

The scientific research activity is briefly resumed, pointing out that I dedicated most of my research career to studies in the field of polymers stability and thermal degradation, with special interest to the thermal treatment and valorisation of polymeric waste and residues, both from synthetic and from natural origin. The main directions of research in the domain of the thesis are shortly introduced, including the main publication results. The knowledge acquired and transferred to scientific community through publications is schematically represented.

The scientometric indicators are presented, including **6** chapters in books, **62** scientific papers published in ISI journals (cumulative impact factor of **199.85**, **2316** total citations, without self citations) from which *19* papers as main author (first and/or corresponding author), with cumulative impact factor of *86.89*, **5** conferences, **30** communications, **42** posters, **5** book reviews, **1** patent, more than **20** research projects, h-index of **27**. Editorial activity is described.

II. Scientific achievements after receiving PhD title

Research work performed after receiving PhD title in the domain of the habilitation thesis was focused on three main directions: *i)* fundamental aspects on thermal degradation of model polymers; *ii)* heteroatoms in pyrolysis oils from model and waste polymers and methods to remove them; *iii)* thermal treatment/valorisation of biomass and its components. Gaining knowledge on degradation mechanisms and on interactions between components in mixtures was of special interest.

i) Insights into fundamental aspects on thermal and catalytic degradation of polymers – studies in a continuous flow reactor

Thermal degradation is studied at laboratory scale mainly in batch reactors, which offer the advantage of versatility and ease of operation. However, plastic treatment at industrial scale would be preferably performed in continuous flow operating mode that allows efficient processing of large quantities of materials and consistent quality of products. A continuous flow process runs at steady state, with constant parameters, that is constant temperature, constant pressure, constant amount of reactor content and constant concentration of chemical species in reactor content and in volatile products. For this reason, a continuous flow reactor is more suitable for the study of polymer degradation compared with batch reactors in which occurring processes are far from equilibrium.

Studies on the macroscopic mechanism of thermal degradation of polyethylene (PE), polypropylene (PP) and polystyrene (PS) in continuous flow reactors were initiated by dr. K. Murata and dr. Y. Sakata from Japan. Joining their research group, I was involved in determining the effect of catalysts and of PVC on thermal degradation of above-mentioned polyolefins.

This section presents results obtained in a continuous flow reactor in studies on thermal degradation of model synthetic PE, PP, PS, with special interest in molecular mass of degradation products, mass rate and macroscopic mechanism of degradation of PE, PP and PS, as well as the effect of poly(vinyl chloride) (PVC) on thermal and catalytic degradation of PE, PP and PS.

The continuous flow reactor offered valuable information on thermal and catalytic degradation of PE, PP and PS, which cannot be obtained by usual batch or semi-batch processes. The observed kinetics and composition of degradation products support the macroscopic mechanism of chain-end scissions at liquid-gas interface, with formation of heavy compounds entrained out of reactor by the flow of volatiles.

ii) Removal of heteroatom containing compounds from pyrolysis oils of polymers in WEEE

Polystyrene and high impact polystyrene (HIPS) are main components of waste from electrical and electronic equipment (WEEE) being followed in amount by acrylonitrile-butadiene-styrene (ABS). While PE, PP and PS are hydrocarbon polymers, ABS has nitrogen in its acrylonitrile units, whose interactions with styrene and butadiene units lead to formation of nitrogen- containing compounds in pyrolysis oils. PVC is also present in WEEE, coming from large and small domestic appliances, but also from the insulation of electrical cables; it leads to corrosive HCl and chlorinated organic compounds. Brominated flame retardants (Br-FR) such as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), tetrabromo bisphenol-A (TBBA) or polybrominated epoxy resins (BERs) were traditional fire retardants used in 1990s in plastic materials to prevent combustion during accidental fires. Antimony oxide (Sb_2O_3) was widely used as synergist to enhance the flame-retardant effect. Br-FR and Sb_2O_3 had special interest and wide use in plastic materials because they ensure higher fire safety for lower quantities of additive. Their market is decreasing because of high environmental concerns however there are still large amounts of products containing these compounds. Bromine (Br), chlorine (Cl) and nitrogen (N) from polymers or flame retardants in WEEE lead to acid or toxic gases such as HCl, hydrobromic acid (HBr), hydrogen cyanide (HCN) and ammonia (NH_3) during thermal decomposition and they can also remain as organic compounds in pyrolysis oils. The amount of these compounds should be decreased as much as possible in order to use WEEE pyrolysis liquids as fuel or feedstock.

This section presents results on pyrolysis of ABS containing brominated flame retardants (ABS-Br), the effect of PVC on thermal degradation of ABS, ABS-Br and polymer mixtures containing ABS-Br, and catalytic removal of heteroatom containing compounds from pyrolysis oils of polymer mixtures with ABS-Br. Debromination of HIPS-Br by reactive ammonia treatment or by alkaline hydrothermal treatment is also presented. Studies continued on real samples, such as pyrolysis of plastic and thermoset fractions of used computers or co-processing of DVDs and CDs with vegetable cooking oil.

It was found that interactions appear at high temperatures of degradation between various components of complex polymeric systems, for example between acrylonitrile and styrene units in ABS, between polymers degrading in similar temperature ranges, between polymers and flame retardants or their synergists. These interactions lead to formation of heteroatom containing compounds (N-, Br-, Cl-, O-) which are not desired in pyrolysis oils. Catalytic upgrading is a suitable way to decrease the amount of heteroatoms in pyrolysis oils. Reactive pyrolysis (in ammonia flow) successfully removed most of the bromine from pyrolysis oils of HIPS-Br. Alkaline hydrothermal treatment (with KOH) was a promising way to obtain good recovery of bromine and of plastic materials, which was only marginally degraded.

iii) **Thermal treatment/valorisation of biomass waste fractions**

Lignocellulosic biomass such as agricultural and forestry residues or energy crops is the cheapest and most abundant form of biomass, which supplies about 14 % of the world's energy needs. It is renewable and environmentally friendly and can be converted into biofuels, as an efficient alternative for fossil fuels. Considerable efforts have been made to convert wood biomass into liquid fuels and chemicals, since the oil crisis in mid 1970s. Knowledge on thermal behaviour, interaction between components and composition of degradation products is of valuable interest.

This section presents results obtained on thermal degradation of various biomasses, co-pyrolysis of pine cones with synthetic polymers, pyrolysis of Tetra Pak and thermal degradation of keratin waste. A special interest was paid to lignin, the second largest source of organic raw materials and the most abundant aromatic natural polymer. Thermal degradation of various lignins is presented, as well as co-pyrolysis of LignoBoost® lignin with synthetic polymers and catalytic upgrading of co-pyrolysis oils from polycarbonate and lignins.

It was found that thermal degradation of biomass is a complex process, due to particular behaviour of its main constituents (hemicelluloses, cellulose, lignin). TG-FTIR/MS can track formation (temperature domains and rate) of individual volatile products, giving insights to the degradation mechanisms. Pyrolysis can convert biomass and its components into valuable products, the process being affected by interactions with synthetic polymers in mixtures. Optimum combination of polymeric materials and experimental parameters can enhance pyrolysis, improving the quantity and quality of products. Catalysts can upgrade the pyrolysis oils by de-oxygenation and hydrogenation reactions.

III. Future directions; challenges and possibilities

Future research plan starts from the solid base of the three main directions developed after receiving the PhD degree, with enlarged vision adapted to nowadays reality and perspective trends.

Environmental degradation is a new domain of interest, which arose from the recent trends in replacing materials based on limited, depleting fossil resources with new materials based on renewable resources, especially biomass, which, in addition, have lower carbon footprint. In this context, I intend to introduce in my domains of interest research studies on environmental degradation, and especially on biodegradation of blends and composites containing natural compounds. A particular interest is to distinguish between the biodegradability and the biocompostability of polymer- based materials. Challenge occurs in the case of bioactive materials, such as bioactive food packaging, that are designed to inhibit microbial spoilage of food in order to preserve quality and extend the shelf life but, as a consequence, are less prone to microbial attack that is necessary for biodegradation of the material itself when become waste after end of use.

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