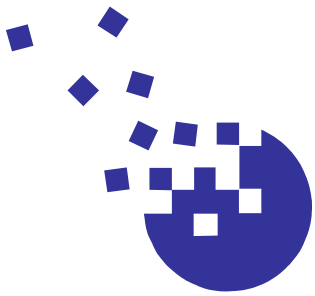

Research Laboratory of Material and Environmental Chemistry

Chemical Research Center
Hungarian Academy of Sciences

Annual Report

2002

Budapest
2003

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INTRODUCTION

The Research Laboratory of Materials and Environmental Chemistry (RLMEC) is a non-profit research institute belonging to the Chemical Research Center of the Hungarian Academy of Sciences.

Mission of RLMEC is to perform high-level basic and applied research in materials science and environmental chemistry.

Our research in materials science is aiming at revealing chemical relationships among composition, microstructure, properties and processing of structural and functional materials. The models include advanced metallic and ceramic materials, traditional and new polymers, special surface layers and coatings, and different composite materials.

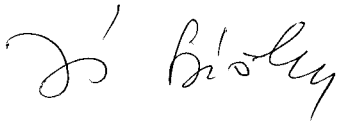
During research in environmental chemistry, we strive to disclose basic chemical, technological and engineering phenomena in order to facilitate development of new processes and technologies of minimum environmental impact. The main research topics are as follows: *(a)* research in environmental analysis and development of new analytical methods for environmnetal protection, *(b)* research on utilization of renewable sources of energy and *(c)* new methods, processes and technologies of waste processing and utilization.

There were remarkable changes in the organization of RLMEC from 1 January 2003. New departments, formerly belonging to the Institute of Chemistry, were joined RLMEC. Thus, polymer research and research in environmental chemistry are now concentrated in RLMEC within CRC HAS.

In the Annual Report, we present details of our activity in the year 2002, in accordance with the new structure of organization.

I warmly recommend this Report to the reader's attention.

Budapest, June 2003.



János Szépvölgyi

Director

1 THE ORGANIZATION[1]

Director	János Szépvölgyi, PhD, DSc
Departments	Department of Materials Chemistry
	Group of Nanolayer Chemistry
	Group of Plasma Chemistry
	Group of Electrochemistry and Corrosion
	Group of Metal Complexes
	Department of Polymer Chemistry and Materials Science
	Department of Applied Polymer Chemistry and Physics
	Group of Polymer Degradation
	Group of Applied Polymer Chemistry
	Department of Environmental Chemistry
	Group of Environmental Techniques
	Group of Thermal Degradation
	Group of Separation Techniques
	Laboratory for Environmental Protection
	Secretariat
Staff	48 scientists (1 OM-HAS, 10 DSc, 15 PhD)
	24 technicians
	6 PhD students
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	P.O.B. 1525 Budapest, Pf. 17.
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Department of Materials Chemistry

Head: János Szépvölgyi, PhD, DSc, scientific adviser

Group of Nanolayer Chemistry
- Imre Bertóti, PhD, DSc, scientific adviser
- András Tóth, PhD, senior research fellow
- Miklós Mohai, research fellow
- Tamás Ujvári, junior research fellow
- László Gulyás, technician

Group of Plasma Chemistry
- Ilona Mohai, PhD, senior research fellow
- Zoltán Károly, PhD, senior research fellow
- Katalin A. Főglein, research fellow
- Loránd Gál, junior research fellow
- Zsuzsanna Laczkó, technician

[1] As for March 31, 2003.

Group of Electrochemistry and Corrosion

Béla Lengyel, PhD, DSc, scientific adviser
György Horányi, PhD, DSc, scientific adviser
Tamás Pajkossy, PhD, DSc, scientific adviser
Sándor Szabó, PhD, DSc, scientific adviser
István Bakos, PhD, senior research fellow
Gabriella Lendvay-Győrik, PhD, research fellow
Gábor Mészáros, PhD, research fellow
Éva Fekete-Dániel, research fellow
Ilona Jáger-Tardi, technician
Edit Rizmayer, technician

Group of Metal Complexes

Klára Dengel-Szentmihályi, PhD, senior research fellow
László Kótai, research fellow
Judit Fodor, junior research fellow
Erzébet Bíró, technician
Judit Lénárt, technician

Department of Polymer Chemistry and Materials Science

Head Béla Iván, PhD, DSc, scientific adviser

Árpád Máthé, PhD, senior research fellow
Márta Szesztay, PhD, senior research fellow
Attila Domján, PhD, research fellow
Gábor Erdődi, junior research fellow
Tamás Fónagy, junior research fellow
Péter Groh Werner, junior research fellow
Sándor L. Szabó, junior research fellow
Tibor Szakács, junior research fellow
Márton Haraszti, PhD student
Péter Mezey, PhD student
Viktória Pálfi, PhD student
Mijid Narmandakh, PhD student
Erzsébet Tyroler, technician
Barbara Kovács, secretary

Department of Applied Polymer Chemistry and Physics

Head Béla Pukánszky, PhD, DSc, scientific adviser

Group of Polymer Degradation

Enikő Földes, PhD, senior research fellow
Szilvia Klébert, junior research fellow
János Móczó, junior research fellow
Erika Selmeczi, technician
Judit Szauer, technician
Mónika Meskó, technician

Group of Applied Polymer Chemistry

Erika Bódi-Fekete, PhD, senior research fellow
Tünde Pozsgai, junior research fellow
László Cseke, technician
Ildikó Erdő-Fazekas, technician
Ede Tatai, technician
Tímea Szalay-Dubniczky, secretary

Department of Environmental Chemistry

Head Gábor Várhegyi, PhD, DSc, science adviser

Group of Environmental Techniques

György Mink, PhD, senior research fellow
László Horváth, research fellow
István Lengyel, technician

Group of Thermal Degradation

Gábor Várhegyi, PhD, DSc, scientific adviser
Marianne Blazsó, PhD, DSc, scientific adviser
Zsuzsanna Novák-Czégény, PhD, research fellow
Emma Pekker-Jakab, PhD, senior research fellow
Ferenc Till, senior research fellow
Erika Dancs-Mészáros Erika, junior research fellow
Sára Stark, technician

Group of Separation Techniques

Eszter Forgács-Tóth, CSc, senior research fellow
Annamária Jakab, junior research fellow
Éva Tarlós, technician

Laboratory of Environmental Protection

Horváth Tibor, PhD, senior research fellow
Miklós Prodán, research fellow
Zoltán Sándor, research fellow
Erzsébet Kéméndi-Fridrich, technician

Secretariat

János Szépvölgyi, PhD, DSc, director
Mihály T. Beck, Professor Emeritus, ordinary member of HAS
Borbála Zelei, PhD, scientific secretary
Andrea Kránicz, secretary
Ágota Mezei-Seres, financial manager
Gábor Babos, technician
József Szűcs, technician

2 RESEARCH ACTIVITIES IN 2002

2.1 Research in materials chemistry

2.1.1 Formation and characterization of nanolayers

Imre Bertóti, Miklós Mohai, András Tóth, Tamás Ujvári

Carbon nitride layers were deposited on silicon targets by DC magnetron sputtering. It was found that the increase of plasma density (*i.e.* electron density, electron temperature, ion current density) decreased the amount of incorporated nitrogen, and it changed the chemical state of nitrogen, as well. According to XPS and FT-IR investigations, the plasma density increased amount of sp^3–type CN clusters.

In the EU project FLAMERET a series of aluminum hydroxide and magnesium hydroxide powder samples coated by zinc hydroxyl-stannate (ZHS) to various extents have been studied by XPS. The surface coverage by ZHS and the thickness of the carbonaceous and ZHS layers were determined for each sample by the XPS MultiQuant program developed in our laboratory. Relationships were found between the surface coverage, the layer thickness and the bulk concentration of ZHS. Thick coatings in the range of several nanometers have been obtained. This accounts for the previously observed high flame retardant and smoke suppressant efficacy of zinc hydroxyl-stannate-coated fillers when applied in various polymeric formulations.

Metal arachidate Langmuir-Blodgett (LB) films were deposited on glass substrates. The extent of salt formation and the build-up of the LB layer were evaluated by quantitative XPS. The surface coverage of the glass substrate by the LB film was assessed by calculations based on a substrate-overlayer model using the XPS MultiQuant program. The attenuation of the Si2p photoelectron signal from the substrate by the 2 and 4 ML LB films was calculated and compared to the measured intensities enabling to evaluate the completeness of the layer. The layer thickness calculated from the measured intensity of constituents was very close to thickness derived from the geometry of the arachidate molecule. This finding confirmed the validity of the model on the one hand, and it referred to the accuracy of our measurements on the other.

2.1.2 Preparation of special ceramic powders in RF thermal plasma

Zoltán Károly, János Szépvölgyi

We established the optimum synthesis conditions of SiO_2 powders of various morphologies in RF inductively coupled thermal plasmas. Both dense and hollow microspheres were produced. The latter ones are of great importance in gas chromatography. Conditions for producing nanosized powders for ceramic processing were established, as well.

2.1.3 Degradation and stability of polymers

Edina Epacher, Enikő Földes, Béla Pukánszky

Effects determining the degree and mechanism of polyethylene (PE) degradation have been studied along with some problems of their stabilization. The effects of chain structure and weak places were analyzed by studying changes in the nascent polymer powder. The chemical properties were investigated by FT-IR. Diffuse reflectance FT-IR Spectroscopy (DRIFT) was also used in these studies. Calibration of DRIFT spectra made possible the quantitative evaluation of chemical changes taking place in the first extrusion. Type and amount of weak places in PE (unsaturated groups, branching, oxygen functionalities) were of decisive importance in terms of stability and the rate of reactions on processing.

Study of Phillips type ethylene copolymers polymerized with different amounts of 1-hexene under similar conditions proved that the vinyl groups are more reactive than the vinylidene and vinylene ones and the branching points. The oxygen built in the polymer during polymerization and/or storage in air at ambient temperature affects strongly the rate and mechanism of degradation on processing, as well as properties of products. The efficiency of stabilizers was studied by comparing the reaction mechanism of two phosphorous secondary antioxidants, phosphite and phosphonite, respectively. Correlation was found between the chemical nature of antioxidants and the changes in the polymer properties.

2.1.4 Morphology of crystalline polymers

Alfréd Menyhárd, Béla Pukánszky, József Varga

Structure, melting and crystallization behavior of the most important semi-crystalline polymers such as LDPE, LPE, iPP, sPP and polyamides have been investigated in details previously. Our research targeted the effects of thermal history, shear forces and the presence of different additives on the crystallization behavior.

PP crystallized exclusively in β-modification (β-iPP) has been prepared first in our laboratory after synthesizing selective β-nucleating agents. Effects of several commercial α-nucleating agents and a β-nucleating agent (Ca-suberate) on the structure and properties of different iPP products were studied. Effectiveness of different α-nucleating agents was determined. It was established that the type and amount of additives strongly affect nucleation. The experimental results indicated that some secondary antioxidants had α-nucleating effect. Investigating the nucleating effect of Ca-suberate in high molecular weight iPP's we found that in homopolymers and block copolymers of iPP's β-modification is formed almost exclusively. However, in random copolymers α-modification is also present, besides β-spherulites. The impact strength of the homopolymer prepared by β-nucleating agent increased by a factor of two, while that of the block and random copolymers actually did not change.

2.1.5 Studies on heterogeneous polymer systems

Erika Fekete, János Móczó, András Pozsgai, Tünde Pozsgai-Fráter, Béla Pukánszky, László Százdi

The main research goal was to determine structure - property correlations in polymer blends, particulate filled polymers, composites filled with fibers, and in nanocomposites. We established relationships among the characteristics of components, the interfacial interactions and the properties of heterogeneous polymer systems.

More recently, we devoted our attention to the interactions of components and to their modification. A linear inverse gas chromatographic (IGC) method was developed for studying the surface characteristics of fillers. Using this method the disperse component of the surface tension, the surface acid-base constants, as well as the dependence of these parameters on temperature and surface coverage were determined for untreated and surface treated fillers, respectively. The IGC method was successfully applied for studying the adsorption of surfactants of different chemical structure. Effects of the chemical structure on the adsorption, the orientation of surfactant molecules, and the structure of adsorbed layer were established. Composites were prepared using the investigated fillers and different polymer matrices. Their mechanical properties were measured. Correctness of the reversible work of adhesion used for describing the interfacial interactions was checked based on dipole-dipole and acid-base interactions of the components. It was established that for fillers of strong surface polarity the Lewis acid-base interaction has to be taken into account besides disperse forces when calculating the strength of interactions. For surface treated fillers of nearly apolar surfaces the acid-base interactions were negligible.

The effect of organoclay preparation on the structure and properties of polymer layered silicate nanocomposites, including orientation of treating agents in the gallery between the clay platelets, was studied in details. The results proved that the aliphatic chains of the treating agent were oriented parallel to the platelets of montmorillonite, and two adsorbed layers of treating agent could sufficiently dislocate the platelets for exfoliation during processing. We can assume that the attractive forces among the treated layers are so weak, that under ordinary processing conditions delamination occurs in all cases.

2.1.6 Biologically degradable polymers

Szilvia Klébert, Béla Pukánszky

With expanding interest in the environmental protection, there is a growing demand for the preparation and application of biologically degradable polymers. Research in this field has been started in our department more recently by focusing on two methods: *(i)* modification of natural polymers and *(ii)* synthesis of aliphatic polyesters. Cellulose acetate was grafted with caprolactone and plasticized starch was prepared for producing biologically degradable composites.

2.1.7 Synthesis of well-defined polymer architectures

Tibor Erdey-Grúz, Tamás Fónagy, Béla Iván,Orsolya Kovács, István Szanka, Márta Szesztay

Allyl-terminated polystyrenes (PSt-allyl) with molecular weights (MW) of 1000, 2000, 10000 and 18000 g/mol were synthesized by atom transfer, radical polymerization (ATRP) of styrene initiated with 1-phenylethyl bromide or 1-phenylethyl chloride and catalyzed by copper(I) halogenides, followed by reaction with allyltrimethylsilane through a carbocationic intermediate. The prepared PSt-allyls were used as comonomers in metallocene catalyzed propylene polymerization in collaboration with the Institute of Polymer Research, Dresden, Germany. The effects of temperature, propene pressure and MW of macromonomers on the structure of graft copolymers were investigated. It was found that the incorporation of polystyrene was increased with decreasing molecular weight of the macromonomer, increasing temperature and decreasing pressure of propylene. Finally, the compatibilisation efficiency of these new copolymers in polystyrene/polypropylene blends was explored. It was found that relatively high amount of graft copolymer was necessary to reach sufficient compatibilisation. Copolymers with shorter polystyrene side chains showed better effect than those with longer side chains.

2.1.8 Quasiliving carbocationic polymerization

Péter Werner Groh, Béla Iván, Árpád Máthé, Zsuzsanna Nagy, Viktória Pálfi, Mijid Narmandakh, Kálmán Tóth, Márta Szesztay

Systematic investigations were carried out on the effect of nucleophilic additives (Lewis bases) on the quasiliving carbocationic polymerization (QLCCP) of isobutylene. We have found differences in the molecular weight distributions and the stabilities of the growing chain ends in the presence of nucleophiles of different chemical structure. This indicates the influence of the Lewis acid coinitiator - nucleophile complex on the polymerization by influencing the quasiliving equilibrium between the propagating and non-propagating chain ends. The use of certain nitrogen-containing, chelating nucleophiles in the QLCCP of isobutylene resulted in isobutylene oligomers with ultra narrow molecular weight distribution.

We have also studied the solvent effect in the QLCCP of isobutylene by applying new solvents or solvent mixtures. According to our results, the reaction has a strong solvent effect. It is due to not only the differences of solvent polarity but the chemical structure of the solvent,

as well. By using benzotrifluoride as reaction medium, we have synthesized polyisobutylenes with well-defined molecular weight and a narrow molecular weight distribution in the temperature range of -20 to 0°C.

The control of QLCCP and the high stability of the growing carbocations in QLCCP make possible synthesis of polymers with functional groups on the chain ends. These functional groups can be transformed to other desired end-groups. For the same reason, QLCCP synthesis of block copolymers for many applications can be carried out by simple sequential monomer addition. The kinetic investigations of QLCCP of isobutylene and styrene resulted in the synthesis of well-defined poly(isobutylene-*block*-styrene) copolymers.

2.1.9 Amphiphilic co-networks

Attila Domján, Gábor Erdődi, Márton Haraszti, Béla Iván, Péter Mezey, Sándor L. Szabó

Amphiphilic co-networks are multicomponent polymer systems composed of covalently bonded hydrophilic and hydrophobic chains. The two immiscible polymers are interconnected by covalent linkages resulting in a unique nanostructured material different from other amphiphilic multicomponent polymeric systems such as block copolymers and interpenetrating networks.

In our experiments the hydrophobic polymer components were polyisobutylene or polydimethylsiloxane, while the hydrophilic parts were poly(methacrylic acid), poly(acrylamide), poly(dimethylaminoethyl methacrylate) or poly(hydroxyethyl methacrylate). Current efforts concentrate on better understanding the structural characteristics of amphiphilic co-networks, and explanations for the new phenomena discovered in these materials.

2.1.10 Research in electrochemistry and corrosion

Béla Lengyel, Tamás Pajkossy, Éva Dániel-Fekete, Gabriella Lendvay-Győrik, Gábor Mészáros

Research in electrochemical and corrosion led to the following results:

- Correlation of flicker noise with the over-voltage of redox systems has been studied. We concluded that an increasing over-voltage broadened the frequency range where the flicker noise exceeded the thermal one.
- Based on measurements of double layer capacitance in aqueous solutions on Pt(111) electrodes, we established that the potential of zero free charge cannot be determined by particular measurements.
- Measurements characterizing corrosion rate of zirconium alloys in high temperature aqueous solutions have been evaluated.
- Electrochemical impedance spectroscopy and standard accelerated corrosion tests were used to study the change of the corrosion protection of water-borne coatings due to outdoor exposure.

2.1.11 Research in electrosorption and electrocatalysis

György Horányi

It was demonstrated that the radiotracer technique could furnish new information on the specific adsorption of simple organic acids on hematite and γ-Al_2O_3 surfaces, respectively. The results obtained with NOM (natural organic matter) analogous organic acids may help in understanding some geochemical processes. Anions formed from organic acids studied in this work played predominant role in the adsorption processes.

The reduction of ClO_4^- was studied at Fe/electrolyte interfaces in acidic medium. The rate and extent of the interaction of ClO_4^- ions with iron resulting in Cl^- ions were commensurable with those of proton discharge leading to formation of H_2. Consequently, the entire literature dealing with corrosion or anodic dissolution of iron in perchloric acid or acidic perchlorate should be revised and the published data should be subjected to a critical analysis. This work is in progress.

As a continuation of our previous work on the adsorption behavior of oxides, the specific adsorption of sulfate and chloride ions was studied on powdered Bi_2O_3, Cr_2O_3, CuO and TiO_2 samples, respectively, by radiotracer technique. A large excess of perchlorate was ensured in the experiments. Similarly to other oxides such as Al_2O_3 and Fe_2O_3, the extent and pH dependence of adsorption is determined by the protonation of the oxide surfaces. Results obtained for Bi_2O_3 contribute to the understanding and interpretation of the behavior of Bi metal and Bi adatom layers in metal/electrolyte interface. Role of the anion adsorption in the dissolution of CuO in acidic medium was demonstrated.

2.1.12 Research in electrocatalysis

Sándor Szabó, István Bakos

During research of rhenium adsorption on Pt surface it was established that from the sulfuric acid solution of $(NH_4)_2ReCl_6$ some rhenium oxide was precipitated instead of Re^0 as expected.

Studies on corrosion properties of Al-Cu bimetallic system were started. Preparation methods of samples were developed to have reproducible experimental results. Corrosion potential and corrosion rate of aluminum were determined for solutions of different chloride content. Corrosion behavior of aluminum in the presence of copper ions was investigated, as well.

Total catalytic total oxidation of chlorinated hydrocarbons and the industrial application of the new process have been studied. A bimetallic catalyst was developed for the purification of air containing volatile, chlorinated hydrocarbons.

2.1.13 Synthesis and characterization of metal complexes

Béla Kazinczy, László Kótai, Klára Szentmihályi, Péter Vinkler

The intramolecular redox reactions of ionic perchlorate and permanganate complexes have been studied by TG-MS and XRD. Copper- and zinc-permanganate complexes containing ammonia ligand were subjected to redox reaction above 100^oC: water, ammonia and ammonium nitrate were evolved and compounds of $MeMnO_2$ type were formed. There was no oxygen formation in particular conditions.

Natural metal complexes (malates, polygalacturanates) were prepared, and investigated by FT-IR, Raman spectroscopy, DSC, TG and XPS. Their free radical scavenger activity was studied by chemiluminescence measurements (H_2O_2/·OH-microperoxidase-luminol system), and by LDL oxidation (H_2O_2-hem-LDL system), respectively.

2.1.14 Analysis of medicinal plants and studies on their efficiency

Pál Apáti, Anna Blázovics, Klára Szentmihályi, Péter Vinkler

Medicinal plants with antiphlogistic activity and used in liver therapy were analyzed by UV spectrometry, GC, GC-MS, HPLC and ICP-OES. Their efficiency was studied *in vitro* (e.g. free radical scavenging activity) and *in vivo*, rerspectively. Our activities were connected to research on gastroenterologic diseases, more precisely to studies on the metabolic changes of essential and toxic elements.

2.2 Research in environmental chemistry

2.2.1 Analysis of organic materials in atmospheric aerosols

Marianne Blazsó

The organic carbon content of fine aerosols plays an important, yet undetermined role in the atmospheric processes. The organic material in troposphere aerosols has been studied in co-operation with the Air Chemistry Group of the Hungarian Academy of Sciences, University of Veszprém, Hungary, by thermally assisted hydrolysis and methylation, coupled to GC/MS. The results help to elucidate the source of organic materials in fine aerosols, moreover, to reveal processes taking place in the atmosphere.

2.2.2 Application of liquid chromatography in the environmental protection

Eszter Forgács-Tóth, Annamária Jakab

We developed new, high-performance liquid chromatography supports covered by plant proteins and cholesterol. Their retention characteristics were determined along with their application in pharmaceutical and environmental analysis. We continued our studies on the relationship between the molecular structure and the chromatographic retention behavior.

New analytical methods were developed and studied to solve some environmental problems. The molecular interactions of environmental pollutants were studied by LC-MS.

The retention parameters of various compounds (drugs, peptides, pesticides and surfactants) were determined on amide embedded ROP silica, polyethylene-coated alumina and monolith silica columns. Relationships among retention and physicochemical parameters were elucidated by statistical methods. It was concluded that the retention of particular compounds was controlled by both sterical and polarity parameters referring to a mixed retention mechanism.

2.2.3 Development of systems for pollution surveillance and control

György Mink, László Horváth, István Lengyel

In the last couple of years, RLMEC developed and installed two monitoring and control systems in the DUNAFERR Iron and Steel Co. One system was dedicated to the on-line analysis of coke furnace gases, while the other one to monitoring and control of cyanides in wastewater. Both systems were improved more recently, based on operational data collected on-site.

2.2.4 Studies on the utilization of biomass materials by thermal methods

Gábor Várhegyi, Emma Jakab, Erika Mészáros, Ferenc Till

Plants improved for energy production were studied by thermogravimetry, thermogravimetry – mass spectrometry and by reaction kinetic analysis in inert gas flow, as well as in the presence of oxygen. The temperature programs were composed of non-isothermal and isothermal sections, to gain information in a wide range of experimental conditions. The samples included poplars, acacia, willow and Micanthus sinensis, and their isolated components such as lignins and extracted materials, respectively. We and interpreted the observed similarities and differences in the thermal behavior of particular samples.

Dependence of wood properties on their origin was studied in international research cooperation. An other cooperation was aimed at preparing high value-added biocarbons.

2.2.5 Research and development in solar thermal area

György Mink, László Horváth

A prototype of a low cost, flat plate collector fabricated from solar grade plastic material has been developed, tested and analyzed in co-operation with the Polytechnic of Dunaújváros. Because of theoretical reasons, the efficiency of the new module is about 20% lower than that of the state-of-the-art solar collectors utilizing selective absorbers. However, for a 20 years lifetime it offers a cost reduction of 30-40% in domestic hot water production, due to the much lower investment and maintenance costs.

In co-operation with the Cagliari University cheap and highly efficient, floating-type solar still modules have been designed and tested in order to utilize shallow ponds (former salt plants) for fresh water production.

2.2.6 Degradation and modification of PVC

Tibor Szakács, Béla Iván

The mechanism of PVC degradation in different solvents was studied. A copolymer of vinyl chloride and 1-chloropropene (~1%) was synthesized, and the effect of incorporated tertiary chlorine atoms as artificial defects on the stability of PVC was investigated. Moreover, the polyene sequences of partially degraded PVC were transformed to epoxy groups in order to test the resulting material as secondary stabilizer of PVC.

2.2.7 Studies on the recycling of plastics and polymer mixtures by pyrolysis

Marianne Blazsó, Emma Jakab, Zsuzsanna Czégény

Our research focused on chemical processes having importance in the pyrolytic recycling of plastic wastes and on reaction conditions promoting or hindering evolution of polluting decomposition products. We performed detailed studies on the interactions of thermal decomposition reactions of different constituents of polymer mixtures by pyrolysis/GC-MS. Evolution of volatiles was followed by pyrolysis-MS or thermogravimetry-MS.

Thermal stability of polyolefins and vinyl polymers was more or less increased when they were pyrolyzed together with PVC, possibly because of the hindrance of radical decomposition reactions by the polyene residue of dehydrochlorinated PVC. Direct effect of hydrogen chloride evolved from PVC resulting in immediate depolymerisation had been observed only in PA-6. Chlorination of the macromolecular moieties leading to chlorinated products upon pyrolysis was rarely detected. Polymers containing polarized moieties may promote dehydrochlorination of PVC. Amide groups in various polyamides and nitrile groups or cycled ladder sequences in PAN similarly help hydrogen chloride elimination by loosing C-Cl bonds.

Brominated bisphenol A segments in brominated epoxy resin partially debrominated under pyrolysis. Change of bromine to hydrogen on the phenolic ring may proceed through a cyclic rearrangement involving the glycidyl ether segment of the epoxy resin. Inorganic bases may promote the reaction.

2.2.8 Theoretical and empirical studies on batch extractive distillation

László Horváth

In co-operation with the Department of Chemical Engineering of the Budapest University of Technology and Economics, we developed a state-of-the-art rectifying system for the separation of azeotropic mixtures with a middle boiling entrained component. Separation of methyl acetate and cyclohexane (a minimum boiling azeotrope) and that of chloroform and ethyl ace-

tate (a maximum boiling azeotrope) using carbon tetrachloride and 2-chlorobutane, respectively, have been studied both theoretically and experimentally, using profile maps and rigorous simulation.

2.2.9 Processing of hazardous organic compounds in RF thermal plasma

Ilona Mohai, Katalin Főglein Zoltán Károly, János Szépvölgyi

Decomposition of $CHCl_3$ and $CFCl_3$ was investigated in a radiofrequency (RF) thermal plasma reactor in neutral and slightly oxidizing conditions, respectively. In neutral conditions highly disperse soot, and chlorinated- and/or fluorinated benzenes were formed as main products. Several polycyclic and aromatic compounds were identified by GC-MS in both the exhaust gas and the toluene extract of the soot.

Thermodynamic calculations were performed on the thermal plasma decomposition of CFC-s and Halons in the presence of argon and/or oxygen. By comparing results of thermodynamic calculations with experimental data, we could interpret the mechanism of soot formation.

Vitrification of metallurgical wastes in thermal plasmas – in both arc and RF-plasma furnaces – was investigated to produce stable and unleacheable materials. We concluded that metallurgical wastes could be converted to vitrified products in oxidative conditions by using glass-forming additives such as silica and alumina.

2.2.10 Utilization of industrial wastes

Béla Kazinczy, László Kótai, Klára Szentmihályi, Péter Vinkler

In this field, the following topics were investigated: *(i)* utilization of processing residues of medicinal plants, *(ii)* recovery of the useful components from galvanic sludge and (iii) recycling of spent baking oil.

Processing residues of medicinal plants were subjected to detailed analysis including ICP-OES, GC and HPLC to establish their composition with a special emphasis on further utilization.

The galvanic sludge contains substantial amounts of zinc. Different chemical methods were developed for its separation. Thus, the sludge being originally a hazardous waste can be utilized as secondary raw material.

It was proved that spent baking oils could be transformed to biodiesel by proper treatment.

3 PARTICIPATION IN NATIONAL RESEARCH PROJECTS

Hungarian Scientific Research Fund (OTKA)

- XPS study of the stability of supramolecular Langmuir-Blodgett systems (T25789)
- Modification of polyethylene surfaces by low-energy, inert and reactive ion beams (T29733)
- Preparation of solid catalysts by structural and surface modification, and their application in transformation of organic compounds (T30156)
- Investigation of layer structures containing C_3N_4 és CN_x (T30424)
- Investigation of mechanical properties of modified surface layers (T30833)
- EIS (Electrochemical Impedance Spectroscopy) method extended to medium amplitude perturbation and its application to corrosion research (T29727)
- Studies on relaxation processes at metal/electrolyte interfaces (T30150)
- Role of classical and modern methods in the contemporary research of electrocatalysis and electrosorption (T31703)
- Studies of rhenium, iridium and rhodium adsorption on other metal surfaces, and acceleration of corrosion by rhenium (T31846)
- Corrosion properties of copper-aluminum bimetallic systems (T37693)
- Structure – property relationships in heterogeneous polymers (T30579)
- Studies of interfacial phenomena in heterogeneous polymers (T29719)
- Studies on factors determining the extent and mechanism of polymer degradation and investigations on certain problems of stabilization (T37687)
- Beta-polypropylene and its binary systems (T34230)
- Quasiliving, radical polymerizations (T29711)
- Research on the biocompatibility of amphiphilic conetworks (F29728)
- Studies on the swelling dynamics of new, amphiphilic conetworks (F31901)
- Synthesis of new, asterisk polymers and studies on their solutions (T33107)
- Studies on the decomposition of hazardous wastes in thermal plasmas (T32272)
- Basic research by thermal analysis for the optimum utilization of biomass fuels (T37705)
- Development of new MINP models for mass transfer networks (F35085)
- Interaction of thermal decomposition reactions in polymer mixtures (T33111)
- Effect of additives on thermal decomposition reactions in waste utilization (T37704)
- Studies on the thermal decomposition of hazardous, polychlorinated organic compounds in high temperature, thermal plasmas (T29734)

Other Hungarian research grants

- Development of human joint prostheses for long service life (NKFP 1/013/2001)
- Research on complex prevention methods for improving the hygienic state in Hungary: in vitro and in vivo investigations on natural antioxidants (NKFP 1/016/2001)

- Design of drugs and diagnostics based on validated target molecules: investigation of natural organic substances and their metal complexes with free radical scavenger activity (NKFP 1/047/2001)
- Development of environmentally friendly, marketable products in the aluminum industry (NKFP 3/035/2001)
- Production and application of composite materials based on natural resources and/or bio-degradable components (NKFP 3A/0036/2002)
- Poliamide-6 nanocomposite (OM K+F ALK-00151/2001)
- Importance of non-nutritive alimentary factors in the therapy of liver and inflammatory bowel diseases: experimental and human studies (Ministry of Welfare, ETT 250/2000)
- Measuring system for the comprehensive research of hybrid separation processes (OM 02335/2000).
- Purification of soil and groundwater contaminated by chlorobenzenes (OM 00919/2002)

4 PARTICIPATION IN INTERNATIONAL RESEARCH PROJECTS

Research Pojects of the European Community

- New surface modified flame-retarded polymeric systems to improve safety in transportation and other areas (FLAMERET; G5RD-CT-1999-00120).
- Novel surface engineered counterface systems for prostheses application (NSE PRO; G5ST-CT-2002-50247).
- Novel arc plasma process for the decomposition of hazardous wastes and for the simultaneous producton of valuable building materials (WASTILE; GRDI-2000-25035)
- Process integrated thermal chemical treatment of halogen-containing materials as source of halogen-free fuels for steel production, and residues for noble metal recovery (HALOCLEANCONVERSION; G1RD-CT-1999-00082)
- Waste management and recycling of WEEE-process integrated thermochemical treatment of halogen-containing materials (HALOCLEANAPPLICATION; G1RD-CT-2002-03014).

Other research cooperations

- Determination of the potential of zero charge of Pt(111) electrodes (MÖB-DAAD program; cooperation with the Department of Electrochemistry, Ulm University, Germany)
- Synthesis and reactions of permanganate salts (MTA-INSA 3/2001-2003; cooperation with Jodhpur University, India)
- Study on preparation and properties of organic adsorbents and catalyst supports (MTA-INSA 8/2001-2003; cooperation with the Indian Institute of Technology, Hyderabad, India)
- Development of polymer composites reinforced with hemp fibre (Hungarian – South African cooperation DAK-2/2001)
- Development of new analytical methods for studying the environmental impact of hazardous materials and drugs (cooperation with the Department of Drug Chemistry, Medical University of Gdansk, Poland)
- Studies on the biological and environmetal effects of anionic surfactants (cooperation with the Insititute of Polymer Chemistry, Bratislavla, Slovakia)
- Electolytic modifiers of the background in capillary electrophoresis (cooperation with the Insititue of Physiology, Prague, Czech Republic)
- Development and application of new methods for stabilizing coloring agents in red wines (cooperation with the National Institute of Agrochemistry, Lisbon, Portugal)

5 PARTICIPATION IN THE UNIVERSITY EDUCATION

In 2002, coworkers of RLMEC delivered the following graduate and post-graduate lectures:

Budapest University Technology and Economics

- Advanced methods for surface modification and investigation (lecture course by Imre Bertóti)
- Introduction to materials science (lecture course by Imre Bertóti)
- Electronics and instrumentation (lecture course by Tamás Pajkossy)
- Electronics and measurement techniques (lecture course by Tamás Pajkossy)
- Environmental chemistry (lecture course by János Szépvölgyi)
- Plastic materials. Processing of plastic materials. Physics of plastic materials. Polymer mixtures and composites (lecture courses by Béla Pukánszky)
- Applications of plastics (lecture course by Erika Bódi-Fekete)
- Plastic materials and environmental protection (lecture course by Enikő Földes)
- Electronics laboratory course (Gábor Mészáros)
- Laboratory courses in application of plastics and technology of plastic materials (Tünde Pozsgai, János Móczó, Szilvia Klébert, Erika Bódi-Fekete, Enikő Földes)

Central European University, Budapest

- Environmental chemistry (PhD course by János Szépvölgyi)

Eötvös Lóránd University, Budapest

- Polymer chemistry and technology. Fundamental macromolecular chemistry. Designed synthesis of polymers. Physical, organic and analytical principles of molecular engineering of macromolecular systems (lecture courses by Béla Iván)
- Electrocatalysis (PhD course by György Horányi)
- Thermal degradation of polymers (lecture course by Marianne Blazsó)
- Laboratory courses in chemical technology (Gábor Erdődi, Sándor Szabó, Béla Iván, Tamás Fónagy, Péter Groh Werner)
- Laboratory course in physical chemistry (Gábor Mészáros)
- Laboratory course in plasmachemistry (Ilona Mohai, Zoltán Károly)

Miskolc University

- Advanced ceramic materials (PhD course by János Szépvölgyi)

Polytechnic of Dunaújváros

- Renewable sources of energy (lecture course by György Mink)

Semmelweis University, Budapest

- The role of metals and metal complexes in free radical processes (PhD course by Klára Szentmihályi)
- Laboratory course in pharmacognosy (Pál Apáti)

Veszprém University

- Advanced ceramic materials (lecture course by János Szépvölgyi)

6 INDUSTRIAL R&D PROJECTS

- **AKZO-NOBEL Coatings Ltd.**
  Characterization of AKZO paint systems
- **BASF AG**
  Participation in solving different R&D problems
- **Béres Pharmaceutical Co.**
  Production of effective bone strengthening medicine
- **Clariant Huningue SA**
  Development of new stabilizers
- **Clopay Plastic Products Co.**
  Studies on interfacial phenomena in polymer composites
- **Du Pont Co.**
  Participation in solving different R&D problems
- **DUNAFERR Rt.**
  Development of monitoring systems for environmental protection
  Processing of metallurgical wastes in thermal plasmas
- **General Electric Hungary Co.**
  Participation in solving different R&D problems
- **IN VITRO R&D Ltd.**
  Production of an effective substance for the therapy of anaemia
- **Kalle Nalo Hungaria**
  Investigation of multilayered polymer foils
- **Middle-Tisza Agricultural Co.**
  Preparation of biofuels from waste vegetable oils
- **MAGYAR LAKK Ltd.**
  Characterization of industrial and commercial paints
- **Ministry of Environmental Protection**
  Studies on the fixation of organic pollutants in soil-plant systems
- **NABI North American Bus Industries Ltd. Co.**
  Comparison of coatings developed from different paints of low solvent content
- **RONA-CRYSTAL**
  Surface analysis of corroded glass surfaces by XPS
- **SANYO Energy Europe Co.**
  Development of polymer/LCP mixtures
- **Tetra Pak Packaging Material Production Ltd.**
  XPS investigations on flame treated, paper packaging materials
- **TVK Co.**
  Development of polyethylene and polypropylene products
- **University of Cagliari**
  Design and construction of a solar still for education and demonstration purposes

7 RESEARCH FACILITIES

Department of Materials Chemistry

- X-ray photoelectron spectrometers (Kratos XSAM 800, VG Escascope)
- Fast atom beam treatment facility
- RF glow discharge treatment facility
- Nanotribology tester (Nanotest 600)
- ICP-OES spectrometer (Jarell-Ash Atomscan 25)
- High temperature reactors for gas-solid reactions
- RF induction plasma systems (Linn, Tekna)
- Spectrometer with CCD-3000 detector (Jobin-Yvon TRIAX 550)
- Electrochemical measuring techniques (potentiostatic and galvanostatic, stationary and transient voltametric facilities, electrode impedance spectroscopy, noise spectroscopy, harmonic analysis)
- Determination of corrosion rate in high-resistance systems
- Rapid corrosion resistance tests
- Methods for the evaluation of lifetime and paint-technological properties of coatings
- Polarography-voltametry

Department of Polymer Chemistry and Materials Science

- Gelpermeation chromatograph (Waters 510)
- Laboratory ozonizer (Yanko Industry Ozone Services)
- Tester of PVC degradation (Donaulab)

Department of Applied Polymer Chemistry and Physics

- Laboratory rolling mill (Schwabentan)
- Single-screw extruder (Haake Rheomex S 3/4")
- Twin-screw compounder (Brabender DSK 42/7)
- Internal mixer (Brabender, 50 ml)
- Laboratory press (Fontijne SRA 100)
- Injection molding machines (Battenfeld BSKM 30/50, BA 200 CD)
- High-speed fluid mixer (Thyssen Henschel FM/A10)
- Vacuum thermoforming machine (VFP 0505 1SL)
- Thermal analyzers (Perkin Elmer DSC 2, DSC 7, TGA6, Mettler DSC 30, TMA 40, TGA)
- Thermomechanical analyzer (Polymer Labs, DMTA II)
- Fourier transform infrared spectrophotometer (Mattson Galaxy 3000)
- UV-VIS spectrophotometer (Hewlett Packard 8452A)
- Rheometry (Göttfert 2002 capillary viscometer, Göttfert MPS-D MFI tester, Brabender Rheotron rotational viscometer, Rheolab rheometer, Physica UDS 200 Universal Dynamic Spectrometer)
- Mechanical testing system (Zwick 1445, Fritz Heckert FPZ 10, Instron 5566)
- Impact testers (Ceast Charpy 6546, Ceast Resil 5.5, Zwick, Izod, Charpy)
- Optical instruments (Hot Stage Mettler FP 82 HT, Polaroid DMC1 digital camera, Hunter-lab ColourQuest 45/0)
- High pressure liquid chromatograph (Knauer HPLC 64)
- Gas chromatograph (Perkin Elmer XLGC)
- Microtome (Reichert-Jung, Polycut)
- Contact angle goniometer (Rame-Hart 100-00-(115)-S Automated Goniometer)

Department of Environmental Chemistry

- Thermobalance-mass spectrometer system (Hiden Hall 300 PCI, Perkin-Elmer TGS-2)
- High pressure thermobalance (Hiden Hall IGA, high temperature furnace)
- Reactive thermobalance (Mettler)
- Analytical pyrolysers (CDS Pyroprobe 2000)
- Gas chromatograph-mass spectrometer system (HP 5985B)
- Gas chromatograph (HP 5880A)
- Laser-diffraction particle size analyzer (Malvern 2600C)
- Fourier transform infrared spectrometer (Perkin Elmer 1700)
- Volumetric adsorption system for studying adsorption and chemisorption
- Differential scanning calorimeters (Setaram DSC 111, Perkin Elmer DSC 2)
- Solar still simulator
- Two-column GC with automatic dosing system (Perkin-Elmer Autosystem XL)
- Semi-preparative HPLC equipment (Waters LC-Module 1)
- HPLC/MS facility (Shimadzu LCMS 2010)
- HPLC equipment (Waters 9110)
- HPLC system (Merck Hitachi)
- Pump for column preparation (Shandon)
- Equipment for evaluating thin-layer chromatograms (Shimadzu)
- UV-VIS-NIR spectrophotometer (Jasco)

Laboratory of Environmental Protection

- UV-VIS spectrophotometer (Unicam)
- ICP-OES spectrometer (Jobin-Yvon Ultrace 138)

8 PUBLICATIONS IN 2002

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