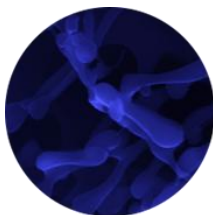




Brochure of ABIOG Partners

4th Meeting of **ABIOG** Project Management Committee & Workshop

18-20 January 2017, Cracow, Poland



EDITORIAL

Brochure of ABIOG Partners - 4th Meeting of **ABIOG** Project Management Committee & Workshop published by the Department of Biotechnology and Physical Chemistry, Faculty of Chemical Engineering and Technology, Cracow University of Technology.

The technical editors were Wiktor Kasprzyk and Szczepan Bednarz.

WELCOME ON THE 4TH ABIOG MANAGEMENT COMMITTEE MEETING & WORKSHOP OF PARTICIPANTS

On behalf of ABIOG project management committee, we sincerely welcome you in Cracow during the 4th project management committee meeting linked with the workshop of selected participants from the V4 countries included in the ABIOG project.

It is a great honor to give place for the next ABIOG meeting at Cracow University of Technology. We hope you will enjoy your stay in Poland.

We believe that this initiative in the frame of Visegrad Found will help us to develop the closer cooperation among our Institutions and to improve the competitiveness in the attracting international projects.

Best Regards,

Polish Members of ABIOG

PROGRAM

January, 18, 2017: Arrival

January, 19, 2017: Workshop

9:30 - 9:35:	WELCOME	
	Szczepan Bednarz	(Poland)
9:35 - 9:45	Introduction of CUT	
	Dariusz Bogdał	(Poland)
9:45 - 10:15	Introduction of PISAS	
	Juraj Kronek	(Slovakia)
10:15 - 10:35	Cristian Peptu	(Slovakia)
10:35 - 11:05	Introduction of IMC	
	Hynek Beneš	(Czech Republic)
11:05 - 11:25	Jana Kredatusová	(Czech Republic)
11:25 - 11:40	<i>Coffee break</i>	
11:40 - 12:10	Introduction of BUTE	
	Balázs Kirschweng	(Hungary)
12:10 - 12:30	Csaba Németh	(Hungary)
12:30 - 12:50	Barnabás Szilágyi	(Hungary)
12:50 - 13:10	Dóra Barczikai	(Hungary)
13:10 - 14:30	<i>Lunch</i>	
	Delegates of CUT	
14:30 - 14:45	Termeh Darvishzad	(Poland)
14:45 - 15:00	Joanna Ortyl	(Poland)
15:15 - 15:30	Katarzyna Matras-Postolek	(Poland)
15:30 - 15:45	<i>Coffee break</i>	
15:45 - 16:00	Agnieszka Leszczyńska	(Poland)
16:00 - 16:15	Tomasz Majka	(Poland)
16:15 - 16:30	DISCUSSION	
18:00 -	<i>Dinner</i>	

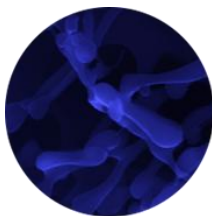
January, 20, 2017: Laboratory visits

9:30 - 12:00 (est.) Laboratory visits, ABI OG administration

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INTRODUCTION TO ABIOG PROJECT



The project develops closer cooperation among the V4 countries in the field of biomaterial science by founding the Advanced Biomaterials Group (ABIOG), which will promote scientific exchanges, research and innovations. The main aim of the project is to create the ABIOG composed of researchers from four Visegrad countries: Poland – Cracow University of Technology, Czech Republic - Institute of Macromolecular Chemistry AS CR, Slovakia - Polymer Institute SAS and Hungary - Budapest University of Technology and Economics, specialized in the field of synthesis and characterization of polymeric biomaterials.

The project is funded by International Visegrad Fund under Small Grant Programme.

For more information please visit www.abiogproject.eu



The International Visegrad Fund is an international organization based in Bratislava founded by the governments of the Visegrad Group (V4) countries - the Czech Republic, Hungary, the Republic of Poland, and the Slovak Republic—in Štířín, Czech Republic, on June 9, 2000.

The purpose of the fund is to facilitate and promote the development of closer cooperation among citizens and institutions in the region as well as between the V4 region and other countries, especially in the Western Balkan and Eastern Partnership regions. The fund operates several grant programs, and also awards individual scholarships, fellowships and artist residencies. Grant support is given to original projects namely in the areas of culture, science and research, youth exchanges, cross-border cooperation and tourism promotion, as well as in other priority areas defined in calls.



Polymer Institute of the Slovak Academy of Sciences Bratislava, Slovakia

Polymer Institute SAS represents an important research and training center for fundamental and applied research in the contemporary topics of polymer chemistry. The Institute activities cover four areas: synthesis and characterization of polymers, composite polymeric materials, polymeric biomaterials and molecular simulation of polymers.

The institute provides the specialized services, which include consultations, infrastructure and innovative solutions for partners from academic institutions, universities and industry both nationally and internationally. Nationally, the institute has a significant position in the area of polymer science and disseminates the information to the public about research activities, obtained results and applications.





Cracow University of Technology Cracow, Poland

Cracow University of Technology was established in 1946 and, as an institution of higher learning granted full autonomy in 1954. Currently CUT is educating over 19 000 students of both full-time and extramural studies as well as doctoral and postgraduate courses. Many of our 1200 researchers and teachers are distinguished specialists participating in intercolonial projects and international research studies. CUT is composed of seven faculties. One of them is Faculty of Chemical Engineering and Technology. The faculty was established in 1966, currently employs 111 researchers and academic staff. More than 1200 students study organic, inorganic and polymers technology as well as nanotechnology and industrial biotechnology.





Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic Prague, Czech Republic

The research activities of the Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic span virtually the whole polymer science.

Main trends of research in the IMC

- Biomacromolecular systems
- Dynamics and self-assembling of molecular and supramolecular polymer structures
- Preparation, characterization and use of new polymeric systems with controlled structure and properties

Going from polymer synthesis through physical chemistry of macromolecular systems to polymer physics and materials processing on one hand, or to biochemistry and biology on the other, one can always find within the Institute an expert in a particular field to get an advice or highly qualified collaboration on a project.





Budapest University of Technology and Economics Budapest, Hungary

The Department of Plastics and Rubber Technology established by Rudolf Balló at 1953, in order to train professionals to the fields of production, processing and application of polymers. The name of the Department changed to Laboratory of Plastics and Rubber and it merged with the Department of Physical Chemistry, forming the new Department of Physical Chemistry and Material Science in 2008. The head of the Department is Mihály Kállay, while Alfréd Menyhárd-Kállay leads the Laboratory. The Department is in close cooperation with the Institute of Materials and Environmental Chemistry, which belongs to the Research Centre for Natural Sciences of the Hungarian Academy of Sciences.

Activities of the Laboratory expanded and changed during the years both from research and education points of view. Pioneer work has been done in the fields of polymer physics, and polymer blends and composites. Our interest turned to bio-related materials lately, in aspects of biopolymers, biodegradation, natural additives and materials for healthcare products.



Functional poly(2-oxazoline)s as advanced biomedical materials

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The research of Department for Biomaterials Research is oriented on study of polymers and biopolymers for different biomedical applications. Our key topics are: a) encapsulation of living cells towards the diabetes treatment, b) biomaterials based on 2-oxazoline chemistry, c) polymers for anti-cancer therapy, d) zwitterionic non-biofouling/biocompatible polymers and hydrogels, e) kinetics and mechanism of free-radical polymerizations of water-soluble monomers, and f) evaluation of biocompatibility of polymers and polymeric materials.

Poly(2-alkyl-2-oxazoline)s (POx) belong to a class of biomedical polymers due to their excellent biocompatibility, low (immuno)toxic effects, and stealth behavior.¹⁻³ Moreover, their preparation via living cationic ring-opening polymerization of 2-oxazolines enables to control over size, topology and functionality of polymers.⁴

Our effort is focused on the synthesis of functional polymers based on 2-oxazolines which can be used for the preparation of conjugates with biomolecules, nanoparticles, and hydrogels.

Acknowledgement: Authors are thankful the Slovak Grant Agency VEGA for the financial support in the project VEGA 2/0163/15

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STRUCTURAL IDENTIFICATION OF AZOFUNCTIONAL ALIPHATIC OLIGOESTERS

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Aliphatic polyesters benefited an intense research in the past decades including thorough investigations by the means of mass spectrometry. Several successful applications of ESI-MS and MALDITOF-MS for the determination of the structural architecture of individual (co)polyester macromolecules, including their topology, composition, chemical structure of the end groups, location of functional groups and comonomer composition distribution, have been reported [1,2]. Moreover, the deep study of fragmentation behavior in collision induced dissociation (CID) conditions made available by the means of ion trap attracts great attention in view of appealing possibilities to elucidate structural details of polyester samples with suitable molecular weight. One particular feature observed by several authors [3,4,5] was the charge exchange fragmentations reactions occurring during the fragmentation processes. Although, the conditions for the appearance of this reactions are not yet clarified their occurrence may present a pattern, useful in structure elucidation by CID fragmentation studies. This prompted us to study a series of model azofunctional oligoesters [6, 7](figure 1) in ESI MS and tandem MS.

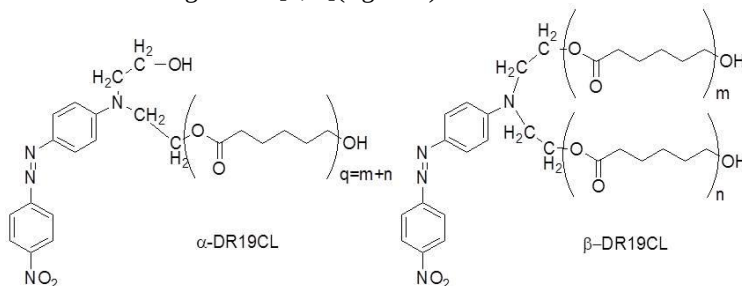


Figure 1. Structural representation of azofunctional oligoesters

The considered structures are well defined oligocaprolactones linked through ester bonds to the azo dye. Our aim is to investigate the dissociation pathways of $[M-Na]^+$ parent ions and also to compare their dissociation under CID conditions. The final goal is to elucidate the structural differences between

azofunctional oligoesters by comparing the results obtained through different analytical methods: NMR, LC UV/VIS, LC MS and LC MS/MS.

Acknowledgement

The research is financed from the SASPRO Programme. The research leading to these results has received funding from the People Programme (Marie Curie Actions) European Union's Seventh Framework Programme under REA grant agreement No. 609427. Research has been further co-funded by the Slovak Academy of Sciences.

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POLYURETHANES DERIVED FROM NATURAL OILS AND RECYCLED POLYOLS

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Polyurethanes (PUR) combining renewable bio-based raw materials (natural oils) and recycled polyols from PUR and polycarbonate wastes were prepared and characterized. The recycled polyols were synthesized using rapeseed, castor, coconut and fish oil derivatives bearing hydroxyl groups on glyceride units. Based on the type of natural oil used, flexible PUR casts, semirigid or rigid PUR foams were prepared [1-3].

Acknowledgement

Financial support of the International Visegrad Fund under Small Grant Programme (grant no. 21620101) is gratefully appreciated.

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MICROWAVE SYNTHESIS OF PCL/LDH NANOCOMPOSITES

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In-situ polymerization of ϵ -caprolactone (CL) in the presence of layered double hydroxide (LDH) modified ionic liquids (IL) has been recently studied by our groups [1]. We found that the successful modification of LDH with phosphonium-based ILs leading to formation of intercalated IL-anion was able to catalyse ring-opening polymerization of CL and simultaneously to promote exfoliation of LDH. The whole process was accelerated using microwave irradiation, since 85 – 95 wt. % yield of polymer (depending on the LDH content) was reached within only 3 min of microwave irradiation. Within the same time, nanocomposites with fully exfoliated nanofiller morphologies were obtained.

Acknowledgement

Financial support of the International Visegrad Fund under Small Grant Programme (grant no. 21620101) is gratefully appreciated.

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Kredatusová, Jana, et al. "Influence of ionic liquid-modified LDH on microwave-assisted polymerization of ϵ -caprolactone." *Polymer* 100 (2016): 86-94.

STABILIZING EFFICIENCY OF QUERCETIN AND RUTIN UNDER PROCESSING CONDITIONS – A COMPARATIVE STUDY

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Stabilizers must be used in order to protect polyolefins during processing. Because of possible physiological effects of the metabolites of synthetic phenolic antioxidants, the interest is focused on the use of natural antioxidants. Quercetin efficiently hindered the degradation processes of PE during processing [1], but high melting temperature and limited compatibility created problems. In our current work we investigated rutin, the glycoside of quercetin, and compared the stabilizing efficiency of the two natural antioxidant.

A Phillips type polyethylene was stabilized with 0 to 1000 ppm rutin or quercetin, respectively, and 1000 ppm Sandostab P-EPQ secondary antioxidant. The polymer and the additives were homogenized then extruded for six times in a single screw extruder. Samples were taken after each extrusion step, and characterized by FTIR, the measurement of color, rheology (MFR), and residual thermo-oxidative stability determination (OIT). All these aspects are discussed in the presentation.

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GASTROINTESTINAL DRUG DELIVERY WITH POLY(ASPARTIC ACID) DERIVATIVES

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Various polymers of natural or synthetic origin are used for the preparation of drug delivery formulations protecting the drug from environmental impacts and providing controlled and/or targeted delivery at the same time in the gastrointestinal tract. Acrylate copolymers have a leading role in this field because their physico-chemical and thermal properties can be controlled within wide limits by their chemical composition. However, there are general disadvantages of the polyacrylates such as the lack of biodegradability and their difficult synthesis, which may also imply considerable environmental pollution.

These drawbacks might be overcome by the application of the derivatives of the biocompatible and biodegradable poly(aspartic acid) (PASP). Contrary to the polyacrylates, PASP derivatives can be synthesized under mild reaction conditions [1]. We prepare dosage forms, such as conventional polymer films and advanced fibrous polymer matrices from PASP derivatives by using techniques like film casting or solvent electrospinning. The results of mechanical tests, water uptake, dissolution rate, and drug release measurements prove that these polymers are good candidates as alternatives of acrylate based polymers in drug formulation.

Acknowledgement

This research was supported by the New Széchenyi Plan (TÁMOP-4.2.1/B-09/1-2010-0002).

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IN SITU GELLING MUCOADHESIVE POLY(ASPARTIC ACID) DERIVATIVES

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Poor bioavailability of traditional ophthalmic drug formulations can be improved with mucoadhesive polymeric dosage forms which adhere to mucosal membranes providing a longer residence time and a controlled rate of drug release. Thiolated polymers and S-protected thiolated polymers can largely enhance the strength of mucoadhesion as they can form covalent disulphide linkages with cysteine rich subdomains of the mucus layer. [1] They also show *in situ* gelling property by oxidation of thiol groups or thiol/disulphide exchange reactions.

In our work poly(aspartic acid) (PASP) was chosen as the backbone of the mucoadhesive polymer derivatives. Thiolated poly(aspartic acid) was synthesised by reacting cysteamine and polysuccinimide and the subsequent hydrolysis of the polymer. S-protected derivative was synthesized by attaching thiopyridyl substructure to the thiol groups of the polymer. Structure of the polymers was confirmed by ¹H-NMR and UV-Vis spectroscopy. *In situ* gelation of the PASP derivatives was monitored by oscillation rheology. Mucoadhesion of the polymers were compared by tensile tests. Release of ofloxacin from the polymer matrix was determined. According to the results, mucoadhesive PASP derivatives may serve as excipients in situ gelling ophthalmic drug delivery vehicles.

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POLY(ASPARTIC ACID) HYDROGELS SHOWING REVERSIBLE VOLUME CHANGE UPON REDOX STIMULUS

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The unique properties of chemically cross-linked poly(amino acid) hydrogels are based on a three-dimensional hydrophilic polymer network that swells but does not dissolve in aqueous medium. Their large water-absorbing capacity, tissue-like soft properties, viscoelastic character, permeability, their expected biocompatibility and biodegradability fulfil the requirements of numerous biomedical applications such as tissue engineering or targeted cancer therapy. Responsive hydrogels exhibit a predetermined response – e.g. volume change – to certain environmental triggers (change in pH, temperature or redox potential).

The thiol-disulphide transformation has large biological relevance. Glutathione is a thiol-containing tripeptide and plays a key role in regulating redox processes of mammalian cells. Basically, the concentration of reduced glutathione differs significantly in the extra- and intracellular compartments and has an elevated level in tumour cells. The resultant concentration gradient is the basis for several possible applications of redox-responsive hydrogels, especially in the field of cancer therapy.

The goal of my work was to synthesise a redox-responsive hydrogel, based on poly(aspartic acid) (PASP), displaying reversible volume change. Thiol-modified PASP was cross-linked in aqueous media with a redox-inert (permanent) cross-linker to prepare PASP hydrogels. Degree of swelling and elastic modulus of the PASP hydrogels were studied upon redox stimulus and reversibility of their redox-sensitivity was investigated as a function of the composition. The PASP hydrogels swelled, but did not dissolve in reducing environment due to the presence of permanent cross-links and I proved their reversible redox-sensitivity.

MOLECULAR ELECTROCHEMISTRY OF ORGANIC COMPOUNDS.

EVALUATION OF ANTIOXIDANTS

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Molecular electrochemistry deals with transformation of molecules initiated by electron transfer. Using combined electrochemical techniques and properly calibrated quantum chemical calculations enabled us to obtain accurate redox potentials and to elucidate the reaction mechanisms of catalytic and non-catalytic reductive degradation of environmentally relevant organic halides [1-3].

Recently, we have developed an electrochemical method for evaluation of the activity of antioxidants [4]. The method is based on measuring the ability of antioxidants to inhibit the formation of 8-oxoguanine, the most frequently used biomarker of oxidative stress. In our studies, the dependence of this inhibition on the antioxidant concentration follows a single-exponential decay model, the parameter of which is related to frequently used inhibition coefficient, IC_{50} , $IC_{50} = \ln 2/k$. Our results revealed also that popular antioxidants, like polyphenols, exhibit also pro-oxidative properties.

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EFFICIENT DUAL RADICAL/CATIONIC PHOTOINITIATOR SYSTEMS UNDER UV AND VISIBLE LIGHT

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The photoinduced polymerization of monomers is gaining popularity as an environmentally friendly and safe method for production of protective polymer coatings on various surfaces. The most important features of polymerization are the efficiency and effectiveness of photoinitiators systems. Nowadays, all of the diaryliodonium and triarylsulfonium salts used in industry for cationic photopolymerization processes absorb UV light in the wavelength range 220-280 nm. This creates a problem, because there are no efficient and simultaneously powerful enough UV light sources that would emit in that range. In industry, common LED systems for UV curing currently focus on the 395 nm and 365 nm wavelengths, which is far from the absorption range of the commercial cationic photoinitiators. Hence, the main problem is finding ways to shift the absorption range of the cationic polymerization photoinitiators towards visible region or to increase efficiency of commercial photoinitiators by use of appropriate photosensitizers. To-date derivatives of thioxanthone have been used most often for sensitization of commercial photo-initiators, but the thioxanthenes cause yellowing of clear coatings. Moreover, a number of commercial photosensitizers suffer from various disadvantages, including toxicity and limited solubility in wide variety of monomers. For these reasons, the development of novel photosensitizers is also a very important issue. In this paper we proposed a high-speed bimolecular photoinitiator systems based on onium salts and new quaterphenyl derivatives.

Acknowledgement

The research are supported by the project SONATA - UMO-2012/07/D/ST5/02300 (NCN).

SEMICONDUCTING INORGANIC NANOCRYSTALS FOR OPTOELECTRONICS AND PHOTOCATALYTIC APPLICATIONS

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One of the most important semiconducting materials is zinc selenide (ZnSe) with a band gap of 2.67 eV and large exciton binding energy (21 meV), which makes it one of the leaders in a wide variety of device applications, such as blue-green LEDs, chemical/biological sensors, various memory devices and in energy transfer [1-2]. Zinc selenide nanocrystals with different morphologies are also characterized by good photocatalytic properties and therefore have drawn researcher's attention in this context [3]. In this study ZnSe inorganic nanocrystals with different morphology (0D, 1D, 2D) were successfully prepared by varied synthesis methods including colloidal synthesis, microwave-assisted solvothermal reaction and hot injection method. As-prepared nanocrystals found application as a nanofillers in transparent PMMA nanocomposites, as a component of active layer in photovoltaic devices or as photocatalyst in the degradation reaction of organic dye Rhodamine 6G (R6G) under UV light.

This work was financially supported by the Foundation for Polish Science (project number HOMING PLUS/2012-6/5) and by National Centre for Research and Development within the V edition of the LIDER programme (project number LIDER/009/185/L-5/13/NCBR/2014).

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MODIFICATION OF MICROFIBRILLATED CELLULOSE (MFC) WITH ACID CHLORIDES AND ITS APPLICATION FOR BIOPOLYAMIDE 4.10 NANOCOMPOSITES

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Microfibrillated cellulose (MFC) has recently been identified as an effective reinforcing filler and modifier of functional properties of polymer composites, e.g. barrier and optical properties. Effective methods of MFC surface modifications are searched in order to provide good dispersibility and miscibility of additive with polymer matrix. In this work microfibrillated cellulose was modified by homologous acid chlorides. The resulted cellulose nanofiller showed fibrillar morphology with hydrophobic character and high crystallinity content. Chemical modification of MFC was confirmed by FTIR and XPS analyses. It was observed that the reactivity of acid chloride towards cellulose esterification slightly decreased with the increasing chain length. However, the total effect on MFC wetting with water was most pronounced for the modifier with the longest alkyl chain. Nanocomposites of biopolyamide PA4.10 and modified MFC were prepared by melt blending. The higher miscibility and resulting improvement of dynamic mechanical behaviour was found for MFC esterified by hexanoyl chloride. PA4.10 composites containing MFC functionalized by longer alkyl chains (over 10 carbon atoms) showed the decrease of storage modulus due to insufficient homogenization and plasticization effect.

Acknowledgement

This research work was supported by Polish National Science Centre under the grant No. DEC-2011/01/M/ST8/06834.

DEVELOPMENT OF NEW STRATEGIES FOR MODIFICATION OF COMPOSITE MATERIALS

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The growing demand for new polymeric materials combining the advantageous properties, such as limited flammability, resistance to aging and thermal stability with an ease of processing requires development of new strategies for modification of composite materials. The investigations carried out in our research group include several topics.

The first relates to the use of electrospinning method for applying thin layers of different thickness on the surface of polyamide and polylactic acid nanocomposites with layered silicates fabricated by melt intercalation.

The second research trend involves the use of a layer-by-layer assembly technique in order to deposit cationic chitosan or phosphorous and copper compounds and anionic montmorillonite polyelectrolyte coatings on polyamide or polylactide and their nanocomposites. This technique could be an alternative for electrospinning and electrospraying methods, which can be also used to cover the composite surface by flame retardants.

Another area of research involves the use of novel method of polymer/montmorillonite nanocomposites recycling by pyrolysis to produce non-graphitized montmorillonite that can be re-used in the preparation of polymer composites. Previous works focus mainly on pyrolysing polymer nanocomposites in order to recycle monomer during high temperature decomposition. We have developed this method to overcome the problem with residues after pyrolysis process. These residues still include layer silicates which can be re-used as suitable fillers for melt intercalation with polymer matrices.

The recent developed research works have been light and high-strength composite ballistic panels, as well as bio-component paper adhesives. Both areas require the development of new innovative solutions based on nano- and biomaterials technology.

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