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FACULTY OF CHEMICAL ENGINEERING AND BIOENGINEERING
OLÁH GYÖRGY DOCTORAL SCHOOL**

Modification of Biopolymers –
Chemistry, Interactions, Structure and Properties

Thesis book

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1. Introduction

The increasing environmental awareness of the society has become an important factor in recent decades affecting legislation, commerce and industry as well as research and development to a great extent^{1,2}. The same trend can be observed in polymer industry as well, as the production and use of biopolymers increases continuously with a very high rate thus all information on these materials is very important. The term "biopolymer" is used in several different ways depending on the application area. The generally accepted definition covers polymers that are either renewable-based, biodegradable or both. Biopolymers have much potential and several advantages, but they possess some drawbacks as well. In spite of increasing production capacity, they are still quite expensive compared to commodity polymers and their properties are also often inferior, or at least do not correspond to the expectation of converters or users. As a consequence, biopolymers must be often modified to meet the expectations of the market. Introducing various fillers as well as small and high molecular weight compounds into biopolymers is a promising way to improve properties and achieve property combinations required for specific applications.

The investigation of interactions, structure and properties of various polymer based heterogeneous systems is the main area of expertise of the Laboratory of Plastics and Rubber Technology at Budapest University of Technology and Economics (BME) and the associated Department of Polymer Chemistry and Physics at the Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, HAS. Following the international trends in polymer science and industry, several projects related to biopolymers

¹ Jiang L, Zhang J. In: Kutz M, editor. Applied Plastics Engineering Handbook. Oxford: William Andrew; 2011. p. 145-158.

² Mohanty AK, Misra M, Drzal LT. *J Polym Environ* 2002;**10**(1-2):19-26.

and other bio-based materials have been started at the Laboratory in recent years. This thesis presents a further step in this direction, focusing on the interaction and structure in heterogeneous biopolymer systems as well as their modification by physical and reactive means.

In order to adjust the properties of biopolymers to the intended application, wide varieties of approaches are used for their modification, like plasticization, the incorporation of fillers and reinforcements, blending and impact modification. In contrast to the development of novel polymeric materials and new polymerization routes, the preparation of heterogeneous polymeric systems is a relatively cheap and fast method to tailor the properties of plastics. As a result, this approach may play a crucial role in increasing the competitiveness of biopolymers.

The incorporation of fillers and reinforcements provides various biocomposites. Although conventional, mineral fillers might also be applied³ for the modification of biopolymers, most studies focus on the potential use of natural lignocellulosic fibers, i.e. wood flour, sisal, flax, etc. into both conventional and biopolymers⁴. Interfacial play a crucial role in the determination of composite properties, affecting structure and micromechanical deformation processes to a great extent⁵. Consequently, investigation and modification of these is in the focus of scientific interest. Interactions can vary in a wide range both in character and strength. Adhesive interactions created by secondary forces are relatively weak, while coupling may result in covalent bonding between the components.

³ Imre B, Keledi G, Renner K, Móczó J, Murariu M, Dubois P, Pukánszky B. *Carbohydr Polym* 2012;**89**(3):759-767.

⁴ Mohanty AK, Misra M, Drzal LT. *J Polym Environ* 2002;**10**(1-2):19-26.

⁵ Renner K. Budapest: Laboratory of Plastics and Rubber Technology, 2013

Plasticization is often used for the modification of biopolymers to improve their processability and/or other properties demanded by a specific application. Plasticizers exchange the intermolecular interactions among polymer chains to bonds between the macromolecules and the small molecular weight compound thus promoting conformational changes resulting in lower glass transition temperature (T_g) and increased deformability. Interactions determine miscibility, which is of great importance in the case of plasticization. Plasticizers tend to migrate to the surface of the products raising environmental and health issues, as well as altering the macroscopic properties of the material as an effect of changing plasticizer content. Migration can be hindered by increasing the molecular weight of the plasticizer, which leads to slower diffusion indeed, but it results in a decrease of miscibility and plasticizing efficiency as well⁶. Another innovative solution to this problem might be the grafting of plasticizer molecules to the polymer chain by reactive processing, i.e. internal plasticization^{7,8}.

Blending is a convenient route to create new materials with the desired combination of properties. Its goals are various from the modification of T_g , improvement of fracture resistance, flexibility, processability to the improvement of some other properties like optical characteristics or flammability. In all these cases however, successful blends should either offer similar performance as the starting material for reduced cost or provide high added value. If possible, interactions are even more important in blends than in other heterogeneous polymeric materials since they determine the mutual solubility of the phases, the thickness and properties of the interphase and the structure of the blend. As a consequence, the proper, and possibly quantitative, characterization

⁶ Liu H, Zhang J. *J Polym Sci B Polym Phys* 2011;**49**(15):1051-1083.

⁷ Hassouna F, Raquez J-M, Addiego F, Toniazzo V, Dubois P, Ruch D. *Eur Polym J* 2012;**48**(2):404-415.

of interaction is of utmost importance for the prediction of blend properties. Most polymer blends can be characterized with a low level of miscibility and interfacial interaction, resulting in inferior mechanical properties, thus they are seldom applied in practice without proper compatibilization. The compatibilizing effect of a compound is usually attributed to an increase in interfacial adhesion and to the formation of smaller dispersed particles leading to improved mechanical properties. Different strategies of compatibilization can be distinguished. In the case of non-reactive methods premade amphiphilic compounds, e.g. block-copolymers, are added to the blend, one constitutive end or block being miscible with one blend component, while the other with the second component. However, the fact that biopolymers often contain various reactive groups makes the use of reactive compatibilization methods plausible and convenient. The method possesses considerable potentials, since structure and properties can be controlled relatively easily by the proper selection of agents, blend composition and processing conditions in a wide range^{9,10}. In this case, the blocky structures acting as compatibilizers form in situ during blending. This might involve the addition of polymers with reactive groups^{11,12}, or small molecular weight chemicals^{13,14} to form the compatibilizer. Another possibility is the chemical modification of one of the components to in order to create reactive groups^{15,16}. The radical grafting of polymers with unsaturated anhydrides resulting in the formation of free anhydride or acid groups is a

⁸ Vidéki B, Klébert Sz, Pukánszky B. *Eur Polym J* 2005;**41**(8):1699-1707.

⁹ Zhang J-F, Sun X. *Biomacromolecules* 2004;**5**(4):1446-1451.

¹⁰ Yao M, Deng H, Mai F, Wang K, Zhang Q, Chen F, Fu Q. *Expr Polym Lett* 2011;**5**(11):937-949.

¹¹ Huneault MA, Li H. *Polymer* 2007;**48**(1):270-280.

¹² Juntuek P, Ruksakulpiwat C, Chumsamrong P, Ruksakulpiwat Y. *J Appl Polym Sci* 2012;**125**(1):745-754.

¹³ Jang WY, Shin BY, Lee TJ, Narayan R. *J Ind Eng Chem* 2007;**13**(3):457-464.

¹⁴ Yao M, Deng H, Mai F, Wang K, Zhang Q, Chen F, Fu Q. *Expr Polym Lett* 2011;**5**(11):937-949.

¹⁵ Shin BY, Jang SH, Kim BS. *Polym Eng Sci* 2011;**51**(5):826-834.

typical example. The reactive polymers obtained are frequently used for the compatibilization of starch based blends containing a large number of hydroxyl groups. Among others, blends containing anhydride-grafted PCL¹⁷, PLA¹⁸ and PHB¹⁹ have been prepared this way. Other functionalities like epoxy¹² or isocyanate groups²⁰ might also be used in various biopolymer based systems.

Reactor blends represent a specific category among compatibilized biopolymer blends. These materials are produced by the synthesis of one polymer in the presence of another. The ring-opening polymerization (ROP) of cyclic esters initiated by the hydroxyl groups of biopolymers like starch²¹, dextran²² or partially substituted cellulose acetate (CA)⁸ is a convenient method for the preparation of block copolymers via reactive processing, although various other combinations are also possible. Several groups have reported improved adhesion, morphology and mechanical properties in systems prepared by this approach.

Biopolymers are in the center of attention, their production and use increases continuously at a very high rate. However, they are surrounded with much controversy and even terms used in the area need further clarification. Modification is a way to improve the often inferior properties of biopolymers, and achieve property combinations required for specific applications. Further study is needed on the miscibility-structure-property relationships of these heterogeneous systems to utilize all potentials of the various modification

¹⁶ Gao HL, Hu S, Su FH, Zhang J, Tang GN. *Polym Compos* 2011;**32**(12):2093-2100.

¹⁷ Avella M, Errico ME, Laurienzo P, Martuscelli E, Raimo, Rimedio R. *Polymer* 2000;**41**(10):3875-3881.

¹⁸ Li H, Huneault MA. *J Appl Polym Sci* 2011;**122**(1):134-141.

¹⁹ Liao H-T, Wu CS. *Des Monomers Polym* 2007;**10**(1):1-18.

²⁰ Zeng J-B, Jiao L, Li Y-D, Srinivasan M, Li T, Wang Y-Z. *Carbohydr Polym* 2011;**83**(2):762-768.

²¹ Dubois P, Krishnan M, Narayan R. *Polymer* 1999;**40**(11):3091-3100.

²² Dubois P, Narayan R. *Macromol Symp* 2003;**198**(1):233-243.

routes. Reactive techniques are versatile and offer very effective ways for modification and compatibilization. The chemical structure of biopolymers also supports the use of this approach. Several questions regarding the underlying molecular processes and reaction mechanisms as well as their effect on macroscopic properties are to be answered yet, thus further development can be expected in this field. The main motive of this Thesis is to give a comprehensive description of the various means for the modification of biopolymers. Both physical and chemical approaches are investigated, with strong emphasis on the determination of interactions, structure and properties as well as the various factors affecting these.

2. Materials and methods

Biocomposites were prepared from PLA and calcium sulfate in a wide composition range, using both unmodified and surface coated filler. The size distribution of the filler was determined by light scattering, while surface characteristics were studied by inverse gas chromatography (IGC). The components were homogenized in a twin-screw compounder, followed by the production of standard specimens by injection molding. The amount of bonded stearic acid on the filler surface prior to compounding and in the composite was compared using diffuse reflectance Fourier transform infrared spectroscopy (FTIR-DRIFT). Mechanical properties of the composites were characterized by tensile and impact testing. The strength of interfacial adhesion was estimated quantitatively with model calculations. Micromechanical deformation processes were followed by acoustic emission (AE) and volume strain (VOLS) measurements. Structure as well as deformation mechanism were confirmed by scanning electron microscopy (SEM).

The blending and reactive modification of PLA as well as cellulose acetate was carried out in an internal mixer followed by compression molding

into plates. A wide range of compounds was used for the modification of PLA, i.e. polystyrene, polycarbonate, poly(methyl methacrylate) and polyurethane, while ϵ -caprolactone for the internal plasticization of CA. Interactions in PLA blends were estimated based on solvent uptake measurements. Glass transition temperature and rheological properties were also determined. Solution state ^1H nuclear magnetic resonance spectroscopy was applied to determine the chemical structure of the grafted and block copolymers acquired by the reactive modification of CA and PLA respectively. Morphology of the blends was studied by SEM, while atomic force microscopy was also applied in the case of reactive and physical PLA/PU blends. Mechanical properties were characterized by tensile testing.

3. Results

In the first study of the Thesis, PLA composites containing uncoated CaSO_4 and the same filler coated with stearic acid are compared. As structure of these composites has been described in an earlier study²³, more effort was spent on the surface characterization of the filler, on the estimation of interfacial adhesion and on deformation processes. Our results have shown that interfacial adhesion is twice as strong in composites prepared with the uncoated particles than in those containing the coated filler. Debonding was found to be the dominating micromechanical deformation process in all the cases. The initiation stress (σ_{AE1}) required to the separation of the phases at the interphase was determined with the help of acoustic emission measurements. Composition dependence of σ_{AE1} , as presented in Fig. 1, differs considerably for the two types of fillers. Characteristic stress increases slightly with filler content for composites containing uncoated CaSO_4 . Such a behavior was explained before with the effect of interacting stress fields leading to a decrease of local

²³ Molnár K, Móczó J, Murariu M, Dubois Ph, Pukánszky B. *Express Polym Lett* 2009;3:49-61.

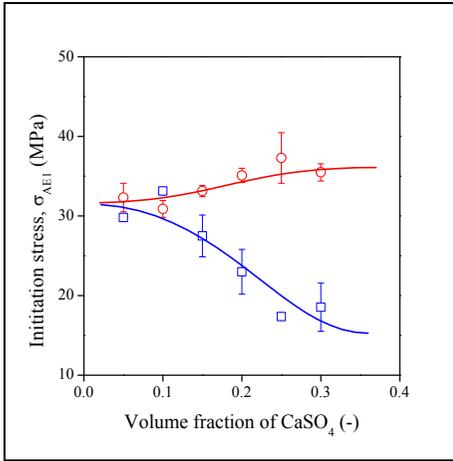


Fig. 1 Effect of filler content and surface coating on the initiation stress for debonding determined by acoustic emission in PLA/CaSO₄ composites; (∇) uncoated, (\circ) coated filler.

mer, locally changing its properties. The plasticizing effect of stearic acid and changes in particle distance all contribute to the decrease of debonding stress, changing macroscopic properties considerably. The final properties and performance of the composites depend unambiguously on the micromechanical deformation processes occurring during loading, on debonding and the subsequent plastic deformation.

Fully degradable PLA blends may be used in agriculture and packaging, but engineering applications require more durability and longer lifetime. As a consequence, PLA is often blended with engineering plastics. The application of such materials also has environmental benefits since they improve carbon footprint considerably. However, the production of such blends with properties satisfying the intended application is possible only if the miscibility

stresses²⁴. On the other hand, coating obviously facilitates debonding. However, the composition dependence cannot be explained solely with this effect, since the strength of interaction is the same at all filler contents. Obviously some other factor or factors also contribute to the initiation of debonding. We found that local plastic deformation is larger around coated particles, suggesting that stearic acid might dissolve in the poly-

²⁴ Pukánszky B, Vörös G.. *Polym Compos* 1996;**17**:384-392.

of the components is controlled and miscibility-structure-property correlations are known. Accordingly, our goal was to study interactions, structure and properties in the blends of PLA with three commercial thermoplastics having different chemical structures. All three blends were found to have heterogeneous structure, but the size of the dispersed particles differs by an order of magnitude indicating dissimilar interactions for the corresponding pairs. We estimated component interactions with three different methods, the determination of the size of the dispersed particles, the calculation of the Flory-Huggins interaction parameter (χ) from solvent absorption and the quantitative evaluation of the composition dependence of tensile strength (parameter C). As presented in Fig. 2, a general correlation was established between interactions and the mechanical properties of the blends.

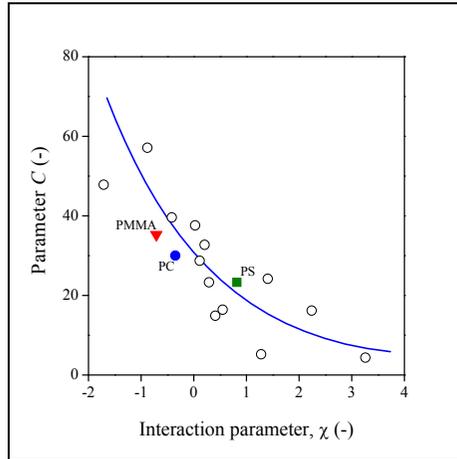


Fig. 2 General correlation between component interactions (χ) and mechanical properties (parameter C) for a wide variety of blends; (○) results of earlier studies.

The rapid physical ageing of PLA results in a brittle material with low impact resistance, thus numerous studies aim to improve this property by either plasticization or blending with various elastomers. Although polyurethane (PU) elastomers possess excellent mechanical properties, while their outstanding biocompatibility makes them able to be used in biomedical applications, these polymers are surprisingly rarely considered for the modification of PLA. Our goal was to improve the properties of PLA by blending with a segmented polyurethane elastomer. In order to compatibilize the blend components by cou-

pling the phases, an innovative reactive processing was developed. The synthesis of PU was carried out in poly(lactic acid) melt. The ratio of isocyanate and active hydrogen containing groups was optimized based on the evaluation of melt viscosity during processing and tensile testing. The isocyanate components react with the hydroxyl end-groups of PLA, as confirmed by NMR measurements, resulting in the formation of PLA-b-PU copolymers. The formation of amide and acylurea groups on the carboxyl end was not detected. Poly(lactic acid)/polyurethane blends prepared by reactive processing and physical blends were characterized using various techniques including microscopy, rotational viscometry, thermal and mechanical measurements. Comparison of compatibilized reactor blends and conventional physical blends clearly showed the benefits of reactive processing. Tensile strength differs considerably for the two kinds of polymers. This property is plotted against PU content in Fig. 3 together with representative AFM micrographs to show the corresponding fine structure of the blends. Properties are very similar at small PU content and differ considerably at the upper end of the composition range with a maximum at 90 vol% PU. The finer distribution of the dispersed phase and some kind of interpenetrating network structure is shown by the AFM micrographs recorded on the reactive blends. Morphology, macroscopic properties

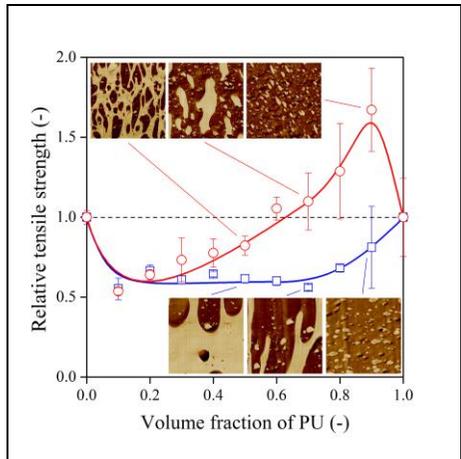


Fig. 3 Effect of the addition of a polyurethane elastomer onto the mechanical characteristics of PLA. Comparison of physical and reactor blends. Changes in structure with composition is shown by AFM phase images; (□) physical (PLA/PU), (○) reactor (PLA-b-PU) blend.

and the quantitative estimation of interfacial interactions all prove that reactive processing was effective and both the structure and the interfacial adhesion of the components improved as an effect. Our results also indicated the development of a submicron structural formation which positively influenced properties at large PU contents.

A similar reactive processing technique was used for the internal plasticization of cellulose acetate. Although many studies aim the modification of CA by grafting with ϵ -caprolactone via reactive processing, the effect of catalyst content on reaction mechanism and properties of the end-product is rarely investigated. In our study, internally plasticized cellulose acetate was prepared by grafting with ϵ -caprolactone at different concentrations of tin(II) bis-(2-ethylhexanoate) catalyst. Our results have clearly shown the crucial effect of catalyst content in the grafting and homopolymer reactions. Both initiation time and rate of the reaction was found to be strongly determined by catalyst content. Depending on reaction conditions catalyst content has an optimum leading to large grafting efficiency, promoting the formation of a small number of longer side chains to the CA backbone, a structure favoring thermoplastic character and biodegradability.

4. New scientific results

1. PLA/CaSO₄ composites are very advantageous from the environmental point of view. The filler particles are often coated with stearic acid to aid the dispersion of the particles and improve processability. With the use of three independent methods we proved the first time that adhesion is twice as strong in composites prepared with the uncoated particles than in those containing the coated filler.

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2. The detailed study of the deformation and failure processes of PLA composites containing uncoated and stearic acid coated particles showed that stearic acid used for the coating of the filler dissolves in the polymer and locally changes its properties. Although debonding is the dominating micro-mechanical deformation process in all composites, local plastic deformation is larger around coated particles. The final properties and performance of the composites depend unambiguously on the micro-mechanical deformation processes occurring during loading, on debonding and the subsequent plastic deformation.
 3. The study of PLA blends prepared with three commercial polymers having differing chemical structure showed that the structure and properties of the blends cover a wide range. We estimated component interactions with three different methods, the determination of the size of the dispersed particles, the calculation of the Flory-Huggins interaction parameter from solvent absorption and the quantitative evaluation of the composition dependence of tensile strength and proved that interactions are strong in the PLA/PMMA pair, weaker in PLA/PC and the weakest for PLA and PS. We established a general correlation between interactions and the mechanical properties of the blends and proved that they are valid also for biopolymer hybrid blends.
 4. Reactive processing is a convenient way to produce new polymers with advantageous properties from biopolymers. The successful synthesis of PLA-b-PU block copolymers in poly(lactic acid) melt was confirmed by NMR spectroscopy. We showed for the first time that the isocyanate component reacts with the hydroxyl end-groups of PLA, but not with the acid group at the other end of the PLA chain thus amide and acylurea groups do not form in the reaction.

5. Polyurethane elastomers are promising candidates for the impact modification of PLA, since the resulting blends can be applied in many areas including biomedicine. Based on the analysis and comparison of morphology, macroscopic properties and the quantitative estimation of interfacial interactions in poly(lactic acid)/polyurethane physical blends and materials produced by reactive processing we proved that a submicron structural formation develops in reactor blends which positively influence properties at large PU contents. The coupling of the phases results in more advantageous morphology in the reactor blends than in traditional physical mixtures and in superior tensile strength in the entire composition range.
6. We proved with experiments carried out in a wide range of catalyst contents that the concentration of tin(II)bis-(2-ethylhexanoate) catalyst determines initiation time and reaction rate both for grafting and homopolymerization. Depending on reaction conditions catalyst content has an optimum leading to large grafting efficiency and favorable chemical structure of the grafted product having a small number of long side chains attached to the CA backbone. The tin octoate catalyst used in our experiments affects the degradation of cellulose acetate only marginally through its high efficiency resulting in increased viscosity and larger friction during reactive processing because of longer grafted chains.

5. Publications

5.1 *The thesis is based on the following papers*

1. Imre B, Pukánszky B. Recent advances in bio-based polymers and composites: Preface to the BiPoCo 2012 Special Section. *Eur Polym J* 2013 In Press (IF: 2.739)
2. Imre B, Pukánszky B. Compatibilization in bio-based and biodegradable polymer blends. *Eur Polym J* 2012; In Press (IF: 2.739)

3. Imre B, Keledi G, Renner K, Móczó J, Murariu M, Dubois Ph, Pukánszky B. Adhesion and micromechanical deformation processes in PLA/CaSO₄ composites. *Carbohydr Polym* 2012;**89**(3):759-767. (IF: 3.628)
4. Imre B, Renner K, Pukánszky B. Interactions, structure and properties in poly(lactic acid)/thermoplastic polymer blends. accepted in *Express Polym Lett* (IF: 1.769)
5. Bedő D, Imre B, Domján A, Schön P, Vancsó GJ, Pukánszky B. Coupling of poly(lactic acid) with a polyurethane elastomer by reactive processing. submitted to *Macromolecules*
6. Imre B, Bedő D, Domján A, Schön P, Pukánszky B. Interactions, structure and properties in poly(lactic acid)/polyurethane blends prepared by reactive processing. accepted in *Eur Polym J* (IF: 2.739)
7. Imre B, Kiss EZ, Domján A, Pukánszky B. The effect of catalyst concentration on the grafting of cellulose acetate with ϵ -caprolactone by reactive processing. submitted to *Cellulose*

5.2 Other publications

1. Imre B, Dominkovics Z, Pukánszky B. A feldolgozási körülmények hatásának vizsgálata rétegszilikát/polipropilén nanokompozitokban, *Műanyag és Gumi* 2008;**45**(12)490-496.
2. Gábor Á, Faludi G, Imre B, Renner K, Móczó J, Pukánszky B. Mikromechanikai deformációs folyamatok politejsav alapú biokompozitokban. *Műanyag és Gumi* 2009;**46**(12):445-448.
3. Kiss EZ, Imre B, Pukánszky B. Cellulóz-acetát reaktív lágyítása ϵ -kaprolaktonnal – a katalizátor-tartalom hatása az ojtási reakcióra. *Műanyag és Gumi* 2010;**47**(4):156-159.
4. Pataki P, Imre B, Földes E, Pukánszky B. Természetes anyagok a műanyagiparban – alapanyagok és adalékok. *Műanyag és Gumi* 2012;**49**(1):12-18.
5. Imre B, Renner K, Pukánszky B. A politejsav módosítása – PLA alapú társított rendszerek. *Műanyag és Gumi* 2013;**50**(3):104-108.

5.3 Conference presentations

1. Imre B, Molnár K, Móczó J, Murariu M, Dubois P, Pukánszky B. Development of PLA based biodegradable composites. 2nd Bratislava Young Polymer Scientists workshop, Krompachy, February 5th 2009.

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2. Imre B, Bányai F, Móczó J, Pukánszky B. A PLA fizikai öregedése. Kutatóközponti Tudományos Napok, Budapest, October 24th 2010.
 3. Imre B, Bedő D, Renner K, Móczó J, Pukánszky B. Impact modification of poly(lactic acid) with polyurethane elastomers. 19th Annual BEPS Meeting, Vienna, September 29th 2011.
 4. Imre B, Móczó J, Pukánszky B. Poly(lactic acid) – investigation and modification of mechanical behavior. Eurotec 2011 Conference, Barcelona, November 14th 2011.
 5. Imre B, Pukánszky B. Biopolymer blends: miscibility, compatibility, performance. International Conference on Bio-based Polymers and Composites 2012, Siófok, May 28th 2012.
 6. Imre B, Molnár K, Móczó J, Murariu M, Dubois P, Pukánszky B. Interfacial adhesion, micromechanical deformations and performance in PLA/CaSO₄ composites. 14th European Conference on Composite Materials, Budapest, June 7-10th 2010. (poster)
 7. Imre B, Faludi G, Renner K, Móczó J, Pukánszky B. Micromechanical deformation processes in PLA based biocomposites, 6th Modification, Degradation and Stabilization of Polymers, Athens, September 5-9th 2010. (poster)
 8. Imre B, Bedő D, Renner K, Móczó J, Pukánszky B. Modification of poly(lactic acid) via reactive processing with polyurethane elastomers. International Conference on Bio-based Polymers and Composites 2012, Siófok May 27-31st 2012. (poster)
 9. Imre B, Renner K, Móczó J, Pukánszky B. Characterization of PLA/wood “green” composites: Structure, physical ageing, micromechanics, and performance, ISPAC 2012, Kerkrade June 11-13rd 2012
 10. Bedő D, Imre B, Pukánszky B. Impact modification of PLA with polyurethane elastomers, Polymeric Materials 2012, Halle September 12-14th 2012.
 11. Imre B, Renner K, Menyhárd A, Móczó J, Pukánszky B. Physical ageing of poly(lactic acid) – molecular processes and macroscopic properties, Polymeric Materials 2012, Halle September 12-14th 2012. (poster)