

## **Modification and functionalization of biopolymers**

OTKA PD 112489 final report 2017

### **1. Background**

The interest in using polymeric materials derived from renewable resources increases day by day because of the considerably improved environmental conscientiousness of society and the fear from the depletion of petrochemical based plastics. Poly(lactic acid), PLA, seems to be the polymer which exploits the most successfully this surge of demand for bio materials and satisfies the requirements of large scale processing and application at the same time. Unfortunately, this polymer has some drawbacks as well, including moisture sensitivity, fast physical ageing, poor impact resistance and relatively high price. As a consequence, many attempts were made to modify it by plasticization, copolymerization, blending, or by the production particulate filled or fiber reinforced composites.

This research work was done in the frame of PD OTKA fund, where young researchers are eligible after receiving their PhD. The research plan was divided into three parts and it was carried out consecutively. In the first stage biopolymers were modified with natural reinforcements. The utilization of various natural fillers in PLA and other matrices allowed the investigation of the effect of component properties on the structure and properties of biocomposites. In the second stage an attempt was made to change deformation processes through the modification of interfacial interactions between the components. The biopolymer was grafted with maleic anhydride functional group in order to produce novel coupling agents. The properties of the new coupling agents were determined and their effect on biocomposite properties was studied as a function of grafting level. In the last part of the research project lignin was utilized in PLA and other polymeric matrices to facilitate the application of this special biopolymer.

### **2. Results and publications**

At the beginning of the research the effect of several natural fiber and filler on the properties of biopolymer based composites were investigated. Grinded corn cob is a waste product of the agriculture industry and it can be found in abundant quantity also in Hungary. Because of the inherent properties of the corn cob, two different deformation processes were identified in PLA/corn cob composites. One was associated to the fracture of the soft particles and at much higher stress the fracture of the hard particles also took place. With several other natural reinforcements – like wood flour – the properties of PLA biopolymer was modified. The thorough study revealed that despite the claims found in the literature storing interaction is formed between the poly(lactic acid) matrix and the natural reinforcements. The magnitude of the interactions was characterized quantitatively with different methods (Faludi, G., Dora, G., Imre, B., Renner, K., Móczó, J., Pukánszky, B.: *J. Appl. Polym. Sci.* 131, 39902 (2014)). With the help of acoustic emission we could prove that despite the strong interaction the very large particle of natural fillers can debond as well. Acoustic emission was a very effective investigation method to characterize the interactions and deformation processes in biopolymer composites in the later research as well, thus we are grateful for the support of the fund in the acquisition of a such device. The deformation processes turned to be very important in the determination of the ultimate properties of any natural fiber reinforced composites. In polypropylene based composites these fibers indicated similar processes which limited the strength of the composites in case of strong interactions (Sudár A., Burgstaller C., Renner K., Móczó J., Pukánszky B.: *Compos Sci Technol*, 103, 106-112 (2014)).

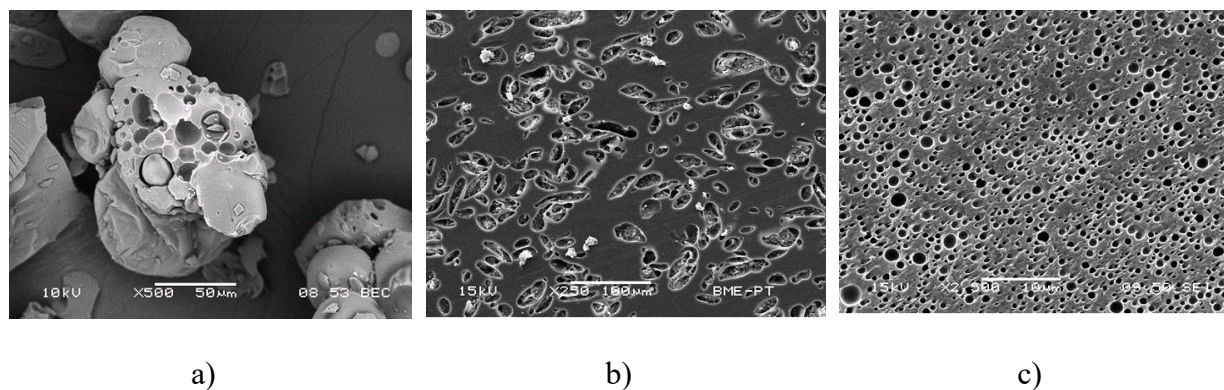
In the second year of the project the research work was continued according to the research plan. Already in the first year several valuable results were published being the most important between them the synthesis of a new coupling agent for poly(lactic acid) (PLA) based composites. Interfacial interactions are modified in numerous ways in polymer/wood composites. In a recent presentation on the third international “Conference on Bio-based Polymers and Composites” a comprehensive overview was provided from the effect of different surface treatment methods on the mechanical properties of PLA/wood composites (Faludi et. al “Improving interfacial adhesion in PLA/wood biocomposites” in BiPoCo2016). Another presentation highlighted the importance of micromechanical deformation processes in fiber reinforced PLA composites (Renner et. al. “Modification of poly(lactic acid) with natural and synthetic fibers” BiPoCo2016) and provided new possibilities in the modification of bio-based polymers like poly(lactic acid). Based on the results collected in the two presentation, two manuscripts are in preparation.

Another important task was of the project to synthesize functionalized biopolymers in order to further improve their properties. The analysis of the results obtained in experiments to produce poly(lactic acid) functionalized with maleic anhydride showed that the chain scission of PLA takes place during reactive modification (Csikós, Á., Faludi, G., Domján, A., Renner, K., Móczó, J., Pukánszky, B. Eur Polym J 68: 592-600, 2015). The occurrence of grafting could not be proved by FTIR spectroscopy, but a detailed NMR analysis showed that the degree of grafting depends on the amount of both reactants; a maximum number of 2.5 MA groups/PLA chain could be grafted under the conditions used in the study. The functionalized polymer proved to be an efficient coupling agent in PLA/wood composites. Efficiency increased with increasing number of functionality and coupling agent amount. Coupling resulted in increased strength and reinforcement. Acoustic emission analysis of deformation processes supported by microscopy proved that the dominating local deformation process is the fracture of the fibers, but a small extent of debonding also occurs in neat, uncoupled composites. The prevention of debonding by coupling resulted improved performance of the composites.

Another study on wood flour reinforced composites proved that wood increases impact resistance slightly, elastomer drastically in two-component materials, but fracture toughness remains small in three-component hybrid systems irrespectively of structure. Depending on particle size and interfacial adhesion, fiber fracture and debonding occur in wood reinforced composites, while mainly plastic deformation takes place in blends. This latter process is suppressed by cavitation, promoted further by the presence of wood fibers, which increase local stresses. The usual concept of three-component materials does not work in wood composites, micromechanical deformations must be controlled to diminish or completely eliminate cavitation and to increase the plastic deformation of the matrix polymer (Sudár, A., Renner, K., Móczó, J., Lummerstorfer, T., Burgstaller, Ch., Jerabek, M., Gahleitner, M., Doshev, P., Pukánszky, B. Compos Struct 141, 146-154 (2016)).

Lignin plays an important role in the project. As the first step of the utilization of this natural compound polypropylene (PP)/lignin blends were prepared in a wide composition range (0–70 vol%) from a PP homopolymer and two liginosulfonates of different compositions by homogenization in an internal mixer and compression molding. Thermodynamic considerations and dynamic mechanical analysis (DMTA) were used for the estimation of interactions and miscibility, while mechanical properties were characterized by tensile testing. Local deformations were followed by acoustic emission measurements, and structure was analyzed by scanning electron microscopy (SEM). The analysis of results obtained by various measurements showed that the structure of PP/lignin blends form during processing by the breakup of large lignin particles which soften at the high temperature of processing. Practically all evidence indicates the development of weak interactions between PP and

lignin; in fact the interactions among lignin molecules are much stronger and prevent any mixing of the two components. As a consequence, dispersed structure forms in the entire composition range studied, a co-continuous structure cannot develop at all, further confirming weak interactions and very poor miscibility. Interfacial adhesion can be improved through the addition of a maleic anhydride grafted polypropylene (MAPP) coupling agent (Fig. 1.).



**Fig. 1.** Particle size and size distribution of lignin dispersed in PP; a) original lignin particles, b) 30 vol% lignin, no coupling, c) 30 vol% lignin, MAPP.

Depending on the strength of interfacial adhesion the blends fail either by debonding or the fracture of the lignin particles. Although coupling improves the stiffness and even more the tensile strength of PP/lignin blends, deformability is very small especially at larger lignin content representing the largest obstacle of practical application. Better dispersion, stronger interactions and modified lignin properties may lead to the improvement of blend properties (Bozsódi B., Romhányi V., Pataki P., Kun D., Renner K., Pukánszky B. *Materials and Design* 103, 32-29 (2016)).

Similarly, lignin was blended with different thermoplastics in the next step of the research. The results of blending experiments carried out with three thermoplastic polymers containing aromatic rings in their structure have shown that  $\pi$  electron interactions are much stronger than dispersion forces acting in PP. The size of dispersed particles was smaller and properties were better in aromatic polymers than in PP. PS containing only aromatic rings and no other functional groups formed the weakest interaction with lignin, while interactions in PC and especially PETG capable of forming also hydrogen bonds was much stronger showing that the combined effect of competitive interactions determine the structure and properties of the blends and lead to the differences observed. In spite of their stronger interactions, the aromatic polymers studied are not miscible with lignin either, heterogeneous structure containing dispersed lignin particles forms at all concentrations. Debonding is the dominating local deformation process in PP, but mainly the failure of the particles occurs at stronger interactions. Deformability is still very small in all the blends studied and they are very brittle. Further improvement is needed in interactions and deformability for the practical use of thermoplastic/lignin blends (Szabo G., Romhányi V., Kun D., Renner K., Pukánszky B: *ACS Sustain Chem Eng* 5: (1) 410-419, 2017).

Beside the intensive research work on lignin and poly(lactic acid) based materials, two additional articles were published in the frame of the project, which were not directly connected to the above mentioned topics, but their results supplied valuable experience and information in the modification and functionalization work of lignin and PLA.

### 3. Conclusions, future work

The intensive research work carried out on biopolymer blends and composites resulted in many precious publications. Until the end of the project 9 articles were accepted and published. The contribution of the fund in these publications is undisputable, since the leader of the project is the corresponding author most of these publications, and none of them could supervene without the acoustic emission device obtained in the project. Until now, the published articles have a sum of impact factor of 33.60 and 48 independent citations were received, although it was only a short 3 year period.

The chemical structure of lignin is complex and depends very much on the extraction technology used for its production. Because of the complicated structure, the proper characterization of lignin is difficult and requires the use of a number of methods. Besides the number of functional groups, the ratio of monomers and molecular weight must be also determined for the complete characterization of lignin. The combination of lignin with thermoplastics should be treated as blend and not composite. Because of their large number of polar functional groups, lignin molecules interact strongly with each other. As a consequence, competitive interactions determine the structure and properties of the blends, and most polymers are immiscible with lignin, because of weaker interactions forming between lignin and the matrix polymer than among lignin molecules. Apparently none of the interactions developing in the blends, including hydrogen bridges, is sufficient to result in complete miscibility. Nevertheless, strong interactions, like the combination of aromatic  $\pi$ -electron interaction and hydrogen bonds, lead to very small dispersed particles and relatively good properties. However, the deformability of the blends is usually poor which might be compensated by the chemical modification of lignin, plasticization, or the use of coupling agents. Lignin can act also as a reactive component in the preparation of various resins and polymers.