Final Report

on the work done in the project OTKA K 120039 on the
"Modification of synthetic and biopolymers by physical and chemical methods"

1. Introduction

Our research group has been continuously working on the modification of polymers since many years. The first projects were on particulate filled polymers and polymer blends. With the passing of the years the projects extended and gradually changed to include various areas of polymer science. First we wanted to obtain deeper knowledge on the factors and processes behind the structure-property correlations of our materials thus went to theoretical calculations and modeling. Later the interest of the scientific community turned towards nanocomposites, and then raw materials from natural resources gained larger importance. Besides our scientific interest also the interaction with our industrial and scientific partners formed the projects in some extent. Both the work and the transformation from one area to the other proceeded continuously, the projects often overlapped, the knowledge obtained in one project was used also in the other, thus the papers published cover a broad area.

This report reflects the variety of projects done in our group during the last few years in the framework of the OTKA contract. Polypropylene (PP) has always been an important commodity polymer, and still is, its modification is constantly in the focus of our attention especially because of the interest of the industry. The stabilization of polyethylene (PE) has always been a traditional topic of the group. The project took a turn a few years ago when we started to explore the possibility of using natural antioxidants for stabilization in agreement with the general tendency and interest in raw materials from natural resources. The work continued successfully in the framework of this project and it seems that it will continue also in the future. Although layered silicate nanocomposites failed to fulfil the expectations and never reached the commercial success hoped for, they are still interesting materials especially in functional applications. The research in this area was extended to other nanofillers, like cellulose nanocrystals and halloysite nanotubes showing some potentials also for practice. In agreement with the general trend in academia and in the industry a large part of our attention was focusing on biopolymer. We studied various aspects of these materials from their preparation, modification and degradation and used a number of natural and synthetic components to create blends and composites from them. Several of the developed materials have functional properties and can be used in packaging, biomedical applications or stabilization. The extensive knowledge obtained in this OTKA project was summarized in book chapters and review papers, most of them prepared on request. This report lists the most important achievements of our research and the related papers.

2. Polypropylene

Polypropylene is one of the commodity polymers used in the largest quantities. The growth rate of its use is also considerable. The reason for the success of this polymer is its versatility, very good balance of properties and excellent price/performance ratio. The properties of the polymer can be modified by various methods, copolymerization, blending, or the use of fillers or reinforcements. Recently PP is reinforced more and more frequently with natural fibers to increase sustainability and to decrease price. Our efforts in this area have been focused on two questions which overlap with each other in some extent, the reinforcement and impact modification of PP and the use of natural fibers in this matrix.

2.1. Reinforcement and impact modification

As mentioned above, PP has a very good balance of properties. A PP homopolymer has a modulus of around 1.5 GPa and a strength about 30 MPa. However, its impact resistance of about 2 kJ/m^2 is not sufficient for some applications and occasionally even its stiffness must be increased. One way to increase impact strength is copolymerization and properties can be further modified by changing the crystalline structure of PP by nucleation. In a project carried out together with our industrial partner, Borealis, we studied the effect of nucleation on the impact resistance of PP copolymers (Horváth 2016). The results showed that efficient nucleation increases the thickness of PP lamellae, but results in increased phase separation as well thus changing also the structure of the amorphous phase of the polymer. The proper combination of ethylene content, the type and amount of the nucleating agent led to a more than twofold increase in impact resistance. Stiffness is usually increased by the addition of fillers or fibers, while impact resistance by blending with elastomers. Unfortunately, both approaches have drawbacks, increased stiffness is usually accompanied by decreased impact resistance and vice versa, larger impact resistance results in a decrease of stiffness. Quite a number of PP raw materials are available on the market which are reinforced with traditional glass (GF) or occasionally carbon (CF) fibers, but PP is increasingly reinforced by wood flour and natural fibers. In a project we compared the reinforcing effect of traditional fibers to that of wood flour and showed that all three reinforcements have advantages and drawbacks (Várdai 2020a). PP reinforced with carbon fibers is very stiff, glass offers a good combination of stiffness and strength, while wood provides stiffness, good price and environmental benefits. Synthetic fibers are not frequently used for the reinforcement of polymers, because their modulus is not as large as that of glass or carbon fibers. In a study we modified PP with PET and PVA fibers and found that they do not increase stiffness very much indeed, but the impact resistance of the polymer improve considerably (Várdai 2020b). The simultaneous increase of stiffness and impact resistance is a crucial quest for plastics used in the automotive industry and the traditional approach is to add a filler or fiber and an impact modifier to the matrix polymer. In an attempt to use the approach, we reinforced PP with wood flour and used elastomer for impact modification (Sudár 2016). The attempt failed completely, although stiffness increased, impact resistance remained always at a very low level. However, based on earlier results, we developed the novel concept of using synthetic fibers

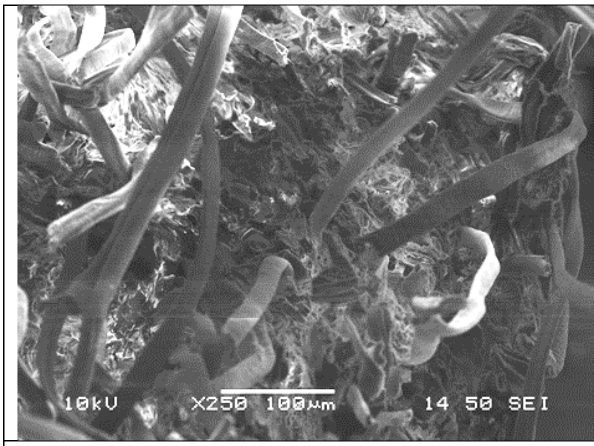

Fig. 1 *Fracture surface of a PP/PET/wood hybrid composite; impact modification by debonding of the synthetic fibers.*

for the impact modification of PP and prepared hybrid composites with wood fibers (Fig. 1). Both the stiffness and the impact resistance of the polymer could be increased simultaneously in this ways yielding a material which can be used successfully for structural purposes in the automotive industry (Várdai 2019).

Fig. 2 *Bagasse fiber used for the reinforcement of PP*

2.2. Natural reinforcements

Natural fibers have large stiffness, they are light and environmentally benign. Car parts prepared from PP often contain flax, hemp, wood flour and more exotic fibers like abaca, coir, or banana, but the search for new reinforcements goes on continuously. In and Indonesian cooperation we obtained sugarcane bagasse fibers (Fig. 2) and used them for the reinforcement of PP (Anggono 2019). The stiffness of PP increased as expected, but its impact resistance remained very small, just like in the case of wood flour. A closer study of the problem revealed that the inherent strength of the fibers is small and they fracture parallel to their axis. Alkali treatment of natural fibers is often used to increase their strength. The effect is clear but the explanations given are contradictory. We treated our bagasse fibers with NaOH and in a detailed study proved that not microfibril angle, crystallinity or crystal modification, but changing composition results in the increased strength of the fibers (Bartos 2020a). We used the alkali treated fibers for the reinforcement of PP and showed that the improvement in the inherent strength of the fibers transfers also to the composites thus increasing composite strength but even impact resistance slightly (Bartos 2020b).

3. Stabilization of PE, natural antioxidants

Polymers must be stabilized to protect them against degradation during processing and their application. Stabilization is a mature technology now, well established packages are used usually containing a phenolic antioxidant and a secondary stabilizer, often a phosphor containing compound, a phosphite, phosphonite or phosphine. However, about a decade ago questions arose about the environmental and health effect of phenolic antioxidants and the industry has not given an answer yet and in fact, it is not prepared to give one, since not much research has been done in this area recently because of the maturity of the technology. A few years ago we proposed the use of natural antioxidants for the stabilization of polyolefins and showed that certain compounds (quercetin, curcumin) are more efficient stabilizers than the currently used synthetic antioxidants. In the OTKA project we continued this research and studied the effect and efficiency of various flavonoid type antioxidants [dihydromyricetin (Fig. 3), silymarin, rutin] in the stabilization of polyethylene (Kirschweng 2016, Kirschweng 2017, Kirschweng 2018). The research

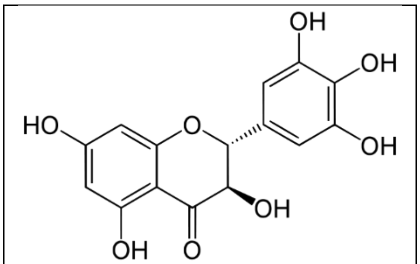

Fig. 3 *Dihydromyricetin, one of the natural antioxidants used in the study*

showed that the efficiency of the antioxidants depends on their structure and varies in a wide range. Physical properties and stability also play a role and compounds with low binding energy of the hydrogen on the active hydroxyl groups are usually quite efficient. We also compared a pure antioxidant to its natural extract and proved, that the extract is slightly more efficient than the pure compound because of several active components as well as the beneficiary effect of the accompanying substances, which improve the solubility and dispersion of the active component in the polymer (Kirschweng 2020). The research with natural extracts from various fruits and especially from agricultural waste continues also in the future.

4. Nanocomposites

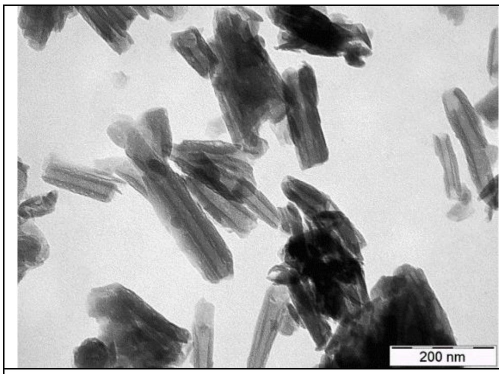

Fig. 4 *Halloysite nanotubes used as carrier for an active molecule.*

Layered silicate nanocomposites created much interest when the researchers of Toyota prepared composites from PA by in situ polymerization and later the company used the material for a part of one of its model. The original idea was that the homogeneous dispersion of nanometer sized particles in a polymer creates large interfaces and thus strong reinforcement at small filler content. Unfortunately, the expectations has never been fulfilled since homogeneous dispersion could be practically never achieved. The strong interactions among the platelets of the silicate prevent complete exfoliation and good dispersion. Research done in the field proved that the key for the preparation of nanocomposites with good properties is the control of interactions. Accordingly, these interactions have been mainly in the focus of our attention in recent years. In an exploratory project we compared the reinforcing effect of various micro- and nanofillers in polyamide and showed that exfoliation, structure and interactions determine properties indeed (Hári 2018a). Nanofillers reinforce the polymer at small concentrations, but microfillers and reinforcements offer similar benefits at lower price. The comparison of the effect of a layered silicate in four different polymer matrices confirmed the key role of interactions which determine structure, local processes and composite properties (Hári 2017). Since interactions are very important, the knowledge of the size of the interface is equally significant, thus we launched a project to revisit the known method used for the determination of the specific surface area of layered silicates by the methylene blue approach (Hegyesi 2017). The study called attention to factors neglected in the past in most research and offered a guide to obtain more reliable results. Interactions can be modified by surface treatment. The edge OH groups of silicate layers were modified by a monofunctional silane compound to control the interaction of the silicate layers (Hegyesi 2019). The results revealed that besides the OH groups also MgOH units play a role in the formation of a house of card structure. Since the lack of complete exfoliation is the major obstacle in the way of composite preparation, we exfoliated the silicate completely in water, modified the surface with a linker and polymerized methyl methacrylate on the surface in the hope to disperse the layers efficiently in a PMMA matrix (Hegyesi 2020). The obtained modified silicate fillers were characterized very thoroughly, and experiments are under way to prepare PMMA/modified silicate composites and determine their properties. Since the results obtained with layered silicates were quite disappointing in most cases, the interest of researchers turned toward other nanofillers like carbon nanotubes, graphene, halloysite (Fig. 4) and cellulose. In an attempt to prepare functional materials with the help of nanofillers, we studied the adsorption of an active molecule on the surface of halloysite nanotubes (Hári 2016). The detailed study of the adsorption process and the structure of the modified filler offered valuable information of its possible use in the stabilization of PE. In cooperation with a Chinese partner we explored the possibility of using cellulose nanocrystals for the reinforcement of PLA (Zhang 2019). Since homogeneity is an issue in all nanocomposites, proper dispersion was achieved by the Pickering emulsion technique.

5. Biopolymers

Although considerable research has been done in a number of areas in the past four years, the majority of the studied focused on projects related to polymers or reinforcements from natural resources, bio-based or biodegradable polymers and our attention shifts and will shift more and more in this direction also in the future. Since a considerable number of projects have been done in this field, we divide them arbitrarily into four groups.

5.1. Aliphatic polyesters

Besides natural polymers (cellulose, starch, lignin), aliphatic polyesters are the most important biopolymers at present. The two most important members of the family are poly(hydroxyl butyrate), PHB, which is produced in an enzymatic process, and poly(lactic acid), PLA, that is the biodegradable polymer produced and used in the largest quantity at the moment. PHB is still relatively expensive and its processing stability is limited thus it is used mainly in medical applications as drug carrier matrix or as implant. In these applications the solubility and diffusion of the active component as well as its release is of utmost importance. During our research we developed several simple and reliable methods to determine the diffusion coefficient of active components (Polyák 2017), the release kinetics of the drug (Polyák 2020a, Polyák 2020b) from PHB, but also a novel technique to follow the degradation of this polymer (Polyák 2017). As mentioned above, PLA is the biopolymer used in the largest quantity mainly in packaging, but also in other applications. One of its drawbacks is its fast physical ageing, which changes properties drastically in about a week. The physical ageing of PLA is usually explained by the change of free volume, but certain phenomena cannot be explained acceptably by this approach. We proposed an explanation which includes also the relaxation of internal stresses (Fig. 5), besides that of the free volume, and can explain all the experimental results published up to now in the literature (Cui 2020). The properties of PLA are not as advantageous as those of

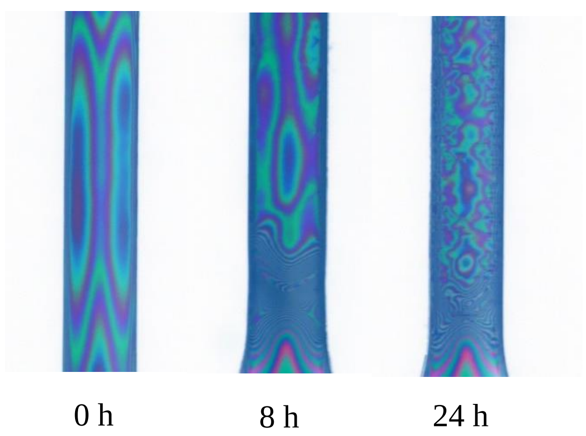

Fig. 5 *Internal stresses developing in PLA and their change during physical ageing.*

the commodity polymers thus it is modified in many ways, but copolymerization, plasticization or blending. In a project we modified PLA with a polyurethane elastomer and proved that reactive blending is more efficient in improving properties than the preparation of a simple physical mixture (Bedő 2017).

5.2. Degradation of aliphatic polyesters

One of the advantages of biopolymers is their biological degradation. Biodegradation is important from the environmental view, but also for scaffolds and implants with controlled lifetime, and in some cases for controlled release of active compounds as well. Accordingly we studied the degradation of aliphatic polyesters in several projects. We found that the hydrolytic degradation of these polymers proceeds with acceptable rate only at extreme pH values, which are impractical for the applications mentioned above (Polyák 2017). On the other hand, degradation can be catalyzed quite efficiently by enzymes. We developed a model to describe the enzymatic degradation of PHB quantitatively (Polyák 2018) and determined the role of the adsorption of the enzyme on the polymer substrate in the degradation process (Polyák 2019). The model developed for PHB could be successfully used for the characterization of the degradation kinetics of PLA in PLA/cellulose nanocrystal composites as well (Hegyesi 2019). In this study we pointed out that a number of factors including pH and the ionic strength of the degradation medium also influence the rate of degradation. The model was successfully applied also to polycaprolactone (PCL) resorbable scaffolds. In these scaffolds, by using halloysite nanotubes a support, we could incorporate the enzyme into the polymer itself for the first time thus allowing the preparation of a device with controlled lifetime (Hegyesi 2020).

5.3. Lignin

Lignin is the second most abundant natural polymer in the world. It is a side product of the cellulose and biofuel industry and a large part of it is burnt in the technology. The value added application of lignin would be of large environmental and financial advantage. It is already used in niche applications like surfactant or additive for concrete, but extensive attempts are made to produce chemicals from them or use them as additives or other components for plastics. In an attempt to utilize lignin as an additive for plastics we prepared polymer/lignin blends from polypropylene (Bozsódi 2016), polymers containing aromatic groups like PS, PC and PET (Szabó, 2017) and ethylene-vinyl alcohol copolymers with various ethylene contents (Podolyák, 2018). In the latter case we could draw conclusions about the role of hydrogen bonding interactions in the determination of the structure and properties of the blends. In ionomer/lignin

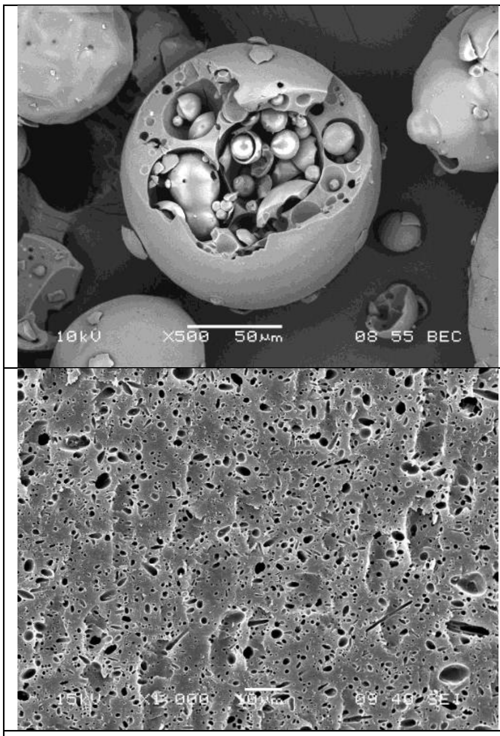

Fig. 6 *Original lignin particles and the structure of a EVOH/lignin blend.*

blends, both ionic and hydrogen bonds can form between the components and their relative number determine properties (Szabó 2018). The results obtained on a wide range of polymer/lignin blends proved that competitive interactions determine structure and properties in these blends and the strongest interactions develop in ionomer/lignin blends (Romhányi 2018). One of the greatest problems before the application of polymer/lignin blends is their rigidity, all blends fail by brittle fracture already at moderate lignin content. In our further work we studied structure evolution in EVA/lignin blends (Fig. 6) and showed the effect of both kinetics and interactions in structure formation (Pregi 2019). In cooperation with Chinese colleagues we prepared PLA/lignin blends by the Pickering emulsion approach and compared their properties to similar blends produced by melt mixing (Li 2019). The better dispersion of lignin in the Pickering blend resulted in far better properties. The work continues with the chemical coupling and modification of lignin as well as towards the development of materials for practical applications.

5.4. Starch

Similarly to lignin, starch is also a cheap agricultural product which is available in large quantities. Many attempts are made to make products from the polymer or use it as a component of plastics. Unfortunately, the large, stiff molecules of starch and the strong interactions among starch molecules complicate the handling of the material, it cannot be processed with the usual processing technologies used in the plastic industry. Starch must be plasticized in order to decrease the interactions among the molecules and this is usually done by glycerol or water, but other hydrogen bonding small molecular weight compounds like amines are also used occasionally. The combination of PLA and starch result in blends which are completely biodegradable, thus many studies have been carried out on them. However, the two components are not miscible and the presence of glycerol further complicates the interaction of the components, structure and properties. We studied these questions in a project and found that the miscibility of the components is limited, they dissolve in each other only in very small amounts, glycerol is located almost exclusively in the starch phase, and properties are not very advantageous (Müller 2016). In order to explore the possibility of preparing real products from the blends, specimens were injection molded from them and their structure and properties were determined in a wide composition range. We observed that the two phases, PLA and plasticized starch (TPS), phase separate during processing and a PLA rich layer develops on the surface of the specimens (Fig. 7). The layer can be even advantageous since it decreases the rate of water absorption, which deteriorates properties otherwise (Józó 2020).

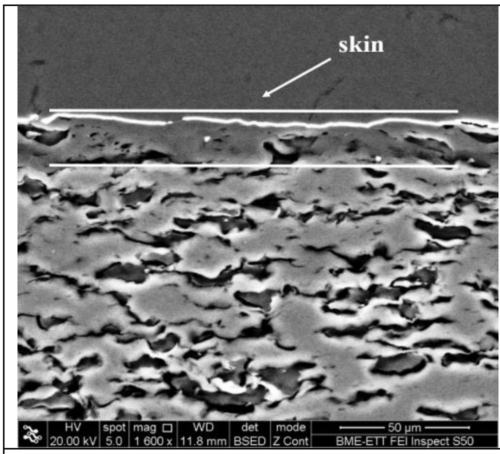

Fig. 7 *Phase separation of PLA and TPS at the surface of a specimen.*

6. Functional materials

Polymers are used mainly for packaging or as structural materials. In recent years considerable effort is focused on providing them with functional properties as well.

Scaffolds and implants contain active components with anti-inflammatory or antioxidant properties, while packaging can also contain antioxidants, but also functions like the identification of the producer or the lifetime of the product. Moisture can deteriorate certain products like some food, drugs or electronic parts, thus the packaging material must absorb all moisture to keep them dry (Fig. 8). We prepared such active packaging materials from high impact polystyrene and zeolite and studied their structure as well as water absorption, both rate and capacity (Kenyó 2018). The study revealed that the absorption capacity of the composites depends mainly on the amount of desiccant, i.e. zeolite, while the rate of adsorption on the structure of the polymer. In another study a wide range of polymers were used as matrix in such zeolite composites to help the selection of the most efficient for the functional application mentioned (Kajtár 2017). The results clearly proved that the main factor determining the rate of moisture adsorption is the free volume of the polymer. Interfacial interactions influence mechanical, but not functional properties. The absorption capacity of the packaging material is determined by the amount of desiccant present and is not influenced by other factors like the free volume of the polymer or interfacial interactions. Other functional materials have been also studied in the project; some of them are mentioned in Section 8 on applications.

Fig. 8 A desiccant PP packaging container for pharmaceutics.

7. Overview and synthesis of the results

Our group has been doing research on the modification of polymers since several decades. Although the topic of the research changes continuously we accumulated considerable general knowledge as well. Our expertise seems to be interesting also for others and we are often invited to write chapters or review articles. Our experience in particulate filled polymers, especially polyolefins, led to the writing of two chapters, one on PE and the other on PP (Móczó 2018, Móczó 2019) in which we summarize our knowledge and experience on the preparation of such materials and on interactions, structure and properties. Our activities related to bio-based polymers and their modification brought to life a series of conferences called Bipoco (Bio-Based Polymers and Composites). The first meeting was organized in 2012 in Siófok, and the last in 2018 in Balatonfüred. Unfortunately, the one planned for 2020 had to be cancelled because of the pandemic. The best papers presented at the conference were published in special issues of the journal European Polymer Journal and the most important new results were summarized in preface papers (Gyarmati 2017, Gyarmati 2019). These papers do not only introduce the articles related to the conference, but also give an outlook for new areas and trends. Our pioneering activity in the field of natural antioxidants caught the attention of the leading scientists of the area and we were invited to prepare a review paper on the topic (Kirschweng 2017). The paper summarizes the natural compounds that have been used as stabilizers for polymers up to now and calls attention to the most important problems, challenges, but also advantages of using natural compounds in polymers. The paper created some interest in the society interested in the stabilization of polymers, but also in other areas like food chemistry. Even larger interest accompanies our feature article on lignin blends (Kun 2017). The paper points out contradictions published in the literature on these materials and calls attention to the utmost importance on component interactions in the determination of the structure and properties of these materials. The paper received almost 100 independent citations since its publication.

8. Application

Although most of the activities of our group is basic research focusing on the determination of general correlations among interactions acting in multicomponent materials, their structure and properties, many of the projects have practical relevance and the results are applied already or they have some potentials to be applied in the future. Research is done with the participation of young scientists, several PhD students worked on various projects in the framework of this contract and their work was supported by many BSc and MSc students. During the timespan of the research seven PhD students (Kenyó Cs., Müller P., Hári J., Kirschweng B., Hegyesi N., Polyák P., Kun D.) completed their studies, while others continue working in various areas, their thesis is under preparation and they will defend it in the nearer or farther future. Some of the papers published have very strong relevance for practice. The project on the thermal analysis of polyacrylonitrile is related to our work on carbon fibers (see Section 2, Polypropylene), but the results can be used in the optimization of carbon fiber production by Zoltek Zrt. (Szepcsik 2018, Szepcsik 2019). The work on nanocomposites yielded a functional material which can be efficiently used in the stabilization of polyethylene (Hári 2018b). The functional, electrospun fibers containing an active compound were developed together with pharmacists from Szeged University and the device can be used efficiently for the treatment of periodontitis (Budai-Szűcs 2020). We also developed a PMMA support for organocatalysis, which allows the fast and efficient recycling of the very expensive catalyst (Nagy 2020). Together with multinational companies we developed novel materials which have been patented by the corresponding companies. The patent on functional packaging material was obtained together with AirSec/Süd Chemie (EP 2204404 B1), while the development of high impact polypropylene copolymers with Borealis AG (EP 2526146 B1). Three patents were obtained on fiber reinforced polypropylene composites also together with Borealis AG (US 10081726 B2, EP 3309211 B1, EP 3309212 B1). We work with several other companies on the development of various materials and technologies and hope that our results will be applied in everyday practice in the future.

9. Summary

The financial support obtained in the framework of the OTKA K 120039 contract offered us the possibility to continue our work on the modification of synthetic and natural polymers having been carried out since many years. The research was and is acknowledged internationally shown by the large number of citations obtained year by year. We continued to organize the biennial Bipoco meeting, always attended by around 200 participants, which extended our international acceptance, allowed us to increase the number of our contacts and to widen our horizon generally. Besides continuing research in some traditional areas, new research topics also gained importance in our activities and our attention shifted more and more towards natural and biopolymers as well as medical applications. Our interest in functional materials have not decreased and we try to use them in stabilization, in the biodegradation of aliphatic polyesters or in medical applications. We continue our work on lignin and develop materials with large renewable content which is very important both to decrease pollution as well as carbon footprint. The work is mostly done by young scientist, staff members, PhD, MSc and BSc students and besides doing high level scientific research, we dedicate considerable efforts to find practical application for the materials and/or technologies developed.