Final report

on the project K 108934 (Competitive interactions in functional polymer systems)

1. Introduction

Recently attention is directed mainly towards the development, production and use of functional materials [1-4]. Several functional polymers have been studied like active packaging compounds, which help to conserve the packaged ware or offering protection against water or oxygen , or controlled release systems [1-5]. Although the use of functional polymers is industrial practice already, relative limited information is available on the basic correlations, on the factors determining the desired properties.

Controlling the moisture-content of packaged wares is extremely important in several areas such as food packaging, while maintaining dry conditions is usually a requirement of packaging for pharmaceuticals and electronic devices [6,7]. Air humidity must be captured in the latter case, which is carried out through the adsorption or absorption of water by a desiccant. Zeolites are used the most frequently as desiccants in polymer composites, however the literature dealing such system is quite limited. Intensive research is conducted also on the development of new desiccants, including hybrid materials, natural polymers, and superabsorbent gels, but the basic correlations are also insufficient in these area. Therefore during the present project several desiccant (zeolites, calcium-oxide (CaO), zeolite/CaO hybrid desiccants, starch, sodium polyacrylate superabsorbent (SAP)) and polymers were used to prepare and study polymer/desiccant composites. The characteristics of desiccants and polymers and their composites were measured in order to determine the factors affecting the functional properties of the investigated polymer composites.

Another important group of functional polymers is polymer nanocomposites which are capable for targeted drug delivery. Halloysite nanotube (HNT) is a naturally occurring aluminosilicate clay with tubular structure. Due to its high mechanical strength, thermal stability, biocompatibility, HNT has a number of exciting potential applications in controlled release devices. Numerous attempts have been made to use halloysite nanotubes as carriers for all kinds of bioactive molecules [8]. During the project we investigated the possible functional application of halloysite nanocomposites. PE/HNTs nanocomposites were prepared and halloysite nanotubes were used as controlled release carriers, and an active agent, a natural antioxidant (quercetin) was applied for filling into the nanotubes in order to reach higher degree of dispersion of antioxidant in polymer matrices.

2. Polymer/ desiccant composites; factors determining functional properties

2.1 Polymer/zeolite composites

During the project five different zeolite (zeolite 3A, 4A, 5A, 10X and 13X) were selected for the investigation. The five zeolites, which included the A and X types are frequently used in industrial practice. Their particle size, size distribution, specific surface area, pore characteristics (size and area) as well as the dispersion component of the surface tension were determined. Water adsorption capacity and kinetics of all desiccants at different humidity conditions were also measured.

Using the five zeolites ten different polymers were selected as possible matrices for zeolite-containing desiccant composites utilized in the preparation of functional packaging materials

Water uptake of composites was determined at 100 % RH and the results were analyzed to identify factors influencing the capacity and rate of water adsorption. The results showed that the desiccants were able to adsorb a considerable amount of water in their free pores. Water uptake of all zeolites and composites could be modeled by Fickian diffusion. The adsorption capacities of the composites depended linearly on the amount of desiccant present in the composite, but were independent of the type of polymer used. On the other hand, zeolite characteristics influence the moisture adsorption of the composites only marginally; adsorption capacity is determined by zeolite content, whereas the rate of adsorption is determined by the properties of the polymer. Composites prepared with X type zeolites have somewhat smaller water adsorption capacity than those containing their A type counterparts. Water initially diffused rapidly into the composites, but this diffusion slowed over time and also with increasing desiccant content. The latter effect can be explained by the increase in the diffusion path as the zeolite content increases. The initial rate of diffusion depended solely on the specific free volume of the matrix, and this factor also strongly influenced the overall rate of water adsorption. However, the latter characteristic also depended on other factors, such as the dispersion of the desiccant in the matrix.

The study of the characteristics of polymer/zeolite desiccant composites prepared with ten different matrices showed that their properties change in a wide range. Stiffness varies between 0.3 and 10 GPa, while strength between l0 and 80 MPa. Because of their larger surface energy X type zeolites have reinforce the polymer more than A type desiccants. The deformability of most composites is small and decreases with increasing zeolite content. For the characterization of interfacial interactions among components in polymer/zeolite composites the investigation of micromechanical deformation processes and contact angle measurements were carried out. The results of the study proved that interfacial adhesion between the polymers and zeolites is not very strong and the composite properties are determined mainly by the matrix characteristics and interfacial interaction plays only a minor role. Accordingly, the matrix of such desiccant composites must be selected mainly according to functional properties and always in view of matrix characteristics.

From the results a PhD thesis and four papers were published and one is submitted:

1. Kenyó C; Kajtár DA; Renner K; Kröhnke C; Pukánszky B: Functional packaging materials: Factors affecting the capacity and rate of water adsorption in desiccant composites, J. Polym. Res. 20: 294, 1-8, 2013
2. Kenyó C; Renner K; Móczó J; Fekete E; Kröhnke C; Pukánszky B: Effect of desiccant characteristics on the properties of PS/zeolite functional packaging materials, Polym. Compos. 35(11): 2112-2120, 2014
3. Kenyó C; Hári J; Renner K; Kröhnke C; Pukánszky B: Effect of Matrix Characteristics on the Properties of High-Impact Polystyrene/Zeolite Functional Packaging Materials, Ind. Eng. Chem. Res. 53: 19208−19215, 2014
4. Kajtár DA, Kenyó C; Renner K; Móczó, J., Fekete, E., Kröhnke, Ch., Pukánszky, B.: Interfacial interactions and reinforcement in thermoplastics/zeolite composites, Composite B. 114:386-394, 2017
5. Kenyó C; Renner K; Móczó J; Fekete E; Kröhnke C; Pukánszky B: HIPS/zeolite hybrid composites as active packaging materials: Structure and functional properties, Eur. Polym. J. (submitted)
6. Kenyó C: Active Packaging Materials: Factors, Mechanism, Efficiency, PhD Thesis, BUTE, Department of Physical Chemistry and Material Science, 2015

2.2 Polymer/hybrid desiccant and SAP composites

LDPE/desiccant and PMMA/desiccant composites were prepared using zeolite 4A, calcium-oxide (CaO) and their combination (hybrid desiccants). Water uptake of composites was determined at different relative humidity (RH) and results were analyzed to identify the factors influencing the capacity and rate of water sorption. The results showed that water uptake of composites can be modeled by Fickian diffusion for only systems containing zeolite. The composites prepared with CaO and hybrid desiccant showed non-Fickian transport, so we used a diffusion-relaxation model proposed by Berens and Hopfenberg [9] for the calculation of water sorption capacity and rates. According to the model calculations sorption capacity and rate of the composites depend on the amount of desiccant present in the composite, the applied RH and in the case of the hybrid desiccants on the CaO/zeolite rate. As was observed in the case of polymer/zeolite composites the adsorption capacities of the composites of hybrid desiccant and CaO depended linearly on the amount of desiccant present, whereas the rate of adsorption is determined by the properties of the polymer. The largest capacity and rate were found in the LDPE/CaO and PMMA/CaO composites, but the chemical reaction between CaO and water during the water uptake results in significant volume change of these composites. Partial substitution of CaO by zeolite can decrease the volume change of the composites, but at the same time it also leads to decreased water sorption capacity and rate. Consequently if we use hybrid desiccant the CaO/zeolite rate must be selected according to the task to be fulfilled.

The results were summarized in a BSc and MSc thesis and published in a hungarian journal:

1. Rácz Ágnes: Hibrid deszikkánst tartalmazó polietilén kompozitok tanulmányozása, Szakdolgozat, BME, 2015
2. Jeney Balázs: Hibrid deszikkánst tartalmazó PMMA kompozitok tanulmányozása, Diplomamunka, BME, 2017
3. Bere J; Rácz Á; Fekete E; Pukánszky B: Hibrid deszikkáns rendszert tartalmazó funkcionális csomagolóanyagok, Muanyag Gumi 51: 231-236, 2014

We also prepared composites from sodium polyacrylate superabsorbent (SAP). Polystyrene (PS), poly-methyl methacrylate (PMMA) and polyethylene (LDPE) composites were produced in a wide composition range and the water absorption capacity and kinetics of the desiccant as well as the composites at different humidity conditions were investigated. The results revealed that factors influencing the capacity and rate of water sorption are very similar to the other investigated composites containing desiccants, but at high relative humidity the sorption capacity of SAP is multiple of zeolite and CaO. The initial rate of water diffusion depended strongly on the specific free volume of the matrix, thus the crystalline PE has the smallest initial rate. Similarly to CaO water uptake of SAP results in significant volume change of the composites.

The results were presented in a BS thesis

1. Jeney Balázs: Szuperabszorbenst tartalmazó polimer kompozitok vizsgálata, Szakdolgozat, BME, 2015

2.3 Polymer/starch composites

Recently a growing interest has been shown in the application of biopolymers as packaging materials in order to reduce the environmental pollution caused by plastic waste, and to achieve sustainable development. PLA is a promising option since it is environmentally friendly and suitable for a number of packaging applications, especially in food packaging. Increasing application area of PLA could be achieved by adding desiccant to pure PLA. Starch is a natural desiccant which is readily available, cheap and biodegradable, therefore PLA/starch and PLA/starch-glycerol composites with different glycerol content were prepared in wide composition range. Water uptake of the desiccant composites was determined at 50 and 100 % RH. Structure and mechanical properties were also investigated and the effect of glycerol content on the measured properties was studied as well. The results showed that starch has significant desiccant effect in PLA. Starch can absorb considerable amount of water, thus the absorption capacity of PLA/starch composites are close to the commonly applied polymer/zeolite desiccant composites. The absorption capacity of the composites depends approximately linearly on the amount of starch present and on the relative humidity. The diffusion of water into the composites is fast initially, but slows down over time, and show Fickian diffusion. Surprisingly the initial and overall rate of desiccant composites was smaller than those of the PLA. Although the absorption capacity of starch-glycerol powders exceed the capacity of starch powder the additional glycerol did not increase the equilibrium water uptake of the desiccant composites. The smaller water absorption of PLA/starch-glycerol composites compering with the PLA/starch composites can be explained by the migration of glycerol from the bulk on the surface of the composites. Besides the desiccant effect starch has also reinforcing effect in PLA, stiffness and strength increase with increasing starch loading. SEM investigation of fracture surface of composites showed only moderate interfacial adhesion between PLA and starch. The composition dependence of mechanical properties of PLA/starch-glycerol composites however depends on the glycerol content of the composites. The modulus and tensile strength decrease with increasing filler content. Glycerol addition weakens the PLA/starch adhesion and softens starch particles. These effects results in the change of the morphology and the dominating deformation mechanism of damage of composites. At large glycerol content a quasi-co-continuous structure can formed.

The results were summarized in two BSc thesis and it has been submitted to the journal “Industrial Crops and Products”:

1. Verasztó Ferenc: A glicerin tartalom hatása a PLA/keményítő kompozitok tulajdonságaira, Szakdolgozat, BME, 2016
2. Kalocsai Tibor: PLA-keményítő és PLA-lágyított keményítő rendszerek: deformációs folyamatok és határfelületi kölcsönhatások, Szakdolgozat, BME, 2016
3. Móczó J; Kun D; Fekete E; Desiccant effect of starch in PLA, Ind. Crops Product (under review).

Polyethylene (LDPE)/maleic-anhidride modified polyethylene (MAPE)/starch and LDPE/MAPE/starch-glycerol composites were also prepared and investigated. Similarly to the PLA/starch composites the LDPE/MAPP/starch composites can absorb considerable amount of water. The absorption capacity of these composites was almost the same as was for PLA composites and depended also on starch content and on the relative humidity, but the rate of water uptake is one order of magnitude lower that the ones of PLA systems. Furthermore at low glycerol content the equilibrium water absorption increased with increasing glycerol content of LDPE/MAPP/starch-glycerol composites, significant glycerol migration was observed only at high glycerol contents. Unfortunately the LDPE/MAPP/starch-glycerol composites became moldy after some month at 100 % RH.

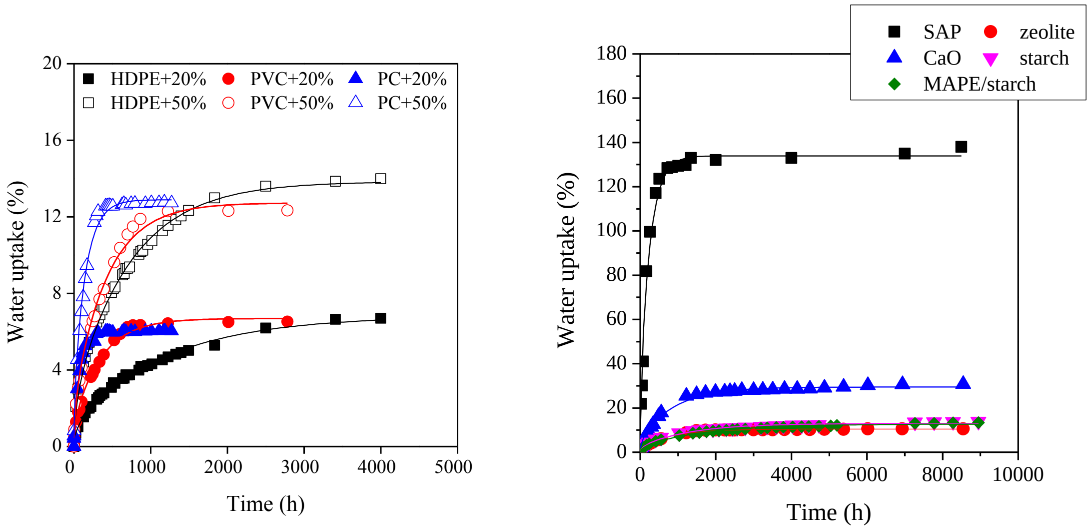
The results were summarized in a MSc. thesis:

1. Sziklai Kristóf: Deszikkánst tartalmazó polietilén kompozitok előállítása és vizsgálata, Diplomamunka, BME, 2016

2.4 Basic correlations, factor determining water uptake, competitive interactions

Comparing the results determined for the different polymer/desiccant composites we can draw several general conclusions.

- The water sorption of almost all polymer composites could be modeled by Fickian diffusion except the composites contained CaO. The composites prepared with CaO and hybrid desiccant showed non-Fickian transport.
- The water sorption capacity of polymer/desiccants composites depends on the type and amount of desiccant present in the composite, but is independent of the type of polymer used (Fig.1).
- The rate of adsorption is determined by the properties of the polymer and desiccant. In the case of composites prepared with the same desiccant the initial rate of diffusion depended solely on the specific free volume of the matrix, and this factor also strongly influenced the overall rate of water adsorption. However, the latter characteristic also depended on other factors, such as the dispersion of the desiccant in the matrix (Fig. 1a).
- The mechanical properties of polymer desiccant composites are determined mainly by the matrix and filler characteristics as well as on the interfacial interactions.
- Water uptake of CaO, CaO/zeolite hybrid desiccant and SAP results in significant volume change of the composites.



a b

Fig 1 Water uptake of polymer/zeolite (a) and LDPE/ 30 V/V % desiccant (b) composites

3. Polymer/halloysite nanocomposites as potential carrier materials for the controlled release of a stabilizer in polyethylene

Quercetin is a very efficient natural antioxidant for PE, but its poor solubility and high melting temperature limits its application. The use of halloysite nanotubes as a support or carrier material seemed to be an obvious solution for the problem. The halloysite nanotubes used as potential carrier material for the controlled release of a stabilizer in polyethylene were thoroughly characterized with several techniques. Specific surface area, pore volume and surface energy determine the adsorption of the active molecule on the surface of the mineral. The high surface energy of the halloysite measured by inverse gas chromatography (IGC) results in strong bonding of the additive onto the surface and difficult release as a consequence. FTIR spectroscopy confirmed strong interaction, an energetically heterogeneous surface and the development of multilayer coverage at large loadings. FTIR and XRD experiments proved the complete lack of intercalation and showed that below 3.5 m/m % quercetin loading most of the molecules are located within the tubes. Molecular modelling of the surface indicated the parallel orientation of quercetin molecules with the surface. Critical concentrations derived from various measurements agreed well with each other further confirming that up to about 4.0 m/m % loading, quercetin is bonded very strongly to the halloysite surface. As a consequence, the dissolution of the active molecules is very difficult or impossible, especially into apolar media like PE, thus neither stabilization nor a controlled release effect can be expected below that concentration.

For modeling the influence of polymers dissolution experiments were carried out for the determination of the effect of solvent characteristics on the amount of irreversibly bonded quercetin. The results proved that adsorption and dissolution depend on competitive interactions prevailing in the system. Solvents with low polarity dissolve only surplus quercetin adsorbed in multilayers. Polyethylene does not contain functional groups, thus the polymer forms weak interactions with every substance; quercetin dissolves into it from the halloysite surface only above a critical surface coverage. Preliminary stabilization experiments confirmed that strong adhesion prevents dissolution and results in limited stabilization efficiency. At larger adsorbed amounts better stability and extended effect were measured indicating dissolution and controlled release. A more detailed stabilization study showed that the melt stabilization efficiency of quercetin used above 4 m/m % calculated for the halloysite does not decrease in the presence of the halloysite support and halloysite nanotubes pretreated with the stabilizer possess controlled release function, ageing is slower in their presence than with separately dispersed components or in the absence of the halloysite.

The results were shown in an MSc and a PhD thesis and three papers were published:

1. Gyürki Ádám: Természetes antioxidánssal módosított halloysit nanocsövek vizsgálata, Diplomamunka, BME, 2015
2. Hári J: Polymer/silicate nanocomposites: competitive interactions and functional application, PhD Thesis, BUTE, Department of Physical Chemistry and Material Science, 2017
3. Kocsis, K., Polyák, P., Hári, J., Janecska, T., Földes, E., Pukánszky, B.: Természetes antioxidánssal módosított halloysit nanocső stabilizáló hatásának vizsgálata polietilénben, Műanyag Gumi 51: 395, 2014
4. Hári, J., Gyürki, Á., Sárközi, M, Földes, E, Pukánszky, B.: Competitive interactions and controlled release of a natural antioxidant from halloysite nanotubes J. Colloid Interface Sci., 462: 123-129, 2016
5. Hári, J., Polyák, P., Mester, D., Mičušík, M., Omastová, M., Kállay, M., Pukánszky, B.: Adsorption of an active molecule on the surface of halloysite for controlled release application: interaction, orientation, consequences, Appl. Clay Sci., 132-133: 167-174, 2016

4. Functional biopolymers

Besides the planned research program we started the investigation other functional polymers, namely functional biopolymers. Starch is considered as one of the most promising biopolymer because it is readily available, cheap and biodegradable. In the last decades, starch has been evaluated in its film-forming ability for applications in the food packaging area. One of the major problems with granular starch is its limited processability, which can be improved by the use of plasticizers, i.e. thermoplastic starch (TPS). The main disadvantages of TPS are its pronounced hydrophilic character and the inadequate mechanical properties. The inferior properties of TPS can be improved by the incorporation of other materials (natural fibers, nanoclays, or other biodegradable polymers). Silicate nanofillers and other carbohydrates are frequently used to improve physicochemical properties of TPS films. In addition blends of starch and other carbohydrates can be applied as edible films in food packaging. On the other way starch composites and blend may be also potential functional biopolymers for several medical and agricultural applications. The aim of the research was to prepare TPS blends and composites with good mechanical and barrier characteristics for food packaging or other applications.

TPS/clay nanocomposites, TPS/wood fiber composites as well as TPS/agar, TPS/Na-alginate and TPS/PLA blends were prepared and investigated. The effect of interfacial interactions as well as component characteristics on the structure and properties of TPS systems were investigated. In spite of the incomplete exfoliation of clays the addition of silicate nanofillers resulted in very strong reinforcement in TPS nanocomposites. Stiffness and strength increased, deformability decreased considerably as the filler content increased. Significant decrease of water vapor and oxygen permeability were found as an effect of clay loading. Similar reinforcing effect was measured at TPS/ agar blends and TPS/wood fiber composites, while the water vapor permeability decreased.

The results are summarized in two BS thesis and two MSc thesis and published in three papers:

1. Bella Éva: Funkcionális biopolimer keverékek, Szakdolgozat, BME, 2015
2. Jenei Andrea: TPS/Nátrium-alginát keverékek készítése és jellemzése, Szakdolgozat, BME, 2017
3. Angyal Lilla: Szerkezet/tulajdonság összefüggések TPS/rétegszilikát nanokompozit filmekben, Diplomamunka, BME, 2016
4. Bella Éva: TPS/agar-agar keverékek előállítása és jellemzése, Diplomamunka, BME, 2017
5. Müller P; Kapin É; Fekete E: Effects of preparation methods on the structure and mechanical properties of wet conditioned starch/montmorillonite nanocomposite films, Carbohyd. Polym. 113: 569-576, 2014
6. Müller P; Bere J; Fekete E; Móczó J; Nagy B; Kállay M; Gyarmati B; Pukánszky B; Interactions, structure and properties of PLA/plasticized starch blends, Polymer 103: 9-18, 2016
7. Fekete E; Kun D; Móczó J: Thermoplastic starch/wood composites: effect of processing technology, interfacial interactions and particle characteristics, Periodica Polytechn. Chem. Eng. (accepted)

5. Utilization of the results

During the project several BSc, MSc and PhD student participated in the research work. As a result of the project ten BSc and MSc and two PhD thesis were written. We intend to use the results in our BSc and MSc programs as well as in our industrial relationships.

6. Summary

Thanks to the project K 108934 we managed to study different functional polymer composites in order to determine the factors affecting the functional properties of them. Intensive research was done on desiccant composites controlling the humidity of packaged wares. Composites were prepared using different polymers and desiccants (zeolites, calcium-oxide, hybrid desiccants, starch, superabsorbent). Characteristics of polymers, desiccants and the composites were thoroughly investigated. The water uptake of polymer composites in the most cases could be modeled by Fickian diffusion, but for the composites prepared with CaO desiccant another diffusion-relaxation model proved to be right. The result showed that the water sorption capacity of polymer/desiccants composites depended on the type and amount of desiccant present in the composite, but is independent of the type of polymer used. The rate of sorption, however, is determined strongly on the specific free volume of the polymer. In the project the halloysite nanotubes used as potential carrier material for the controlled release of a stabilizer (quercetin) in polyethylene were also exhaustively characterized with several techniques. The results proved that up to about 4.0 m/m % loading, quercetin is bonded very strongly to the halloysite surface. As a consequence, the dissolution of the active molecules into the PE is impossible, but above this concentration a controlled release of the stabilizer can be achieved.

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