Active packaging materials: factors, mechanism, efficiency

Thesis book

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Introduction

Plastic packaging materials form an important part of the economy and our everyday life. They have numerous functions like making possible the safe distribution of products, protecting them from the environment, informing the customer, etc.\(^1,2\). Similarly to other areas, the packaging industry is under continuous development and change. The tendency is shown by the title of the leading article in Plastics Engineering "plastic packaging is becoming stronger, smarter and greener"\(^3\). In agreement with this title and due to the ever increasing demand of the public new solutions, including functional and smart packaging materials have been developed in recent years. The latter respond to changes in the environment, while the former fulfill some function improving the performance of the packaging. The number of such materials increases rapidly and they are used already in everyday practice. The main functions targeted for various products are oxygen scavenging\(^4\), humidity control\(^5,6\), regulating ethylene content\(^7\), antimicrobial effect\(^8\), adsorption of odorous materials, or the opposite, the release of desirable aromas\(^9\). Intensive research and development work is carried out on these materials all over the world, but mostly in industry.

\(^3\) Markarian, J., *Plast Eng* 70(6), 8-14 (2014)
**Antimicrobial packaging** (AMP) is closely related to food packaging and can be classified into two types: those containing antimicrobial agents that migrate to the surface of the packaging material and thus can come into contact with the food, and those that are effective against food surface microbiological growth without the migration of the active agent into the food\(^{10}\).

Ethylene is a growth hormone that functions in the sprouting of plant seedlings as well as during the growth of plants and fruits. The amount of ethylene present in the atmosphere influences the respiration rate of the plant, thus respiration can be altered by controlling ethylene concentration. Commercial agents for *ethylene removal* include KMnO\(_4\), activated charcoal, bentonite, zeolite, etc.

The removal of odors from the interior of packages may be both advantageous and disadvantageous. In the latter case, aroma capture may remove desirable components of the contained food thus leading to a convenience loss for the consumer. Accordingly, two of the main functions of such packaging systems are holding the desirable odors in the package while removing undesirable ones, which may be sometimes released by the packaging materials themselves. Some well-known examples for odor removal materials are activated carbon, which is extremely effective and commonly used, vitamin E (alpha-tocopherol) or BHT (butylated hydroxy-toluene).

*Aroma emission* is another important field of active packaging. The controlled release of desirable aromas from packaging materials is used to enhance the flavor perception of the contained food at the time of opening and shortly thereafter. Various flavors are used in the packaging industry and most of them are introduced into the packaging material during processing (e.g. extrusion).

Moisture control is one of the most important forms/purposes of active packaging. Humidity may cause the deterioration of the properties of packaged products, especially in the case of semi-prepared foods and pharmaceuticals. Dry atmosphere should be maintained to avoid damage, which is usually achieved by desiccants in the packaging industry. They can be classified in two groups based on their moisture uptake mechanism: adsorbents and absorbents. The former adsorb water physically on the surface of the adsorbent, while absorption is a chemical process, absorbents react with water or bind it.

Often used absorbents are calcium sulfate (CaSO$_4$), calcium chloride (CaCl$_2$) and calcium oxide (CaO). Adsorbents are able to bind considerable amount of water on their extensive, high energy surface. Active carbon, silica gel, clays, and zeolites are often used for this purpose; silica gel, and zeolite are the desiccants most frequently applied in practice. Intensive research is carried out to develop new desiccants including hybrid (adsorbent/absorbent) materials, natural polymers (starch, cellulose derivatives), and superabsorbent gels (acrylates, cellulose compounds).

Moisture controlling packages can be produced by the introduction of desiccants into polymer matrices. Dispersing desiccants in polymer matrices results in particulate filled polymer composites. The properties of such systems are determined by four factors: component properties, composition, structure, and interfacial interactions. All of these factors are equally important in influencing composite properties and they must be adjusted to suit the application.

Zeolites are used the most frequently as desiccants in polymer composites, however the literature dealing with such systems is quite limited. Most of the articles published focus on the mechanical properties of the compo-

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sites\textsuperscript{12,13,14,15}, and only a few discuss humidity control\textsuperscript{16,17}. Usually commodity polymers, e.g. polypropylene\textsuperscript{14-17}, polyethylene\textsuperscript{12-13} or polystyrene\textsuperscript{18}, are used as matrices in such desiccant composites; other matrices are rarely mentioned\textsuperscript{19,20}. These studies focused on the effect of matrix characteristics on the properties of desiccant composites and the possible influence of the zeolite was neglected, since only a single, specific zeolite was used in all cases. Zeolites can come from natural resources or can be produced synthetically. Many of their characteristics, including pore size and volume, particle size, specific surface area, surface energy, the ratio of silica and aluminum atoms, etc., may change in a wide range and influence the properties of polymer/zeolite composites.

Controlling oxygen permeability is especially important in the pharmaceutical and food packaging industry. The atmosphere within the sealed package should be free of oxygen, because it can react chemically with the contained food or pharma, and cause long-term oxidative effects. Limiting oxygen content is not always an easy task, since most foods contain air, and oxygen is often present in the headspace of the package. After recognizing that problem, oxygen removers came to the front of research. The materials applied to remove oxygen or preventing it from entering the package, and blocking

\textsuperscript{12} Biswas, J., Kim, H., Choe, S., Macromol. Res. 11, 357–367 (2003)
\textsuperscript{15} Acosta, J. L., Morales, E., Ojeda, M. C., Linares, A., J. Mater. Sci. 21, 725–728 (1986)
undesirable reactions can be classified into four groups: antioxidants, interce-
tors, absorbers, scavengers.

The permeability \((P)\) of gases and vapors through polymeric materials
depend upon two factors; the solubility \((S)\) of a gas or vapor in the polymer and
the rate of diffusion \((D)\). The oxygen permeability \((OTR)\) of polymers varies in
a wide range covering several orders of magnitudes\(^{21}\). The differences in oxy-
gen barrier properties mostly depend on the chemical composition and molecu-
lar structure of the polymers. The easiest way to minimize oxygen concen-
tration within the package in an active packaging system is to use polymers with
limited permeability like PA, PVDC, PAN or EVOH. Dry ethylene-vinyl alco-
hol copolymers (EVOH) offer extremely good protection against oxygen\(^{22}\).
Their good barrier properties are related to large crystallinity (~70 %) and the
large concentration of functional groups. This latter results in strong inter- and
intramolecular forces and thus large cohesive energy density \((CED)\)^{23}.

The barrier properties of EVOH copolymers depend on ethylene con-
tent\(^{24}\), crystallinity\(^{23}\), temperature and humidity\(^{25}\). All these factors influence
the OTR of EVOH, but humidity has a most pronounced effect. The permea-
tion rate of the polymer may increase by orders of magnitude with increasing
humidity. This effect represents the major drawback of ethylene-vinyl alcohol
copolymers as oxygen barrier materials. Numerous attempts have been made to
overcome this problem; they can be classified in three groups: blending EVOH

\(^{21}\) Massey, L.K.: Permeability Properties of Plastics and Elastomers - A Guide to Packaging and
Barrier Materials (2nd Edition), William Andrew Publishing/Plastics Design Library, Norwich
(2003)
\(^{24}\) Cava, D., Cabedo, L., Gimenez, E., Gavara, R., Lagaron, J.M., Polym Test 25(2), 254-261
(2006)
\(^{25}\) Muramatsu, M., Okura, M., Kuboyama, K., Ougizawa, T., Yamamoto, T., Nishihara, Y., Saito,
with other polymers\textsuperscript{26}, preparing multilayer films\textsuperscript{27}, incorporation of nano-fillers\textsuperscript{28,29}.

Active packaging materials become more and more a part of our life. In spite of the increasing need of controlling humidity within packages, very little systematic work has been reported in the literature on this issue according to our best knowledge. Neither the effect of polymer nor that of desiccant characteristics have been thoroughly investigated yet. As a consequence, the goal of our study was to carry out systematic experiments with desiccant composites prepared with selected zeolites and polymers to determine the effect of desiccant content, the properties of the matrix polymer, and desiccant characteristics on the rate and capacity of water adsorption, but also on other composite properties.

Controlling the oxygen permeability of packages also needs further development. Applying EVOH is possible, but as described above, the water sensitivity of this copolymer is a major drawback in its application as oxygen barrier material. Various approaches have been tried to overcome this problem. A detailed literature study of the topic has not indicated any solution, or even attempt, in which a small molecular weight additive was used to improve the barrier properties of poly(ethylene-co-vinyl alcohol) against oxygen. As a consequence, the goal of our study was to carry out systematic experiments with a specific small molecular weight additive to determine its effect on the barrier and other properties of EVOH.

\textsuperscript{27} Dhawan, S., Barbosa-Cánovas, G.V., Tang, J., Sablani, S.S.:; \textit{J Appl Polym Sci} \textbf{122}(3), 1538-1545 (2011)
Materials and methods

Different polymers with various chemical compositions, mechanical and rheological properties were selected as possible matrix for zeolite containing desiccant composites in order to cover a wide range of properties important in fulfilling their function and to prepare functional packaging materials. The series of zeolites, they included the most often used synthetic zeolites, i.e. 3A, 4A, 5A, 10X and 13X, were used as desiccants.

The components were homogenized in an internal mixer. Torque and temperature of mixing were recorded during homogenization and used for evaluation. 1 mm thick plates and 100 μm thick films were compression molded from the homogenized material. The zeolite content of the composites changed between 0 and 50 vol%.

The molecular weight of polymers was determined by gel permeation chromatography, density was measured using a pycnometer at room temperature. The water vapor transmission rate (WVTR) was determined on 100 μm thick films. The surface tension of the polymers (\(\gamma_S\)) was determined by static contact angle measurements. The butadiene content of HIPS copolymers was determined by the measurement of their iodine value according to the ASTM D 5902-2005 standard. The structure of the copolymers was studied by transmission electron microscopy (TEM). Structure, size and size distribution of polybutadiene droplets were determined from the micrographs by image analysis.

Water adsorption characteristics of zeolites were determined in an atmosphere of 100 % rh. by the measurement of the weight of samples as a function of time. Their chemical composition was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Their pore size and volume samples were characterized by water and nitrogen adsorption. The particle size and size distribution of the zeolites were also measured. The surface tension of
zeolites was determined by inverse gas chromatography (IGC).

The water adsorption of the composites was followed by the measurement of weight in an atmosphere of 100 % RH on 20 x 20 x 1 mm specimens as a function of time. Mechanical properties were characterized by tensile testing. The distribution of the zeolites in the composites and failure mechanism were studied by scanning electron microscopy (SEM). Micrographs were recorded on fracture surfaces created during tensile testing.

Modified poly(ethylene-co-vinyl alcohol) polymer (EVOH) were prepared from high ethylene content (48 mol%) EVOH and an additive [N,N’-bis(2,2,6,6-tetramethyl-4-piperidyl)-isophthalamide (Nylostab SEED)] in a wide composition range. The components were homogenized in a twin-screw compounder. The extruded strand was cooled in air and then pelletized. The pellets were compression molded to plates of 1 mm and films of about 100 μm thickness. All materials were dried at 100 °C for 4 hours in an oven before processing and then kept in a desiccator until further use.

Melting and crystallization characteristics and the possible nucleation effect of the additive were determined by differential scanning calorimetry (DSC). Crystallinity was calculated from the enthalpy of fusion (157.8 J/g) of the PVOH single crystal of 100 % crystallinity [1]. Crystalline structure was also studied by X-ray diffraction (XRD). Molecular interactions were studied by Fourier transform infrared spectroscopy (FTIR). Molecular modeling was used to check possible interactions between the additive and the polymer and to estimate their strength. The density of the polymer was measured at room temperature in n-hexane using a pycnometer. Oxygen transmission rate (OTR) was detected at 23 °C and 50 % relative humidity. Mechanical properties were characterized by tensile testing.
3. Results

In the first study of the Thesis, polymer/zeolite desiccant composites prepared with ten different matrices were characterized. The results showed that the desiccant can adsorb considerable water in its free pores. Adsorption capacity of the composites depends linearly on the amount of desiccant present, but it is independent of the type of the polymer used. More complicated is the effect of polymer characteristics on the rate of water adsorption. The diffusion of water into the composites is fast initially, but slows down with time and also with increasing desiccant content. This latter effect can be explained with the increase of the diffusion path as zeolite content increases. Permeation of substances through polymers is an important phenomenon in many application areas including packaging. In studies related to gas, and first of all to oxygen diffusion the free volume of the polymer turned out to be the most important characteristics determining permeation. Lee [8] determined the permeability of oxygen through various polymers and obtained a very good correlation between permeation and specific free volume \( v_{sf} \) indeed. We plotted the logarithm of water vapor transmission rate (WVTR) against the reciprocal value of \( v_{sf} \) of the neat polymers (Fig. 1). The correlation is quite good, a straight line with a negative slope is obtained as predicted by theory. The
meation of water through all of the polymers used as matrix in desiccant composites is determined by their free volume. Subsequently we plotted the rate of adsorption values ($a$ and $b$) of the composites against $v_{sf}$ in the same way. The initial rate of diffusion depends only on the specific free volume of the matrix and this factor influences strongly also the overall rate of water adsorption. However, this latter characteristic depends also on other factors like the dispersion of the desiccant in the matrix. Matrix type and zeolite content must be selected according to the task to be fulfilled; fast adsorption can be achieved only with polymers having large free volume.

Similarly to the properties of the polymer used as matrix, very little attention has been paid to the effect of desiccant characteristics on the functional properties of desiccant composites. The systematic study of five zeolites and their polymer/desiccant composites proved that the water adsorption capacity of zeolites depends on the total volume of the pores ($V_t$), the relatively close correlation between the two quantities is presented in Fig. 2. The rate of adsorption depends on a different property of zeolites, on the equilibrium constant of adsorption. Zeolite characteristics influence the moisture adsorption of the composites only marginally; adsorption capacity is determined by zeolite content, while the rate of adsorption by the properties of the polymer. Matrix properties influence mainly application related properties, reinforcement and ductility is better in HIPS than in PS composites.
Structural materials are being replaced in increasing quantities by functional materials, which, besides their excellent mechanical properties, also fulfill some function thus increasing their value [1]. The mechanical properties of all heterogeneous materials are strongly influenced by interfacial interactions [7]. Because of the importance of interactions and adhesion, several attempts have been made to determine or estimate them in polymer/zeolite composites, but these results are clearly contradictory. In view of these contradictions the goal of this part of our study was to estimate interfacial interactions and reinforcement in polymer zeolite composites potentially used as desiccant packaging materials. Interfacial adhesion was estimated by various means including the measurement of surface characteristics, cyclic loading experiments and the evaluation of the composition dependence of mechanical properties by appropriate models. The results showed that composite properties change in a wide range; stiffness varies between 0.3 and 10 GPa, while strength between 10 and 80 MPa. The deformability of most composites is small and decreases with increasing zeolite content. Interfacial adhesion between the matrix polymer and the zeolite is not very strong, although quantitative determination is hampered by various factors. Most of the composites fail by debonding, brittle matrices by debonding and/or matrix fracture, while considerable shear yielding has been observed in LDPE composites. Zeolite is dispersed adequately in all matrices and the only structural phenomenon affecting properties is the possible embedding of zeolite into the elastomer phase of HIPS. Composite properties are determined mainly by matrix characteristics and interfacial adhesion plays only a relatively minor role.

Both glassy PS and high impact polystyrene (HIPS) have large specific free volume and they are successfully used as matrices for desiccant composites in practice. The results of another study also showed differences in the performance of the two kinds of polymer, i.e. PS and HIPS, and indicated that dispersed structure and elastomer content might influence both functional and
application properties. The results showed that the water absorption capacity of the composites increases strongly with zeolite, but decreases slightly with increasing polybutadiene content. The overall rate of water adsorption decreases with increasing zeolite content and it is influenced quite significantly by the amount of elastomer as well. Zeolite and elastomer contents determine both functional and application properties, but structural parameters also play a role. The size of the dispersed butadiene droplets, the amount of PS embedded into them as well as the encapsulation of the zeolite into the droplets also influence all properties in smaller or larger extent.

During the literature study on the oxygen permeability of polymers, we have not found any indication of using a small molecular weight additive for the improvement of the barrier properties of poly(ethylene-co-vinyl alcohol) against oxygen. The general idea and goal of our project was to explore this possibility and use of N,N’-bis(2,2,6,6-tetramethyl-4-piperidyl)-isophthalamide (Nylostab SEED) to decrease OTR of EVOH copolymer. The additive proved to be an efficient nucleating agent in polyamides. Nucleation of EVOH might increase crystallinity thus decreasing oxygen permeability and water sensitivity as well. The compound contains several functional groups, which may interact with the –OH group of EVOH thus changing free volume and offering a further route to modify oxygen permeability.

The results showed that oxygen transmission decreased considerably when the additive was added at less than
2.0 wt% concentration (Fig. 3). The decrease resulted from the interaction of the hydroxyl groups of the polymer and the amide groups of the additive. Above 2 wt% the additive forms a separate phase leading to the deterioration of properties. The success of the approach represents a novel way to control oxygen permeation in EVOH and in other polymers with similar functional groups capable of strong interactions.

4. New scientific results

1. With the help of a systematic study of polymer/desiccant composites prepared with ten different matrices we proved unambiguously that the adsorption capacity of the composites depends linearly on the amount of desiccant present, but it is independent of the type of the polymer used. [1]

2. With a detailed analysis of the desiccant characteristics of polymer/zeolite composites we showed the first time that the diffusion of water into the composites is fast initially, but slows down with time and also with increasing desiccant content due to the increase of diffusion path. The rate of diffusion depends basically only on the specific free volume of the matrix. [1]

3. We investigated the application characteristics of desiccant composites and showed that composite properties are determined mainly by matrix characteristics and interfacial adhesion plays only a relatively minor role. [3]

4. With a detailed study of five zeolites and their desiccant PS composites we proved that the water adsorption capacity of zeolites depends on the total volume of the pores, while the rate of adsorption on thermodynamics, on the equilibrium constant of adsorption. On the other hand, the adsorption characteristics of desiccant composites do not depend on zeolite properties. [2]

5. We carried out systematic measurements with a number of polystyrene matrices and showed that the water absorption capacity of their desiccant composites increases strongly with zeolite, but decreases slightly with increasing polybutadiene content, while the overall rate of water adsorption shows the opposite tendency. [3]
6. With a more detailed analysis of HIPS/zeolite composites we proved that the embedding of the zeolite into the polybutadiene droplets is the thermodynamically favored process and experimental results confirmed that considerable embedding occurs during composite preparation. The extent of embedding depends on zeolite content, but also on the morphology of the HIPS matrix. Embedding influences only the initial rate of water adsorption which decreases slightly with increasing extent of encapsulation. [7th Chapter of the Thesis]

7. We proposed a novel way to control oxygen permeation in EVOH by the use of a small molecular weight additive, which has never been done before. With the detailed analysis of the experimental results we could prove that contrary to our original assumption the decrease in oxygen permeation did not result from increased crystallinity, but from the interaction of the hydroxyl groups of the polymer and the amide groups of the additive. The dissolution of the additive in the amorphous phase of the polymer led to decreased crystallinity, but also in the decreased mobility of amorphous molecules thus decreasing permeability. [4]

5. Publications

5.1 The thesis is based on the following papers

1. Kenyó, C., Kajtár, D., 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(11), 1-8 (2013) (IF: 1.920, Total Citation: 3, Independent Citation: 0)

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) (IF: 1.632, Total Citation: 1, Independent Citation: 0)


4. Péter, Zs., Kenyó, C., Renner, K., Kröhnke C., Pukánszky, B.: Decreased oxygen permeability of EVOH through molecular interactions, *eXPRESS Polym Lett*, 8(10), 756-766, (2014) (IF: 2.761, Total Citation: 1, Independent Citation: 0)
5.2 Other publications

5. Renner, K., Kenyó, C., Móczó, J., Pukánszky, B.: Micromechanical deformation processes in PP/Wood composites: particle characteristics, adhesion, mechanism, *Compos A* **41**(11), 1653-1661 (2010) ([IF:3.071], Total Citation:37, Independent Citation:28)

6. Pusztai E., Kenyó, Cs., Nagy, J., Wágner, Ö., The effect of some disiloxane chain extenders on the thermal and mechanical properties of cross-linked poly(siloxane-urethane)s, *EXPRESS Polym Lett* **7**(5), 456-470 (2013) ([IF:2.761], Total Citation:1, Independent Citation:0)


5.3 Conference presentations


