Active packaging materials: factors, mechanism, efficiency

Ph. D. Thesis

by

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Chapter 1

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. [1-3]. The importance of packaging is shown by the fact that industrially relevant journals dedicate entire issues to the problems of packaging [4-6]. About 35-40% of all plastics produced is used by the packaging industry and about 30% of all packaging materials is prepared from plastics (Fig. 1.1). Plastic materials are around for a long time and changed the philosophy as well as the technology of packaging completely. 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” [4].

![Pie chart showing world consumption of packaging materials by sectors](image)

**Figure 1.1**  
*World consumption of packaging materials by sectors [7]*

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 [8-11]. 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 [12-14], humidity control [15-19], regulating ethylene content [20], antimicrobial effect [21-24], adsorption of odorous materials, or the opposite, the release of desirable aromas [25, 26]. Intensive research and development work is carried out on these materials all over the world, but mostly in industry.
Controlling the humidity of the packaged ware is extremely important in several areas. The quality of food have been preserved by drying for several hundred years, but recently moisture control became an issue in the pharmaceutical and electronic industries as well. Controlled and given moisture content is desirable for certain food products [15, 17, 18], while dry conditions must be maintained mostly in pharma [16, 19, 27] and electronics [28]. Water being present in the atmosphere must be captured in the latter case which is done either by the adsorption or absorption of water [29].

In spite of the social and economic importance of active packaging materials controlling humidity, very little systematic work has been reported in the literature, at least according to our knowledge. Most of the research and development work is done in the industry and the most important results are never published. As a consequence, very little reliable information is available about the most important parameters controlling the functional and application properties of such materials. The few scientific papers published are based on specific ideas of using certain components or focusing on selected problems. The results obtained are often contradictory and general conclusions cannot be drawn from them [30, 31]. The parameters most important for these functional packaging materials, i.e. adsorption rate and capacity, are difficult to extract from such papers and the reliability of the results is questionable. And the same applies to other functional packaging materials including those with improved barrier properties.

Desiccant composites are heterogeneous materials and the Laboratory of Plastics and Rubber Technology at the Budapest University of Technology and Economics has extensive experience in this area. Some years ago Süd Chemie AG (Germany) contacted the laboratory and initiated joint research and development work in the area of active packaging materials. An agreement was signed between an affiliate of the company, AirSec SAS (France), and the laboratory to improve the efficiency of their desiccant packaging materials used in the pharmaceutical and electronic industry. The main goal of the research was to carry out systematic experiments with desiccant composites prepared from various zeolites and polymers in order to explore the factors determining the most important characteristics of such packaging materials. Besides desiccant composites, other materials and problems were also investigated during the years, like using natural materials in packaging, improving barrier properties, solving technological and quality problems, etc. The systematic work carried out on packaging materials resulted in some practical [32], but also in important scientific results, which have not been published or known earlier. This thesis is based on and contains the most important results of the scientific work resulting from this cooperation.

1.1. Active packaging

1.1.1. Definitions

Active or intelligent packaging usually means devices having active functions beyond the conventional, passive ones such as containment, protection or providing information (nutritional data, advertisement, etc.). For the better understanding of the possibilities offered by active and intelligent packaging these terms must be properly
defined. Robertson [33] defines active packaging as “packaging in which subsidiary constituents have been deliberately included in or on either the packaging material or the package headspace to enhance the performance of the package system”, while intelligent packaging is referred to by him as “packaging that contains an external or internal indicator to provide information about aspects of the history of the package and/or the quality of the food”. These terms are quite accepted in the field of active packaging, thus we apply them also in this Thesis.

1.1.2. Classification

The range of active packaging is extremely broad today, thousands of attempts have been made to produce various active packaging materials. Most of the studies and patents are produced in Japan and the US, but Europe is closing up in recent years. Most of this research can be classified into six major categories [1, 9, 10]:

- oxygen scavenging,
- moisture control,
- ethylene removal from fresh-food packaging,
- antimicrobials,
- odor removal,
- aroma emission.

Besides moisture control agents and oxygen scavengers, which will be discussed more in detail later, antimicrobial packaging (AMP) constitutes one of the largest group among active packaging materials. AMP is closely related to food packaging. Han et al. [34] defined the purpose of AMP to extend the lag phase and reduce the growth rate of microorganism in order to extend shelf life and to maintain product quality and safety. Antimicrobial packaging materials 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 [9]. Hotchkiss [35] collected some of the antimicrobial agents which can be potentially used in active packaging materials (Table 1.1).

Ethylene is a growth hormone that functions in the sprouting of plant seedlings as well as during the growth of plants and fruits. Many fresh products emit relatively large amounts of ethylene; this emission varies according to plant type. 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 KMnO₄, 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). These latter can also be applied as antioxidant additives in packaging materials extending the shelf life of the product by reacting with peroxides and free radicals.

Table 1.1 Antimicrobial agents [35]

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic acids</td>
<td>propionic, benzoic, sorbic</td>
</tr>
<tr>
<td>Bacteriocins</td>
<td>nisin</td>
</tr>
<tr>
<td>Spice extracts</td>
<td>thymol, p-cymene</td>
</tr>
<tr>
<td>Thiosulfonates</td>
<td>allicin</td>
</tr>
<tr>
<td>Enzymes</td>
<td>peroxidase, lysozyme</td>
</tr>
<tr>
<td>Proteins</td>
<td>conalbumin</td>
</tr>
<tr>
<td>Isothiocyanates</td>
<td>allylisothiocyanate</td>
</tr>
<tr>
<td>Antibiotics</td>
<td>imazalil</td>
</tr>
<tr>
<td>Fungicides</td>
<td>benomyl</td>
</tr>
<tr>
<td>Chelating agents</td>
<td>EDTA</td>
</tr>
<tr>
<td>Metals</td>
<td>silver</td>
</tr>
<tr>
<td>Parabens</td>
<td>heptylparaben</td>
</tr>
</tbody>
</table>

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. In the case of such materials volatility is a crucial characteristic, as it influences the performance of the flavor. The best performance is achieved by fragrance molecules with a length of 6 to 18 carbons atoms [9]. Aromatic materials may interact with plastics in two ways: solubility of the aroma compound in the packaging material or diffusion into or permeation through the plastic packaging material by the components of flavors. Various flavors are used in the packaging industry and most of them are introduced into the packaging material during processing (e.g. extrusion).

1.2. Moisture control

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 [29]. The former adsorb water physically on the surface of the adsorbent, while absorption is a chemical process, absorbents react with water or bind it.

1.2.1. Types of desiccants

Desiccants can be classified also according to the application. Some desiccants are used in a sachet placed inside a sealed package, while others are incorporated directly into the package material. This latter solution is spreading continuously, because direct interaction between the product and the desiccant can be avoided in this way, thus the desiccant does not alter the properties of the wrapped product.

Often used absorbents are calcium sulfate (CaSO₄) [36], calcium chloride (CaCl₂) [37] and calcium oxide (CaO) [38]. These materials absorb water either to bind it as hydrate or to react with it chemically to form a new compound. Adsorbents are able to bind considerable amount of water on their extensive, high energy surface. Active carbon [39], silica gel [40], clays [41], and zeolites [42] are often used for this purpose; silica gel [30], and zeolite [31] are the desiccants most frequently applied in practice. Intensive research is carried out to develop new desiccants including hybrid (adsorbent/absorbent) materials [37, 43, 44], natural polymers (starch, cellulose derivatives) [45, 46], and superabsorbent gels (acrylates, cellulose compounds) [47-49].

Moisture controlling packages can be produced by the introduction of desiccants into polymer matrices, as mentioned above. New properties can be achieved in a rather simple, and time efficient manner by this type of modification, while the development of new polymer synthesis routes is a time and money consuming process. 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.

1.2.2. Water adsorption

The most important phenomenon in moisture control by the use of desiccant composites is the diffusion of water through a heterogeneous material. Park and Crank [50] described the mathematical theory of diffusion in isotropic substances. Their hypothesis is based on the assumption that the rate of transfer of the diffusing substance through unit area of a cross section is proportional to the concentration gradient measured normal to it:

\[ F = -D \frac{\partial c}{\partial x} \]  

(1.1)
where $F$ is the rate of transfer per cross section, $c$ the concentration of the diffusing substance, $D$ the diffusion coefficient and $x$ the space co-ordinate measured normal to the surface.

The sorption or desorption kinetics of two component systems can be expressed analytically if one of the factors mentioned above ($F$, $D$ or $c$) is kept constant. If we assume that diffusion coefficient ($D$) is constant, we obtain the following equation

$$M_t = M_\infty \left( 1 - \frac{8}{\pi^2} \sum_{m=0}^\infty \frac{1}{(2m+1)^2} \exp\left( -\frac{D(2m+1)^2\pi^2 t}{L^2} \right) \right)$$

where $M_t$ is the time dependent weight increase, $M_\infty$ the final water uptake reached after infinite time, $L$ the thickness of the sample, and $t$ the time of adsorption. This equation is suitable for moderate or long times, while equation (3) describes the initial rate of sorption at short times

$$\frac{M_t}{M_\infty} = 4 \left( \frac{Dt}{L^2} \right)^{1/2} \left( \pi^{-1/2} + 2 \sum_{m=0}^\infty (-1)^m \text{erfc} \left( \frac{mL}{2(Dt)^{1/2}} \right) \right)$$

Only a few desiccants can be applied in practice, when completely dry atmosphere must be achieved, because most of them are not active enough at low humidity (< 20 %) (Figs. 1.2 and 1.3). As the figures show, CaO and zeolite are the best candidates being used as desiccants. However, the incorporation of the former is disadvantageous in polymers, because of its water sorption mechanism. CaO reacts with water instantaneously in an exothermic reaction and forms a new compound Ca(OH)$_2$ [51]. This process is accompanied by volume increase, which along with the nascent heat, can lead to the deterioration of the mechanical properties (strength, deformability, etc.) of the composites. This undesirable phenomenon can be avoided by the use of zeolites instead of CaO. Zeolites are adsorbents, thus they bind water without any volume change on their extensive surface area in their pore system [52].

1.2.3. Polymer/zeolite composites

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 composites [42, 53-64] and only a few discusses humidity control [30, 31]. Usually commodity polymers, e.g. polypropylene [57-62], polyethylene [42, 54-56] or polystyrene [53], are used as matrices in such desiccant composites; other matrices are rarely mentioned [63, 64]. Some papers are summarized in Table 1.2 showing the type of the matrix and the filler, the surface treatment applied, and the average particle size of the desiccant.
Figure 1.2 Comparison of commercial desiccants at 25°C [29]. A) CaSO₄, B) zeolite, C) clay, D) silica gel, E) CaO

Figure 1.3 Comparison of commercial adsorbents at 25°C [29]. A) activated alumina (granulated), B) activated alumina (spheres), C) silica gel, D) zeolite 5A, E) active charcoal
Biswas et al. [54-56] compared the properties of LLDPE/zeolite, LDPE/zeolite and HDPE/zeolite composites and the possible applicability of these materials as microporous, breathable films. The authors compounded zeolite with the polymers in a twin-screw extruder by melt extrusion. Mechanical properties were characterized by tensile testing. They concluded from the results that stronger interfacial adhesion develops in LLDPE/zeolite than in LDPE/zeolite or HDPE/zeolite composites. Their conclusions were based on SEM micrographs recorded on cryogenically fractured surfaces. However, the results and the conclusions seem to be rather contradictory. Interfacial interactions between the polymer and the filler are created mainly secondary, van der Waals forces. The strength of adhesion is proportional to the reversible work of adhesion if only secondary interactions act between the components. This quantity can be calculated from the surface tension of the components. The strength of interaction between the components cannot be very dissimilar for the polymers used by the authors, because all polyethylenes have very similar surface tension and the same filler was used throughout the study. The same group investigated also the effect of the surface coating of the zeolite on the properties of polymer/zeolite composites [42]. Stearic acid was used as coating material. They measured the mechanical, thermal and rheological characteristics of the composites and studied their morphology as well. Surface coating enhanced the flexibility of the composites. As a result, composites containing the coated zeolite had larger impact strength than the ones prepared with the uncoated filler.

Stronger interfacial adhesion was claimed to develop between polymer matrices and inorganic fillers as a result of modification with stearic acid. However, this conclusion contradicts experience and published results [36, 65]. As mentioned above, adhesion between the polymer and the filler depends on the surface tension of the components. The surface coating of the filler with a surfactant results in decreased surface energy and decreased particle/particle as well as polymer/particle interactions.

Pehlivan et al. [31] studied the water adsorption of polypropylene (PP)/zeolite composites. The samples were prepared by compression molding from powder and the desiccant was surface modified with polyethylene glycol (PEG) before composite preparation. The authors measured significantly different adsorption capacities by water immersion and in an atmosphere of 100 % Rh (24.5 and 13.5 wt%, respectively). Similar differences were observed in the rate of adsorption as well, without unambiguous explanation. Composites containing unmodified zeolite were not investigated in this study, which makes the interpretation of the results even more difficult. Mathiowitz et al. [30] also studied PP composites containing zeolite treated with PEG and compared it to silica gel. Their main conclusions were that desiccant composites bind water and that composites prepared with the zeolite are more efficient than those containing the silica gel.

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 [66]. 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 [67].

**Table 1.2 Collection of the published literature**

<table>
<thead>
<tr>
<th>Matrix type</th>
<th>Filler type</th>
<th>Surface treatment (wt%)</th>
<th>Average particle size (μm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>zeolite 13X</td>
<td>-</td>
<td>2–3</td>
<td>[53]</td>
</tr>
<tr>
<td>HDPE</td>
<td>zeolite 4A</td>
<td>-</td>
<td>0.5–3</td>
<td>[42, 54, 56]</td>
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<tr>
<td>LLDPE</td>
<td>zeolite 4A</td>
<td>-</td>
<td>2–3</td>
<td>[42, 54, 55]</td>
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<tr>
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<td>zeolite 4A</td>
<td>-</td>
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<tr>
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<td>zeolite</td>
<td>-</td>
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<tr>
<td>PP</td>
<td>natural zeolite</td>
<td>PEG 4000</td>
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<td>natural zeolite</td>
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<td>-</td>
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<td>zeolite 4A</td>
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1.2.4. Factors affecting the water adsorption of zeolites

Zeolites are microporous, aluminosilicate materials, which occur naturally but are also synthesized on a large scale [68]. More than two hundred unique zeolite frameworks have been identified [69], but the A, X and Y types are used the most frequently in practice. Their framework is built up by tetravalent silicon ions. A part of the silicon is replaced by trivalent aluminum ions in their structure thus the zeolite lattice possesses some residual negative charge as a result. The cations, which compensate the negative valence of the anionic framework are located in the inner cavities of the lattice. The porous structure can accommodate a wide variety of cations, such as Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and other alkali or alkaline earth metal ions. The interconnected pores are accessible only for small molecules, because the largest pore size of a zeolite is about 10 Å (10\(^{-9}\) m). The pores are not just small, but also uniform, as shown by Fig. 1.4. This unique pore structure can be modified during synthesis by cation exchange; pore size may vary from 3 to 10 Å. The small diameter of the pores and the long channels result in large specific surface area (500–1000 m\(^2\)/g).

In his comprehensive work Neimark [70] showed that not only the pore diameter of the zeolites can be modified by cation exchange, but their water adsorption capacity as well. The variation in water uptake is not as much related to the size of the cations as to their hydration capacity. Consequently, the water adsorption capacity of zeolites is determined by the strength of specific interactions between water and the compensating cation. According to Neimark [70] the strength of interaction changes in the order: Mg\(^{2+}\) > Li\(^+\) > Ca\(^{2+}\) > Na\(^+\) > K\(^+\). Stach et al. [71] confirmed these results by exchanging the cations (Na\(^+\) to Mg\(^{2+}\)) of A, X and Y type zeolites. The results of their work are summarized in Table 1.3. A considerable increase (50 %) was achieved in adsorption capacity by cation exchange.

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Si/Al ratio</th>
<th>Composition</th>
<th>Adsorption capacity (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaA</td>
<td>1.00</td>
<td>Na(_{12}[(\text{AlO}_2)_12(\text{SiO}_2)_12]) × 27H(_2)O</td>
<td>0.286</td>
</tr>
<tr>
<td>MgA</td>
<td>1.00</td>
<td>Mg(_{6}[(\text{AlO}_2)_12(\text{SiO}_2)_12]) × 27H(_2)O</td>
<td>0.419</td>
</tr>
<tr>
<td>NaY</td>
<td>2.43</td>
<td>Na(_{56}[(\text{AlO}_2)_56(\text{SiO}_2)_56]) × 268H(_2)O</td>
<td>0.335</td>
</tr>
<tr>
<td>MgY</td>
<td>2.43</td>
<td>Mg(_{28}[(\text{AlO}_2)_56(\text{SiO}_2)_56]) × 268H(_2)O</td>
<td>0.418</td>
</tr>
<tr>
<td>NaX</td>
<td>1.25</td>
<td>Na(_{86}[(\text{AlO}_2)_86(\text{SiO}_2)_86]) × 264H(_2)O</td>
<td>0.338</td>
</tr>
<tr>
<td>MgX</td>
<td>1.25</td>
<td>Mg(_{43}[(\text{AlO}_2)_86(\text{SiO}_2)_86]) × 264H(_2)O</td>
<td>0.449</td>
</tr>
</tbody>
</table>

Moise et al. [72] divided the water adsorption process into three basic steps. In the first step water is adsorbed on the hydrophilic sites of zeolites accompanied by high adsorption heat that decreases as water fills the pores. The second step corresponds to the formation of a \(\text{H}_2\text{O}\) monolayer on the pore walls. Hydrogen bonds form between water
molecules and oxygen atoms in the zeolite framework. The third step, filling of the pores, occurs after the completion of the monolayer. The entire adsorption process depends strongly on the nature and density of the exchangeable cations.

![Figure 1.4](image)

**Figure 1.4**  *Pore size distribution of common adsorbents [73]*

The Si/Al ratio of zeolites is also an important factor influencing water adsorption capacity. The amount of Al within the framework may vary in a wide range from Si/Al = 1 to ∞; the completely siliceous forms being polymorphs of SiO₂ [73]. The composition of the framework depends on synthesis conditions. Si/Al ratio can be modified also after synthesis. As the Si/Al ratio of the framework increases, the hydrophobicity of zeolite increases as well. Hunger et al. [52] measured the water uptake, the pore volume and the Si/Al ratio of different type of commercially available zeolites. Their results are collected in Table 1.4.

The results clearly show that adsorption capacity decreases with increasing Si/Al ratio. However, the effect of pore volume must be also kept in mind. The two parameters influence the water adsorption capacity zeolites in different ways. Small Si/Al ratio means large concentration of compensating cations which influences the adsorption process considerably, while pore volume determines maximum capacity achieved at the complete filling of the pores. This latter is a theoretical value, because the pores are never filled completely.
Table 1.4 Effect of Si/Al ratio and pore volume on the adsorption capacity of zeolites

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Composition</th>
<th>Si/Al ratio</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Adsorption capacity (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaA</td>
<td>Na$<em>{12}$[Al$</em>{12}$Si$<em>{12}$O$</em>{48}$]</td>
<td>1.00</td>
<td>0.287</td>
<td>0.260</td>
</tr>
<tr>
<td>NaX</td>
<td>Na$<em>{88.1}$[Al$</em>{88.1}$Si$<em>{103.9}$O$</em>{384}$]</td>
<td>1.18</td>
<td>0.311</td>
<td>0.298</td>
</tr>
<tr>
<td>NaY</td>
<td>Na$<em>{53.3}$[Al$</em>{53.3}$Si$<em>{138.7}$O$</em>{384}$]</td>
<td>2.60</td>
<td>0.310</td>
<td>0.292</td>
</tr>
<tr>
<td>Na, K-erionite</td>
<td>Na$<em>{4.89}$K$</em>{4.11}$[Al$<em>{9}$Si$</em>{27}$O$_{72}$]</td>
<td>3.00</td>
<td>0.190</td>
<td>0.159</td>
</tr>
<tr>
<td>Na-mordenite</td>
<td>Na$<em>{8}$[Al$</em>{8}$Si$<em>{40}$O$</em>{96}$]</td>
<td>5.00</td>
<td>0.169</td>
<td>0.126</td>
</tr>
<tr>
<td>NaZSM-5</td>
<td>Na$<em>{6}$[Al$</em>{6}$Si$<em>{90}$O$</em>{192}$]</td>
<td>15.00</td>
<td>0.102</td>
<td>0.077</td>
</tr>
</tbody>
</table>

1.3. Oxygen scavenging [9]

1.3.1. Type of oxygen scavengers

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, the extent of which increases as temperature rises. 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 undesirable reactions can be classified into four groups:

- antioxidants,
- interceptors,
- absorbers,
- scavengers.

Antioxidants are able to react with peroxide radicals in the presence of light and oxidize themselves to generate nontoxic, stable compounds. It is crucial to stop the formation of free radicals, because they can initiate chain reactions, which might deteriorate the properties of packaged products. Antioxidants terminate these chain reactions by removing free radical intermediates and inhibit other oxidation reactions.

Interceptors prevent oxygen from reaching the food product by themselves being oxidized before the oxygen reacts with the food. The definition of interceptors is similar to that of the antioxidants, they are frequently used as synonyms.

Absorbers are quite different from the previously described oxygen removing materials. Oxygen absorbers trap oxygen physically, not by chemical reaction.
Scavengers are usually termed as compounds, which are incorporated into the packaging material. These are chemically combined with the package structure and they effectively remove oxygen from the inner environment. Some of these products are able to remove the oxygen from the wrapped product itself.

1.3.2. Permeation of gases through polymers

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 \( D \) [74]. Solubility is determined by the interaction between the permeant molecule and the polymer, while the rate of diffusion depends on the size of the permeant molecule and the relative amount of amorphous phase of the polymer. Accordingly, permeability is defined as

\[
P = D \cdot S
\]  

(4)

The permeation of a gas through a polymer matrix can be divided into the following steps (Fig. 1.5):

1. absorption into the polymer,
2. diffusion through the polymer matrix,
3. desorption through the polymer wall and evaporation from the surface.

The oxygen permeability (OTR) of polymers varies in a wide range covering several orders of magnitudes (Table 1.5) [75]. The differences in oxygen barrier properties mostly depend on the chemical composition and molecular structure of the polymers.

![Permeation of gases through a polymer matrix](image)

**Figure 1.5** Permeation of gases through a polymer matrix

The easiest way to minimize oxygen concentration within the package in an active packaging system is to use polymers with limited permeability like PA, PVDC, PAN or EVOH. As Table 1.5 shows, dry ethylene-vinyl alcohol copolymers (EVOH) offer extremely good protection against oxygen [76-80]. Their good barrier properties are related to large crystallinity (~70 %) and the large concentration of functional groups [81]. The large number of hydroxyl groups in EVOH copolymers results in strong inter- and
intramolecular forces and thus large cohesive energy density (CED) [81]. The free volume of the polymer also plays a crucial role in the permeation process. Close correlation exists between the free volume and the permeability of polymers (Fig. 1.6). According to the figure, the free volume of ethylene-vinylalcohol copolymers is very small due to their large CED and crystallinity.

Table 1.5 Oxygen permeability of commonly used polymers [74]

<table>
<thead>
<tr>
<th>Polymer type</th>
<th>Permeability (cm³/mm/m²/24 h/bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>742</td>
</tr>
<tr>
<td>PC</td>
<td>92</td>
</tr>
<tr>
<td>PP</td>
<td>59</td>
</tr>
<tr>
<td>HDPE</td>
<td>43</td>
</tr>
<tr>
<td>PETG</td>
<td>6</td>
</tr>
<tr>
<td>PVC</td>
<td>4</td>
</tr>
<tr>
<td>PET</td>
<td>1</td>
</tr>
<tr>
<td>EVOH (wet)</td>
<td>0.8</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>0.4</td>
</tr>
<tr>
<td>PAN</td>
<td>0.4</td>
</tr>
<tr>
<td>PVDC</td>
<td>0.1</td>
</tr>
<tr>
<td>EVOH (dry)</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Figure 1.6  Correlation between the free volume and permeability of polymers [80]
1.3.3. Oxygen permeation of EVOH copolymers

The barrier properties of EVOH copolymers depend on:

- ethylene content [75, 81, 82],
- crystallinity [80],
- temperature [79, 83],
- humidity [77, 81-89].

All these factors influence the OTR of EVOH, but humidity has a most pronounced effect. The permeation rate of the polymer may increase by orders of magnitude with increasing humidity (Fig. 1.7). This effect represents the major drawback of ethylene-vinyl alcohol copolymers as oxygen barrier materials [87]. Numerous attempts have been made to overcome this problem; they can be classified in three groups:

- blending EVOH with other polymers,
- preparing multilayer films,
- incorporation of nanofillers.

A frequently used approach to decrease the oxygen permeability and water sensitivity of EVOH is modification by blending [85, 86, 90-99]. EVOH is usually combined with polyamide (PA), poly(vinyl alcohol) or polyethylene. Yeh et al. [98] prepared PE/EVOH, PA/EVOH and PA/EVOH/PE blends by reactive extrusion and investigated their oxygen transmission rate. Blending resulted in a decrease in the permeability of polyethylene bottles compared to neat PE, but the desired improvement could not be achieved from the EVOH point of view. Generally, blending EVOH with various polymers results in decreased crystallinity of the copolymer along with decreased barrier properties.

Multilayer film production is another option to increase the barrier properties of ethylene-vinyl alcohol copolymers in humid environment. These films consist of an EVOH barrier layer between polyolefin outer layers combined by adhesive functional polymers [82, 100, 101]. The outer layers are almost impermeable for water, thus they can protect the inner, barrier layer from the undesired effect of moisture. However, when semi prepared foods are sterilized [100, 102] in plastic packaging systems [containing ethylene-vinyl alcohol copolymer (EVOH) as the barrier layer], the sterilization step temporarily diminishes the effectiveness of the oxygen barrier, because high temperature and moisture are involved. At high temperatures, the outer layers become more permeable to water, which can be present in large quantities, and deteriorate the barrier properties of EVOH. This effect, known as retort-shock, has adverse consequences for the shelf life of the product. Oxygen scavengers incorporated into the packaging material can solve this problem and protect the packaged food against oxygen [103]. Multilayer film development led to the production of packaging films with 9 or 10 layers combining EVOH, polyamide (PA) and polyolefins [104]; microfilms with 30-1000 layers of 0.02-5 μm thickness also appeared on the market recently [105]. Increasing the number of barrier layers with different functions results in decreased permeability of the packaging along with increased shelf life of the product [106].
Another approach to decrease the permeability of EVOH is the production of layered silicate nanocomposites [107-113]. Lucciarini et al. [99] prepared EVOH/clay nanocomposites by loading 5 wt% of clay into the matrix using a twin-screw extruder. Surface modified layer silicates are supposed to exfoliate completely in EVOH. Surface modification increases the degree of exfoliation, but according to our knowledge completely exfoliated structure could not be prepared up to now. Exfoliated nanoclays are expected to increase tortuosity and improve barrier properties. Unfortunately it is difficult to control of structure of polymer/layered silicate nanocomposites [114], complete exfoliation is rarely achieved [115], organophilic silicates are quite expensive and they often discolor the product [116]. Another disadvantage of incorporating layered silicates into polymer matrices is that they increase considerably the stiffness of the composites. EVOH copolymers with small ethylene content are very stiff inherently thus compounding it with the silicate may result in a very brittle material.

1.4. Summary and goals

Active packaging materials become more and more a part of our life. Both society and economy demands the development of newer and newer packaging solutions. 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

Figure 1.7  The effect of ethylene content and humidity on the barrier properties of EVOH [69]
Introduction

25

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. Other issues related to interfacial adhesion and composite structure have also been addressed in the work.

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. The presented examples, however, emphasize the need for additional solutions resulting in further decrease in the oxygen permeability of EVOH without deteriorating other properties. 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.

1.5. Scope

As mentioned in the introduction the application of functional packaging materials spreads with increasing rate in most branches of industry including food, pharma and electronics. A large variety of functions are applied from the control of humidity through the release of active components to antiseptic characteristics. Desiccant materials represent an important segment of active packaging materials and they are applied already in industrial practice. On the other hand, like so often, research lags behind industry and basic correlations controlling the properties of such materials are not really known yet. The results of systematic research are not reported in the literature and the information on specific materials and questions is often contradictory. Both development and the improvement of existing products need more intensive and organized research. Desiccant composites are heterogeneous materials with all the consequences. The Laboratory of Plastics and Rubber Technology has many years of experience in the study of such materials. Many questions which are essential for desiccant composites has been studied in detail by the laboratory that published many papers on mechanical properties, deformation mechanisms, interphase formation and other questions. The cooperation between Süd Chemie AG and the laboratory was built upon this experience, which had to be extended only slightly to include the study of the specific properties of functional packaging materials. Most of the work has been done on desiccant composites, but an approach to improve the oxygen barrier properties of poly(vinyl alcohol) was also explored during the project. This Thesis is based on the results achieved in this cooperation and it summarizes its most important conclusions.

Desiccant composites are prepared from all kinds of polymers, but mainly from commodity plastics in order to keep price at a reasonable level. The desiccant is often
selected randomly depending on the availability or price of the material. Silica gel or zeolite is used the most frequently in such composites. However, the combination of a commodity polymer with the most abundant desiccant does not allow the thorough study of factors determining either functional or application properties and even less the determination of general correlations, which might help to find the optimum selection of materials and compositions. The most important functional properties of desiccant composites are their water adsorption capacity and the rate of adsorption. According to our knowledge the effect of polymer and desiccant properties on these characteristics have never been explored systematically. As a consequence, we selected a wide range of polymers for the first part of the study and combined them with a zeolite frequently used as desiccant in the first part of the project (Chapter 3). The polymers were thoroughly characterized with a large variety of methods. Composites were prepared in a wide range of desiccant content and their functional properties were investigated as a function of zeolite loading. Various approaches were applied for the characterization of the rate of water adsorption, and adsorption was described quantitatively with the help of appropriate models. An attempt was made to find general correlations between matrix properties and the desiccant characteristics of the composites.

Although the functional properties of desiccant composites are extremely important for the intended application, packaging materials and the packaging itself must fulfill other requirements as well. The packaging must withstand all mechanical and occasionally thermal loading to which it is exposed during production, filling and use. This requires certain mechanical properties, which depend on the characteristics of the components, but also on composition and interfacial interactions. The experiments to determine the effect of these factors on the mechanical properties of desiccant composites prepared with the same variety of polymers as before are described in Chapter 4. During the design of the experiments, their execution and in the evaluation of the results special attention was paid to interfacial interactions and deformation mechanism. Particulate filled polymers usually fail by debonding and among others, debonding stress is determined by the strength of interaction. However, the determination of the strength of interfacial adhesion is not straightforward in these desiccant composites, thus considerable effort was dedicated to the problem. Large extent of easy debonding must be avoided to prevent the catastrophic failure of the product. The influence of polymer characteristics on adhesion and deformation mechanism is discussed in detail in the chapter.

Besides the properties of the matrix polymer, desiccant characteristics also influence composite properties and very little is known about this question too. In order to extend our knowledge, PS composites were prepared with commercial zeolites frequently used as desiccants in industrial practice. The results of the study are reported in Chapter 5. Similarly to matrix polymers, also zeolites were characterized very thoroughly and characteristics were related to both the functional and the application properties of the composites.

Polystyrene and high impact polystyrene are excellent candidates as matrix materials for desiccant composites. They are commodity polymers with acceptable price and reasonable mechanical properties. Polystyrene has large specific free volume thus the
rate of diffusion of small molecular weight materials is reasonably fast in it, allowing the preparation of desiccant composites with fast adsorption. Although neat PS homopolymers are very brittle, their high impact counterparts have larger deformability and fracture resistance, although at the price of decreased stiffness. However, substances used as desiccants usually increase the stiffness of the polymer anyway. On the other hand, the structure of HIPS is rather complex, it has a salami like character with dispersed polybutadiene particles which contain small PS inclusions. Butadiene content, the particle size of the droplets, the amount of PS inclusions all may influence the properties of desiccant composites, but according to our knowledge, no information has been published on the correlation of HIPS structure and composite properties. **Chapter 6** summarizes results obtained on desiccant composites prepared from two PS homopolymers and seven HIPS copolymers. The dispersed structure of the copolymers was characterized in detail and correlations were established between structure and composite properties. The results showed that desiccant characteristics are influenced mainly by the desiccant, while application properties by the matrix. The correlations established indicated that besides the factors mentioned above, other structural factor or factors may also play a role in the determination of the properties of HIPS composites. Adding a filler to a two component polymer/elastomer blend complicates structure even further, the zeolite may be dispersed in the PS matrix separately from the elastomer or it can be encapsulated by the latter phase. In **Chapter 7** we report the results of experiments and model calculations dedicated to the exact characterization of structure and its effect on composite properties. The extent of zeolite encapsulation was estimated from the stiffness of the composites with the use of an appropriate model and then composite properties were studied as a function of this factor. The results showed that encapsulation influences mainly application, but not functional properties.

The previous paragraphs clearly showed that most of the work done in the framework of this Thesis focused on desiccant composites. However, the field of active packaging includes also a number of other materials among others those with good oxygen barrier properties. Any company working in the area is interested in such materials and wants to extend its portfolio with packaging materials having as wide variety of functions as possible. Small oxygen permeability is important in food packaging and in the pharmaceutical industry. Such packaging is usually made from a polar and/or crystalline polymer. Oxygen diffuses only through the amorphous phase of the polymer thus we assumed that increased crystallinity would result in decreased permeability. Barrier properties can be enhanced also by the incorporation of particles which increase the diffusion path of the gas. Layered silicate nanocomposites were claimed to possess excellent barrier properties, but the claims have been rarely substantiated by results. Moreover, such composites have several drawbacks including the need of proper homogenization, inhomogeneous dispersion, inappropriate mechanical properties, changed color, the possible exudation of the surfactant into the ware, etc. **Chapter 8** reports a different approach to the problem, the use of a small molecular weight additive in small amount to decrease the oxygen permeability of an ethylene-vinyl alcohol copolymer frequently used as polymer in oxygen barrier applications. The basic idea was to increase the crystallinity of the polymer thus decreasing oxygen permeation, but extensive characterization of the materials and detailed analysis of the results revealed...
that our initial assumption was wrong. The chapter reports the results of this analysis and our most important conclusions.

In the final chapter of the thesis, in Chapter 9, we briefly summarize the main results obtained during the work, but refrain from their detailed discussion, because the most important conclusions are drawn and reported at the end of each chapter. This chapter is basically restricted to the listing of the major thesis points of the work.

1.6. References


35. Hotchkiss, J.: Recent Research in MAP and Active Packaging Systems, in 27th Annual Convention, Australian Institute of Food Science and Technology, Canberra (1994)


Introduction


Chapter 2

Experimental part

In this chapter we summarize all those materials and experimental methods, which were used in Chapter 3 to 7 and Chapter 8 separately. Characteristics of these materials are detailed here also. Techniques dedicated to the solution of a particular problem are described in the corresponding chapter.

2.1 Experimental part of Chapter 3 to 7

2.1.1 Materials

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. All the polymers are collected in Table 2.1 and the last column indicate the chapter in which they appear in the Thesis.

Table 2.1 Polymers used in the Thesis

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>Producer</th>
<th>Trade name</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>TVK (Hungary)</td>
<td>Tipelin FA24451</td>
<td>3, 5</td>
</tr>
<tr>
<td>HDPE</td>
<td>TVK (Hungary)</td>
<td>Tipelin BA55013</td>
<td>3, 5</td>
</tr>
<tr>
<td>PP</td>
<td>TVK (Hungary)</td>
<td>Tipolen H 649 F</td>
<td>3, 5</td>
</tr>
<tr>
<td>PS1</td>
<td>Dow (USA)</td>
<td>Styron 686 E</td>
<td>3, 4, 5, 6</td>
</tr>
<tr>
<td>PS2</td>
<td>Ineos Nova (Switzerland)</td>
<td>Empera 116</td>
<td>3, 5, 6</td>
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<tr>
<td>HIPS67a</td>
<td>Dow (USA)</td>
<td>Styron 485</td>
<td>3, 4, 5, 6</td>
</tr>
<tr>
<td>HIPS86a</td>
<td>Dow (USA)</td>
<td>Styron 1175</td>
<td>3, 5, 6, 7</td>
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<tr>
<td>HIPS98a</td>
<td>Dow (USA)</td>
<td>Styron 1200</td>
<td>6, 7</td>
</tr>
<tr>
<td>HIPS47a</td>
<td>Dow (USA)</td>
<td>Empera 416</td>
<td>6, 7</td>
</tr>
<tr>
<td>HIPS65a</td>
<td>Ineos Nova (Switzerland)</td>
<td>Empera 524</td>
<td>6, 7</td>
</tr>
<tr>
<td>HIPS120a</td>
<td>Ineos Nova (Switzerland)</td>
<td>Empera 613</td>
<td>6, 7</td>
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<td>HIPS104a</td>
<td>Ineos Nova (Switzerland)</td>
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<tr>
<td>SAN</td>
<td>Dow (USA)</td>
<td>Tyril 880</td>
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<td>PC</td>
<td>Bayer (Germany)</td>
<td>Macrolon 2658</td>
<td>3, 5</td>
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<td>PMMA</td>
<td>Arkema (France)</td>
<td>Ortoglas HFI 7</td>
<td>3, 5</td>
</tr>
<tr>
<td>PVC</td>
<td>BorsodChem (Hungary)</td>
<td>Ongrovil S 5258</td>
<td>3, 5</td>
</tr>
</tbody>
</table>

* In the case of the HIPS polymers, instead of their trade name we use ten times their butadiene content in the abbreviation.
The series of zeolites used as desiccants were obtained from the Luoyang Jianlong Chem. Ind. Co., China, and they included the most often used synthetic zeolites, i.e. 3A, 4A, 5A, 10X and 13X. The desiccants were thoroughly characterized with a wide range of techniques; their most important characteristics are collected in Table 2.2.

**Table 2.2**  Characteristics of the zeolites used as desiccant in the study

<table>
<thead>
<tr>
<th>Type</th>
<th>Cation</th>
<th>Si/Al ratio</th>
<th>Particle size (μm)</th>
<th>Pore diameter (Å)</th>
<th>Pore volume (cm³/g)</th>
<th>(M_w^b) (%)</th>
<th>(K^c)</th>
<th>(\gamma_{sd}^d) (mJ/m²)</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>K⁺, Na⁺</td>
<td>1.00</td>
<td>4.5</td>
<td>3.0</td>
<td>0.27</td>
<td>26.2</td>
<td>42.2</td>
<td>219</td>
<td>4</td>
</tr>
<tr>
<td>4A</td>
<td>Na⁺</td>
<td>1.23</td>
<td>4.0</td>
<td>3.8</td>
<td>0.28</td>
<td>27.5</td>
<td>47.6</td>
<td>216</td>
<td>4, 6, 7</td>
</tr>
<tr>
<td>5A</td>
<td>Ca²⁺, Na⁺</td>
<td>1.25</td>
<td>4.5</td>
<td>4.3</td>
<td>0.29</td>
<td>27.8</td>
<td>29.4</td>
<td>217</td>
<td>3, 4, 5</td>
</tr>
<tr>
<td>10X</td>
<td>Ca²⁺, Na⁺</td>
<td>1.39</td>
<td>4.7</td>
<td>7.4</td>
<td>0.36</td>
<td>34.3</td>
<td>57.2</td>
<td>235</td>
<td>4</td>
</tr>
<tr>
<td>13X</td>
<td>Na⁺</td>
<td>1.43</td>
<td>4.3</td>
<td>8.1</td>
<td>0.33</td>
<td>33.3</td>
<td>33.5</td>
<td>240</td>
<td>4</td>
</tr>
</tbody>
</table>

*a* Si/Al ratio was calculated from ICP-OES results.

*b* the final water uptake reached after infinite time

*c* the equilibrium constant of water adsorption

*d* dispersion component of surface tension determined by IGC

### 2.1.2 Sample preparation

Before composite preparation, the zeolites were dried at 300 °C for 16 h in vacuum. The components were homogenized in a Brabender W 50 EH internal mixer attached to a Haake Rehocord EU 10 V driving unit at 190 °C for 10 min. 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 at 190 °C using a Fontijne SRA 100 laboratory machine. The zeolite content of the composites changed between 0 and 50 vol%.

### 2.1.3 Characterization

#### 2.1.3.1 Matrices

The most important characteristics of the polymers used are listed in Table 2.3. Their molecular weight was determined by gel permeation chromatography in THF (except PE and PP) using a Waters e2695 Separation Module. The measurements were done at 35 °C with 0.5 ml/min flow rate using Styrage columns. PE and PP are insoluble in THF, thus their molecular weight was determined different circumstances. The PE and PP samples were dissolved in 1,2,4-trichloro-benzene (TCB) (1 mg/mL) at 160 °C for 2 hours and stabilized with 2,6-di-tert-butyl-4-methylphenol (BHT) (100 mg/L). Calibration was done in both cases with polystyrene standards. Density was
measured using a pycnometer at room temperature. The water vapor transmission rate (WVTR) of the polymers was determined on 100 µm thick films using a Mocon Permatran W1A equipment. Results were calculated for 20 µm thickness according to industrial practice. The surface tension of the polymers (γS) was determined by static contact angle measurements. Normal alkanes were used for the determination of the dispersion component of surface tension (γSd), while six different solvents (water, glycerol, ethylene glycol, dimethyl sulfoxide, formamide, and 1-bromonaphthalene) were applied for the estimation of the polar component (γSp).

### Table 2.3 Characteristics of the polymers used in Chapters 3–7

<table>
<thead>
<tr>
<th>Polymer</th>
<th>MFR (g/10 min) at Value</th>
<th>Mw/Mn</th>
<th>Density (g/cm³)</th>
<th>WVTR</th>
<th>Free volume νsf (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>0.28 190/2.16</td>
<td>17160</td>
<td>6.89 0.92</td>
<td>15.2</td>
<td>0.110</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.35 190/2.16</td>
<td>18620</td>
<td>6.57 0.96</td>
<td>3.6</td>
<td>0.088</td>
</tr>
<tr>
<td>PP</td>
<td>2.50 230/2.16</td>
<td>92620</td>
<td>4.84 0.90</td>
<td>6.4</td>
<td>0.092</td>
</tr>
<tr>
<td>PS1</td>
<td>2.50 200/5.0</td>
<td>127970</td>
<td>2.44 1.04</td>
<td>138.3</td>
<td>0.166</td>
</tr>
<tr>
<td>PS2</td>
<td>2.50 200/5.0</td>
<td>127970</td>
<td>2.44 1.04</td>
<td>138.3</td>
<td>0.166</td>
</tr>
<tr>
<td>HIPS67</td>
<td>12.00 200/5.0</td>
<td>77525</td>
<td>2.68 1.02</td>
<td>111.7</td>
<td>0.167</td>
</tr>
<tr>
<td>HIPS86</td>
<td>2.80 200/5.0</td>
<td>95840</td>
<td>2.54 1.04</td>
<td>100.8</td>
<td>0.168</td>
</tr>
<tr>
<td>HIPS98</td>
<td>5.00 200/5.0</td>
<td>77525</td>
<td>2.68 1.02</td>
<td>111.7</td>
<td>0.167</td>
</tr>
<tr>
<td>HIPS47</td>
<td>21.00 200/5.0</td>
<td>95840</td>
<td>2.54 1.04</td>
<td>100.8</td>
<td>0.168</td>
</tr>
<tr>
<td>HIPS65</td>
<td>10.50 200/5.0</td>
<td>95840</td>
<td>2.54 1.04</td>
<td>100.8</td>
<td>0.168</td>
</tr>
<tr>
<td>HIPS120</td>
<td>6.00 200/5.0</td>
<td>77525</td>
<td>2.68 1.02</td>
<td>111.7</td>
<td>0.167</td>
</tr>
<tr>
<td>HIPS104</td>
<td>4.80 200/5.0</td>
<td>95840</td>
<td>2.54 1.04</td>
<td>100.8</td>
<td>0.168</td>
</tr>
<tr>
<td>SAN</td>
<td>3.50 230/3.8</td>
<td>75510</td>
<td>2.39 1.07</td>
<td>169.3</td>
<td>0.161</td>
</tr>
<tr>
<td>PC</td>
<td>13.00 300/1.2</td>
<td>24730</td>
<td>2.07 1.20</td>
<td>105.7</td>
<td>0.149</td>
</tr>
<tr>
<td>PMMA</td>
<td>11.00 230/3.8</td>
<td>43470</td>
<td>1.88 1.16</td>
<td>140.7</td>
<td>0.135</td>
</tr>
<tr>
<td>PVC</td>
<td>– –</td>
<td>55270</td>
<td>2.41 1.44</td>
<td>25.7</td>
<td>0.128</td>
</tr>
</tbody>
</table>

* in conditions first number represents the temperature in °C, while the second is the applied weight in kg

* expressed in (g 20 µm/m²/24 h)

The butadiene content of HIPS copolymers was determined by the measurement of their iodine value according to the ASTM D 5902-2005 standard; unsaturations were reacted with iodine chloride in chloroform and the residual chloride was titrated with sodium thiosulfate. In Chapter 6, the structure of the copolymers was studied by transmission electron microscopy (TEM). 100 nm thick slices were cut at -100 °C with a Leica Ultramicrotome and then stained with osmium tetroxide for 4 hours. Micrographs were recorded with a FEI Morgagni 268D electron microscope. Structure, size and size distribution of polybutadiene droplets were determined from the micrographs.
by image analysis using the Image Pro Plus 6 software (Media Cybernetics, USA). The most important structural characteristics of HIPS copolymers are collected in Table 2.4. **Table 2.4 Structural characteristics of the HIPS polymers used in the Thesis**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Particle size (µm)</th>
<th>Embedded PS&lt;sup&gt;a&lt;/sup&gt; (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Most frequent</td>
</tr>
<tr>
<td>HIPS67</td>
<td>1.2 ± 0.7</td>
<td>0.50</td>
</tr>
<tr>
<td>HIPS86</td>
<td>2.6 ± 2.3</td>
<td>1.13</td>
</tr>
<tr>
<td>HIPS98</td>
<td>1.0 ± 0.5</td>
<td>0.70</td>
</tr>
<tr>
<td>HIPS47</td>
<td>1.7 ± 0.8</td>
<td>0.95</td>
</tr>
<tr>
<td>HIPS65</td>
<td>0.6 ± 0.2</td>
<td>0.55</td>
</tr>
<tr>
<td>HIPS120</td>
<td>2.4 ± 1.2</td>
<td>1.65</td>
</tr>
<tr>
<td>HIPS104</td>
<td>1.5 ± 0.7</td>
<td>1.10</td>
</tr>
</tbody>
</table>

<sup>a</sup> The determination of the amount of encapsulated PS is described in Chapter 7.

### 2.1.3.2 Fillers

Water adsorption characteristics of zeolites were determined in an atmosphere of 100 % relative humidity 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). To characterize pore size and volume samples were vacuumed at 300 °C for 24 hours down to 10<sup>-5</sup> Hgmm, and water and nitrogen adsorption was measured using a Hydrosorb (Quantachrome, USA) apparatus at 20 and -195 °C, respectively. The particle size and size distribution of the zeolites were determined using a Malvern Mastersizer 2000 equipped with a Sirocco powder analyzer. The surface tension of zeolites was determined by inverse gas chromatography (IGC). The fillers were agglomerated with water and the 800–1200 µm fraction was used for the packing of the column. The dispersion component of surface tension was determined by the injection of n-alkanes at various temperatures between 200 and 280 °C. Unfortunately, none of the polar solvents eluted from the column thus the polar component of surface tension of zeolites could not be determined with this method. The density of the zeolites was measured by helium pycnometry.

### 2.1.3.3 Composites

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. The zeolite content of the composites was checked by thermal gravimetry (TGA). 15 mg samples were heated to 650 °C with 80 °C/min rate in oxygen and kept there for 5 min to burn off the polymer. Mechanical properties were characterized by tensile testing using an Instron 5566 machine at 115 mm gauge length and 5 mm/min cross-
head speed on specimens with 1 x 10 mm dimensions. In Chapter 5–7, cross-head speed was 0.5 mm/min during the determination of stiffness, while properties at larger deformations, i.e. yield stress and strain as well as tensile strength and elongation-at-break were determined at 5 mm/min. In Chapter 5, debonding stress was estimated by cyclic loading experiments. The specimen was deformed up to different, increasing deformations at 0.5 mm/min cross-head speed. After reaching the desired deformation it was removed from the grips, was let to relax for 15 min and then deformed to the next, larger elongation. Young’s modulus was determined in each deformation step and debonding stress as well as the amount of debonded filler were derived from the deformation dependence of stiffness. In Chapter 5 and 7, the distribution of the zeolites in the composites and failure mechanism were studied by scanning electron microscopy using a JEOL JSM 6380 LA apparatus. Micrographs were recorded on fracture surfaces created during tensile testing.

2.2 Experimental part of Chapter 8

2.2.1 Materials

The poly(ethylene-co-vinyl alcohol) polymer (EVOH) used in the experiments was the Eval G156 grade acquired from Eval Europe, Belgium. Its ethylene content is 48 mol%, density 1.12 g/cm³ and its melt flow index is 6.4 g/10 min at 190 °C and 2.16 kg. The additive, N,N’-bis(2,2,6,6-tetramethyl-4-piperidyl)-isophthalamide (Nylostab SEED, in further discussion Seed) is the product of Clariant, Germany. The chemical structure of the additive is shown in Scheme 1. It is a sterically hindered amine (HALS) product, a crystalline material with melting temperature of 272 °C and density of 1.12 g/cm³. Experiments were carried out at 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, 2.5, 5.0, 7.5 and 10.0 wt% additive contents.

2.2.2 Sample preparation

The components were homogenized in a Brabender single screw extruder at 30 rpm and 260-270-280-260 °C zone temperatures. The extruder was equipped with a die of single orifice of 3 mm diameter. 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 at 190 °C using a Fontijne SRA 100 machine. All materials were dried at 100 °C for 4 hours in an oven before processing and then kept in a desiccator until further use.

Scheme 1 Chemical structure of the additive used in the experiments (SEED)
2.2.3 Characterization

Melting and crystallization characteristics and the possible nucleation effect of the additive were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7 apparatus. The measurements were done on 3-5 mg samples cut from the 1 mm thick plates. Two heating and a cooling run were carried out at 10 °C/min heating and cooling rate, respectively, in the temperature range of 30-300 °C. 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 patterns were recorded using a Phillips PW 1830/PW 1050 equipment with CuKα radiation at 40 kV and 35 mA in the reflection mode. The traces were recorded in 0.04° steps with a sampling interval of 1 s and a rate of 0.04°/min in the 2θ range of 3-43°. Crystallinity was calculated from the XRD traces with the method proposed by Brückner [2].

Molecular interactions were studied by Fourier transform infrared spectroscopy (FTIR). The measurement were carried out in the attenuated total reflection (ATR) mode and the spectra were recorded in the wavelength range of 4000-400 cm\(^{-1}\) with 16 scans in 4 cm\(^{-1}\) steps using a Perkin Elmer Spectrum 100 apparatus. Molecular modeling was used to check possible interactions between the additive and the polymer and to estimate their strength. To reduce the necessary time and computer capacity to a reasonable level, we selected a small molecular weight model compound (1,4-buthandiol) representing the repeating unit of the polymer. We focused only on specific interactions, i.e. hydrogen bonds, and neglected dispersion interactions in the analysis. All the geometry optimizations for the model system were performed at the density functional theory (DFT) level using the MPW1B95 (modified Perdew and Wang exchange and Becke’s 1995 correlation) functional [3] as well as the 6-31++G** basis set [4].

The density of the polymer was measured at room temperature in n-hexane using a pycnometer. A Systec Instruments Model 8000 apparatus (Thame, Oxfordshire, England) was applied for the permeation measurements. The test area and thickness of the sample were 50 cm\(^2\) and about 100 μm, respectively, for all specimens. Oxygen transmission rate (OTR) was detected at 23 °C and 50 % relative humidity. Mechanical properties were characterized by tensile testing using an Instron 5566 machine at 115 mm gauge length and 5 mm/min cross-head speed on specimens with 1 x 10 mm dimensions. The haze of the samples was determined with the help of a ColorQuest (HunterLab, Reston, US) apparatus.
Chapter 3

Factors affecting the capacity and rate of water adsorption in desiccant composites

3.1. Introduction

As described in Chapter 1, the number of detailed studies focusing on the factor, which determine the water adsorption characteristics of desiccant composites, is very limited. Accordingly, the goal of our study was to carry out systematic experiments with desiccant composites prepared with a selected zeolite and to determine the effect of desiccant content and the properties of the matrix polymer on the rate and capacity of water adsorption. Ten different polymers were selected for the study and desiccant content was varied in a wide range from 0 to 50 vol%.

3.2. Results and discussion

3.2.1. Water adsorption

The rate and amount of water adsorbed by a desiccant composite are determined by the characteristics of the components. Previous studies in the area showed that the capacity of the composites is much larger than that of the matrix polymers and increases with desiccant content [1, 2]. Much less reliable information is available for adsorption rate and the contribution of the components has not been clearly defined yet [2]. The water adsorption isotherm of the 5A grade zeolite used in the study is shown in Fig. 3.1. Adsorption is relatively fast and the desiccant adsorbs 23.8 wt% water of its weight. We regard this value as the theoretical capacity of the zeolite under our conditions. The claim that water adsorption is fast is difficult to judge from the isotherm presented in Fig. 3.1. However, as results will show later equilibrium adsorption is reached after much longer times in the composites than in the zeolite.

The water uptake of polycarbonate composites is presented in Fig. 3.2 as a function of time and zeolite content. We can see the much slower rate of adsorption mentioned above and also that maximum adsorption is more or less proportional to the zeolite content of the composite. Similar adsorption isotherms were recorded in composites prepared from the other polymers as well. During quantitative evaluation we assumed Fickian adsorption and the equation derived from Fick's second law, i.e. Eq. 1.2 was solved for $m = 2$ to obtain the following correlation

$$M_i = M \times \left(1 - \frac{8}{\pi^2} \left(\exp(-a t) + \frac{1}{9} \exp(-9 a t) + \frac{1}{25} \exp(-25 a t)\right)\right)$$

(3.1)

which was fitted to the experimental data. \( a \) (s\(^{-1}\)) is a constant characterizing the overall rate of water adsorption. The solid lines in Figures 3.1 and 3.2 are the fitted correlations. It is obvious from the agreement of measured and calculated values that water adsorption can be described by Fickian diffusion reasonably well.

Figure 3.1 Water adsorption isotherm of the zeolite 5A used in the study

Figure 3.2 Water adsorption of polycarbonate composites at various zeolite contents. Symbols: (○) 10, (△) 20, (▽) 30, (◇) 40, (◁) 50 vol%
In order to compare the effect of the type of the polymer used as matrix material, adsorption isotherms are plotted as a function of time in Fig. 3.3 for three polymers at two different zeolite contents. Fitted correlations are presented in this figure as well. The comparison of the results obtained for the three polymers shows that the adsorption capacity of the composites depends mainly on the amount of desiccant present and only slightly on the type of the polymer used as matrix. On the other hand, the rate of adsorption, indicated by the initial slope of the adsorption isotherms, depends on the properties of the polymer and in a much lesser extent on the amount of desiccant added. Since both adsorption capacity and the rate of adsorption are important for practice, quantitative analysis must be carried out in order to analyze the factors influencing them. One way to do this is the fitting of Eq. 3.1 to the experimental results. Adsorption capacity can be estimated quite accurately by the extrapolated water uptake, i.e. \( M_\infty \), while the overall rate of adsorption can be characterized by parameter \( a \). However, the initial rate of adsorption differs considerably from the overall rate and none of the current theories can describe equally accurately both. A common practice to characterize the initial rate of adsorption is to fit another form of Fick’s law to the experimental results, as described in the introduction part of the thesis (see Eq. 1.3).

If we plot the water uptake as a function of the square root of time, we should obtain a straight line the slope of which, \( b \ (s^{-1/2}) \), is proportional to the initial rate of water adsorption. Eq. 3.3 was fitted to the water adsorption of all composites; an example is shown in Fig. 3.4 for three PP composites. A reasonable fit is obtained again, thus the initial rate of adsorption can be determined in this way. Fig. 3.4 also shows that the initial rate of water adsorption increases with zeolite content.

![Figure 3.3](image_url)  
**Figure 3.3** Effect of polymer type and zeolite content on the water adsorption of various desiccant composites. Symbols: (□) HDPE, (○) PVC, (△) PC
Factors affecting the capacity and rate of water adsorption

The results shown in the previous section indicated qualitatively that the water adsorption capacity of desiccant composites depends mainly on their zeolite content, while the type and characteristics of the polymer influence the rate of adsorption much more. In order to see the correlations and the effect of these factors much better we plotted maximum water uptake against zeolite content for three polymers in Fig. 3.5. According to the figure adsorption increases with zeolite content linearly for all three polymers indeed and it is completely independent of the type of polymer used as matrix. Very similar correlations were obtained for all the polymers used as matrix material in this study.

Much more complicated is the effect of polymer characteristics on the rate of water adsorption. The initial rate of adsorption is plotted against zeolite content in Fig. 3.6 for the same three polymers as in Fig. 3.5. Adsorption rate is the fastest in the PC composites, while much slower in PVC and especially in HDPE. These relationships were more or less visible already in Fig. 3.3, but the calculation and plotting of parameter $b$ against zeolite content reveals them much more clearly. We must also note that the increase in the rate of adsorption slows down with increasing desiccant content in PC, while it accelerates slightly in PE. The inherent properties of the polymer obviously influence water adsorption strongly, but the dominating one cannot be identified from the results presented up to now. We must call the attention also to the fact here, that the

![Figure 3.4](image-url) Determination the initial rate of water adsorption in PP/zeolite composites with various desiccant contents. Symbols: (⊙) 10, (△) 30, (∇) 50 vol%
rate of water adsorption is at least one or two order of magnitudes faster for the neat zeolite \( (b = 0.16 \text{ s}^{-1/2}) \) than for the composites.

**Figure 3.5**  Effect of matrix type and zeolite content on the water adsorption capacity of desiccant composites. Symbols: (□) HDPE, (○) PVC, (△) PC

**Figure 3.6**  Influence of the type of the polymer used as matrix and zeolite content on the initial rate of water adsorption \((b)\) in desiccant composites. Symbols: (□) HDPE, (○) PVC, (△) PC
Factors affecting the capacity and rate of water adsorption

Even more surprising is the effect of these parameters, or more exactly that of zeolite content, on the overall rate of water adsorption \( a \) as shown by Fig. 3.7. Overall rates are in the same magnitude than initial rates and the relative order of the composites is also the same, i.e. adsorption is the fastest in PC and the slowest in HDPE, but the rate of water uptake decreases with increasing zeolite content instead of increasing. The difference among the polymers is also larger; water adsorption is very slow in PVC and HDPE and much faster in PC. The rate of water adsorption is between the values presented in Figs. 3.6 and 3.7 for the other polymers as well. Although the comparison of Figs. 3.6 and 3.7 calls the attention to the importance of determining both the initial and the overall rate of water adsorption, it does not explain the difference; further analysis is needed to explain the phenomenon.

3.2.3. Discussion

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. The fractional free volume \( v_{ff} \) is the ratio of the free volume to the specific molar volume \( v \) of the polymer, i.e.

\[
v_{ff} = \frac{V - V_0}{v}
\]

(3.2)
where \( v_0 \) is the occupied volume. The occupied volume can be determined by the method of Bondi [3] from the van der Waals volume \( (v_W) \) of the polymer, \( v_0 = 1.3v_W \). Both the specific molar volume and the van der Waals volume are listed by van Krevelen and te Nijenhuis [4] in their book. Often not the fractional free volume, but the specific free volume, \( v_{sf} \), is used for the characterization of the polymers which is the fractional free volume related to the molecular weight of the repeat unit \( (M) \), i.e. \( v_{sf} = v_{ff}/M \). Cohen and Turnbull [5] applied the free volume theory of Doolitle [6] to describe diffusion in polymers

\[
D = C \exp\left(-\frac{\gamma v^*}{v_{sf}}\right)
\]  

(3.3)

where \( C \) and \( \gamma \) are constants and \( v^* \) is the free volume needed for diffusion. Fujita [7] expressed the mobility of the diffusing gas \( (M_p) \) with the approach

\[
M_p = A \exp\left(-\frac{B}{v_{sf}}\right)
\]  

(3.4)

where \( A \) and \( B \) are constants independent of the concentration of the diffusing gas. Mobility is related to permeability \( (P) \)

\[
P = D S = SRT \exp\left(-\frac{B}{v_{sf}}\right)
\]  

(3.5)

where \( S \) is the solubility of the diffusing matter in the matrix. We can see from Eq. 3.5 that if we plot permeability against the natural logarithm of \( v_{sf} \), we should obtain a linear correlation with a negative slope. Lee [8] determined the permeability of oxygen through various polymers and obtained a very good correlation between permeation and \( v_{sf} \) indeed (see Fig. 1.6). Free volume can be calculated as indicated above or can be determined by positron annihilation spectroscopy [9]. However, this latter approach is difficult or even impossible to use for certain polymers, since, for example, chlorine or nitrile groups hinder the formation of ortho-positrons.

We used the above presented approach to analyze the effect of polymer characteristics on the water adsorption of desiccant composites. First we calculated the specific free volume of our polymers from data listed by van Krevelen and te Nijenhuis [4]. In the case of copolymers (HIPS, SAN) we calculated average values taking into account their composition. Weight averages were used in the calculation. Crystallinity was also taken into account, since diffusion occurs only in the amorphous phase in polymers. Calculated specific free volumes are listed in the last column of Table 2.3.

In order to check the approach, first we plotted the logarithm of water vapor transmission rate (WVTR) against the reciprocal value of \( v_{sf} \) of the neat polymers (Fig. 3.8). The correlation is surprisingly good, a straight line with a negative slope is obtained as predicted by theory and the deviations of the individual points from the line are very small. We can safely conclude that the approach can be applied also in our case, and the permeation 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
Factors affecting the capacity and rate of water adsorption

Adsorption values \((a\) and \(b\)) of the composites against \(v_{sf}\) in the same way. **Fig. 3.9** shows initial rates plotted in this way for composites containing 30 vol\% zeolite. A very good linear correlation is obtained again with somewhat larger, but not very large deviations. We can conclude that the initial rate of adsorption is determined mainly by the free volume of the polymer. Similar correlations were obtained at other zeolite contents as well, but also for overall values of adsorption rate, although the deviations from the straight line were larger in this latter case. Nevertheless, the tendency was always the same proving that diffusion in the matrix determines both the initial and the overall rate of water adsorption in desiccant composites.

![Figure 3.8](image)

**Figure 3.8** Correlation between the water vapor transmission rate of the polymers used as matrices for desiccant composites and their specific free volume. Symbols: (□) HDPE, (○) PP, (△) LDPE, (▽) PVC, (◇) PS, (△) HIPS2, (▽) PC, (●) HIPS1, (☆) PMMA, (●) SAN

Only one question remains that we have to explain, the different composition dependence of the initial and the overall rate of water adsorption. The adsorption of all composites is much slower than that of the neat zeolite and one would expect that diffusion is determined by the diffusion rate of the polymer. The expectation is fulfilled for the initial, but not for the overall rate of adsorption. Obviously, diffusion slows down with increasing desiccant content at longer times in the latter case. Although water adsorption is claimed to proceed in three steps and slow down with time for the neat zeolite [10], this stepwise diffusion cannot cause the effect observed in the composites, since overall rate for the zeolite is at least one order of magnitude larger than for the composites. The only reasonable explanation is the increase of diffusion path with increasing desiccant content. Fillers were shown to slow down diffusion through compo-
sites because of increasing tortuosity of the path [11]. Diffusion occurs from the edges thus particles located there are filled with water fast. Diffusion proceeds through the polymer as a consequence and water molecules must go around particles saturated with water. The effect is obviously much larger for polymers in which diffusion is fast (PC) than in polyolefins, in which it is very slow.

![Figure 3.9](image)

**Figure 3.9**  
*Effect of the free volume of the matrix polymer on the initial rate of water adsorption of desiccant composites containing 30 vol% zeolite. Symbols are the same as in Fig. 3.8*

### 3.3. Conclusions

The study of polymer/zeolite desiccant composites prepared with ten different matrices showed that the desiccant can adsorb considerable water in its free pores. 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. 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. 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.
3.4. References

Chapter 4

Effect of desiccant characteristics on the properties of PS/zeolite composites

4.1. Introduction

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 few papers published compose two desiccant at most [1-5], and even those have not been characterized properly. As a consequence, the goal of our study was to carry out systematic experiments on desiccant composites prepared with a series of zeolites and to determine the effect of their characteristics on the rate and capacity of water adsorption, but also on other composite properties. Two different polymers were selected for the study, a polystyrene (PS) and a high impact polystyrene (HIPS), to investigate the effect of the elastomer phase on composite properties.

4.2. Results and discussion

4.2.1. Desiccant characteristics

As mentioned before, the capacity and rate of water adsorption are the most important functional properties of desiccant composites. The characteristics of zeolites may change in a wide range and it is safe to assume that some of them influence composite properties as well. The synthetic zeolites used in this study include the A and X types used most frequently in industrial practice. The characteristics of the desiccants are collected in Table 2.2 and they include the type of compensating cations, Si/Al rate, pore size and volume and characteristics related to water adsorption (capacity, \(M_\infty\); equilibrium constant of adsorption, \(K\)). The type of the compensating ions and Si/Al ratio have been proved to influence the adsorption characteristics of zeolites quite strongly [6-8]. However, the diameter of the ions do not differ significantly in our case and although Si/Al ratio changes from 1.0 to 1.4. This change is very small compared to the possible range from 1 to infinite. Accordingly, we do not expect these parameters to influence the water adsorption capacity of our zeolites. However, considerable difference can be seen in capacity (\(M_\infty\)) for A and X types, respectively, caused by some other factor. Both pore size and total pore volume differ for the two types of zeolites and the surface energy (\(\gamma_{sd}\)) of X types is also somewhat larger than that of A type zeolites. The

particle size of the desiccants is very similar; we did not expect and did not find any effect of this parameter on desiccant and other properties.

The water adsorption isotherm of two different types of zeolite is presented in Fig. 4.1. As the figure shows, water adsorption is very fast and more than 30% water is adsorbed at least by the X type zeolites. The capacity of the two zeolites differs considerably. As explained above the difference may result from dissimilar pore size, volume or surface energy. A detailed analysis of the results proved that the dominating factor in the determination of the water adsorption capacity of the zeolites used in this study is the total volume of the pores (\(V_t\)). We did not find any correlation between adsorption capacity and pore diameter or surface tension, or in fact any other characteristics of the desiccant, but total pore volume. The relatively close correlation between the two quantities is presented in Fig. 4.2. The zeolites used form two groups according to their type and the difference in adsorption capacity is about 10%.

![Figure 4.1](image)

**Figure 4.1** Comparison of the water adsorption isotherm of two different types of zeolites used as desiccants in the study. Symbols: (○) 4A, (△) 10X

Besides capacity, the rate of water adsorption is another important attribute of desiccant composites. Similarly to capacity, this characteristic might be influenced by the type of the desiccant as well. In the determination of the rate of water adsorption we assumed Fickian type adsorption and fitted Eq. 3.1 to our experimental adsorption isotherms. Just as before, we determined the initial rate of adsorption from a different form of Fick's law, from Eq. 1.3
Figure 4.2  Effect of the total pore volume of the zeolite on its water adsorption capacity

Comparing all the characteristics determined for the zeolites to the initial rate of water adsorption we found that it is independent of most characteristics and correlates mainly with the equilibrium constant of water adsorption (K) defined as

$$\Delta G = -RT \ln K$$  \hspace{1cm} (4.1)

where $\Delta G$ is the free enthalpy of adsorption, $R$ the universal gas constant and $T$ absolute temperature. The correlation is shown in Fig. 4.3. It is interesting to note that the zeolites cannot be divided into two groups and the points belonging to A and X types are located randomly along the correlation (see also Table 2.2). We can also conclude that the rate of adsorption changes much less with desiccant characteristics than adsorption capacity, the determined values are very similar to each other. The examination of the factors determining the water adsorption characteristics of zeolites showed that capacity depends quite significantly on the type of the zeolite, but adsorption rate does not. Accordingly, we can expect also the adsorption capacity of desiccant composites to depend on the type of the zeolite and X types are expected to perform better than the more common A types.

4.2.2. Water adsorption of composites

The water adsorption isotherms of a series of composites are presented in Fig. 4.4. The comparison of the isotherms to those presented in Fig. 4.1 may lead to several conclusions. Water adsorption in HIPS/zeolite desiccant composites can be described quite well by the equation based on Fick's law. The rate of adsorption is con-
siderably slower in the composites, than for neat zeolites, and it is in the same order of magnitude as that of the neat polymer \( (\alpha = 0.03-0.04 \text{ s}^{-1}) \), i.e. it is determined by the characteristics of the matrix. In accordance with earlier results (see Chapter 3), adsorption capacity is determined mainly by the amount of zeolite present, the amount of adsorbed water seems to be proportional to zeolite content. Naturally, Fig. 4.4 alone does not allow the determination of the effect of the matrix polymer or that of the type of zeolite, but it shows quite well the effect of desiccant content.

![Graph showing correlation between equilibrium constant (K) and initial rate (b) of moisture adsorption](image)

**Figure 4.3** Correlation between the equilibrium constant \( (K) \) and the initial rate \( (b) \) of moisture adsorption

Water adsorption capacity determined by the fitting of Eq. 3.1 to the adsorption isotherms \( (M_{ao}) \) is plotted against zeolite content in Fig. 4.5 in order to compare the effect of the two parameters, i.e. zeolite and matrix type, mentioned above. The determining role of desiccant content is very clear from the figure, linear correlation exists between water adsorption capacity and zeolite content. Some differences can be seen in the slope of the line depending on the type of zeolite used. However, quite surprisingly, composites containing X type absorb less water than those prepared with A type zeolites and the effect depends also on the type of polymer used. The adsorption capacity of the 13X type zeolite \( (\triangledown, \blacksquare) \) is much smaller than that of the rest and the effect is more pronounced in neat PS than in the impact polymer. Slight differences can be seen in the other cases as well, but the influence of polymer and zeolite type is much weaker than in the case of zeolite 13X; in fact composites prepared from HIPS and the 10X zeolite have the same adsorption capacity as those containing A type zeolites.
Figure 4.4  Water adsorption isotherms of HIPS/4A desiccant composites

Figure 4.5  Effect of zeolite content on the water adsorption capacity ($M_\infty$) of polystyrene desiccant composites. Full symbols PS, empty symbols HIPS; (□) 3A, (○) 4A, (◇) 5A, (△) 10X, (▽) 13X
Fig. 4.2 showed a very clear correlation between the adsorption capacity of zeolites and their total pore volume. The capacity of desiccant composites is plotted against the pore volume of the zeolite in Fig. 4.6 at two different desiccant contents. Contrary to the neat zeolites, the water adsorption capacity of the composites decreases with increasing total pore volume of the zeolite. Although the correlation is not very strong, it is unambiguous. It is quite difficult to find a plausible explanation or even a tentative one for the phenomenon; it definitely needs further study and considerations. Nevertheless, we can conclude that the water adsorption capacity of desiccant composites prepared from various zeolites depends practically only on the amount of zeolite present and only slightly on the type of desiccant used. The rate of moisture adsorption seemed to be somewhat larger in HIPS than in neat PS composites, but the differences fall within the standard deviation of the measurement thus the correlations are not shown here. In order to come to a definite conclusion about the effect of elastomer content on desiccant properties, further, more systematic experiments must be carried out as a function of elastomer content.

![Figure 4.6](image_url)  
**Figure 4.6** Correlation between the total pore volume of the zeolite and the water adsorption capacity of its composites. Zeolite content: (○) 10, (□) 30 vol%  

4.2.3. Application properties

The rate and capacity of water adsorption are the most important functional properties of desiccant composites. However, if we want to use these composites in packaging for any purpose, they should meet the requirements of the specific application. These requirements usually include characteristics related to processing, but also
stiffness, strength and toughness. Mechanical properties of such composites depend very much on the interfacial adhesion of the components, thus interactions must be analyzed as well, especially since several contradictory statements have been published in the literature on this issue [9].

Torque measured during the homogenization of the composites, which is proportional to viscosity, is plotted against zeolite content in Fig. 4.7 for the composites prepared from neat PS. The correlation is the same and even the values are similar for the HIPS composites, in spite of the considerable difference in the molecular weight of the two polymers (see Table 2.3). The viscosity of the composites prepared with the X type zeolite is considerably larger than that of the materials containing the A type. Since particle sizes are very similar (see Table 2.2) irrespectively of type, the main reason must be the surface energy of the zeolite being substantially larger for the X than for the A type. Larger viscosity, especially at the large zeolite content necessary for efficient desiccation, might result in difficulties in processing and the steep increase of torque at 50 vol% filler content indicates some homogenization problem, the slight aggregation of the desiccant.

![Equilibrium torque vs Zeolite content](image.png)

**Figure 4.7** Influence of the type of zeolite on equilibrium torque measured during the homogenization of desiccant composites in neat PS matrix. Symbols: (○) 4A, (△) 10X

The modulus of the polymer increases with increasing zeolite content and its composition dependence is independent of the type of zeolite (not shown). The stiffness of composites prepared with the two polymers, i.e. PS and HIPS, obviously differs from each other because of inherent differences in matrix properties. However, modulus is
not very sensitive to slight differences in dispersion and/or interfacial adhesion thus the result is expected. On the other hand, the strength of composites prepared with the two matrices differs significantly as shown by Fig. 4.8 for two desiccants (4A and 10X). The strength of composites prepared from neat PS decreases slightly with increasing zeolite content ($\bullet$, $\Delta$). On the other hand, the tensile strength of composites based on HIPS increases with increasing desiccant content ($\bigcirc$, $\triangle$), i.e. true reinforcement can be achieved in this matrix polymer. The effect of A and X type zeolites also differs from each other, the reinforcing of the second being stronger than that of the first. The observed differences can be explained by the inherent property of the matrix, on the one hand, and by dissimilar interfacial adhesion on the other. Always larger reinforcement is achieved in soft matrices, than in stiff polymers, while the larger surface energy of the X type zeolite results in stronger interfacial interactions, leading to larger reinforcement.

![Composite strength plotted against zeolite content for polystyrene/zeolite composites. Effect of matrix and zeolite type. Full symbols PS, empty symbols HIPS; ($\bigcirc$, $\bullet$) 4A, ($\triangle$, $\Delta$) 10X](image)

The extent of reinforcement and the influence of adhesion can be expressed quantitatively by the model developed earlier to describe the composition dependence of tensile strength in particulate filled composites [10]

$$
\sigma_T = \sigma_{T0} \lambda^n \frac{1 - \varphi}{1 + 2.5 \varphi} \exp(B \varphi)
$$

(4.2)

where $\sigma_T$ and $\sigma_{T0}$ are the true tensile strength ($\sigma_T = \sigma \lambda$ and $\lambda = L/L_0$) of the composite and the matrix, respectively, $n$ is a parameter expressing the strain hardening tendency of the matrix, $\varphi$ is the volume fraction of the zeolite and $B$ is related to its relative load-
bearing capacity, i.e. to the extent of reinforcement, which depends among other factors, also on interfacial interaction. We can write Eq. 4.2 in linear form

\[
\ln \sigma_{T_{\text{red}}} = \ln \frac{\sigma_T}{\ln (1 - \varphi)} = \ln \sigma_T + B \varphi \tag{4.3}
\]

and the plot of the natural logarithm of reduced tensile strength against filler content should result in a straight line, the slope of which is proportional to the load-bearing capacity of the filler and under certain conditions to the strength of interaction. The strength of the four series of composites of Fig. 4.8 is plotted in the form indicated by Eq. 4.3 in Fig. 4.9. We obtain straight lines indeed with slight deviations at the largest desiccant content, because of the slight homogenization problems mentioned earlier. The calculation was executed for all composites and the results are collected in Table 4.1. We can see that reinforcement \((B)\) is much larger in the softer matrix, as expected and predicted by the model used.

![Figure 4.9](image_url)

**Figure 4.9** Reduced tensile strength plotted against zeolite content in the representation of Eq. 4.3 for the composites of Fig. 8. Full symbols PS, empty symbols HIPS; (○, ●) 4A, (△, ▲) 10X

The mode of deformation and failure is also important aspects of most applications. In particulate filled composites the dominating deformation mode is debonding, the separation of the matrix and the filler at the interface under the effect of external load. The critical stress initiating debonding can be predicted by the correlation [11]

\[
\sigma^D = -C_1 \sigma_T^2 + C_2 \left( \frac{E W_{AB}}{r} \right)^{1/2} \tag{4.4}
\]
where $\sigma^D$ and $\sigma^T$ are debonding and thermal stresses, respectively, $E$ the Young's modulus of the matrix, $W_{AB}$ the reversible work of adhesion, $r$ the radius of the particles, while $C_1$ and $C_2$ are geometric constants related to the debonding process. Using the Eq. 4.4 we predicted debonding stress for our composites and listed the results in Table 4.1. If we compare debonding stress to the strength of the matrix, we can see that the former is larger in all cases thus debonding does not occur, but the composites fail either by the yielding or fracture of the matrix. These conclusions are further confirmed by SEM micrographs recorded on the fracture surface of composites created during tensile testing (Fig. 4.10). All the filler particles are covered by the matrix indicating good interfacial adhesion irrespectively of the presence or absence of an elastomer phase. Easy debonding may lead to premature failure, thus good adhesion and the mechanism mentioned above can be very advantageous if the composites do not become brittle as a result of filling.

Table 4.1  Reinforcement and debonding stress depending on interfacial adhesion for PS and HIPS/zeolite composites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Zeolite</th>
<th>Tensile strength (MPa)</th>
<th>Debonding stress (MPa)</th>
<th>Parameter B</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>3A</td>
<td>38.3</td>
<td>51.0</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>4A</td>
<td></td>
<td>50.9</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>5A</td>
<td></td>
<td>50.8</td>
<td>2.95</td>
</tr>
<tr>
<td></td>
<td>10X</td>
<td></td>
<td>51.8</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>13X</td>
<td></td>
<td>51.9</td>
<td>2.99</td>
</tr>
<tr>
<td>HIPS</td>
<td>3A</td>
<td>11.8</td>
<td>36.7</td>
<td>4.30</td>
</tr>
<tr>
<td></td>
<td>4A</td>
<td></td>
<td>36.6</td>
<td>4.14</td>
</tr>
<tr>
<td></td>
<td>5A</td>
<td></td>
<td>36.6</td>
<td>4.35</td>
</tr>
<tr>
<td></td>
<td>10X</td>
<td></td>
<td>37.3</td>
<td>5.76</td>
</tr>
<tr>
<td></td>
<td>13X</td>
<td></td>
<td>37.4</td>
<td>5.65</td>
</tr>
</tbody>
</table>

Although the 1 mm thick plates prepared and used in these experiments do not allow the reliable determination of impact or fracture resistance, we can estimate the ductility of our materials from the stress vs. strain traces. Relative toughness (related to the corresponding matrix property) is compared for all composites in Fig. 4.11 for two desiccants, 4A and 10X. We can see that HIPS composites perform much better than those produced with the neat PS, as expected. Accordingly, if fracture resistance is an important requirement for the intended application, impact modified PS should be selected as matrix, since it performs better than the unmodified material.
Effect of desiccant characteristics

Figure 4.10  *SEM micrographs recorded on the fracture surface of polystyrene/zeolite composites containing 30 vol% desiccant. The surfaces were created in tensile testing. a) PS/4A, b) HIPS/4A*

Figure 4.11  *Composition dependence of the ductility of polystyrene/zeolite composites. Effect of matrix and zeolite type. Full symbols PS, empty symbols HIPS; (⊙, ●) 4A, (△, ▲) 10X*

4.3. Conclusions

The systematic study of five zeolites and their desiccant PS composites 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, zeolite characteristics influence the moisture adsorption of the composite only marginally; adsorption capacity is determined by zeolite content, while
the rate of adsorption 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. The dispersion of the zeolite is very good both in PS and in HIPS composites. Mechanical properties are excellent mainly because of the good interfacial adhesion between the components. Because of their larger surface energy, composites containing X type zeolites have larger viscosity and they reinforce the polymer more than the A type desiccants. Matrix properties influence mainly application related properties, reinforcement and ductility is better in HIPS than in PS composites.

4.4. References


Chapter 5

Interfacial interactions and reinforcement in thermoplastics/zeolite composites

5.1. Introduction

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]. A wide range of functions can be introduced into these materials like electrical and thermal properties, piezoelectric response, desiccant characteristics, antiseptic properties, etc. Occasionally the filler may fulfill more than one function as in the preparation of breathable films, in which they help the formation of voids to let vapor pass through the film, but prevent the permeation of liquids, while act as desiccant at the same time. Zeolites were used for this purpose in more than one case [2-6].

Obviously, the components of the material and the ensuing composite must meet some requirements in order to fulfill their functions. Desiccant characteristics require large specific surface area and high surface energy to bind efficiently as much water as possible. On the other hand, matrix-filler adhesion cannot be excessively strong, otherwise debonding does not occur during the preparation of breathable films, and the required voids do not form. All packaging materials must possess certain mechanical properties to fulfill their role, stiffness, strength, deformability and fracture resistance must exceed certain minimum values. The mechanical properties of all heterogeneous materials are strongly influenced by interfacial interactions [7], which play an important role in the preparation of breathable films, but influence desiccant properties as well. Because of the importance of interactions and adhesion, several attempts have been made to determine or estimate them. Unfortunately, published information is controversial sometimes coming even from the same authors. Biswas et al. [2-5, 8, 9] prepared zeolite composites with various matrices including linear low density (LLDPE), low (LDPE) and high density (HDPE) polyethylene as well as polypropylene (PP). They drew their conclusions about adhesion from the composition dependence of tensile properties and from scanning electron micrographs (SEM). They claim strong interaction in LLDPE, but weak in the rest of the polyolefins. The conclusion is difficult to believe, since the surface energy of all polyolefins is small and very similar, interactions are created by van der Waals forces, thus it they must be practically the same for all the polymers tested. Moreover, the authors neglected the fact that the composition depend-

Kajtár, D., Kenyó, C., Renner, K., Móczó, J., Fekete, E., Kröhnke, C., Pukánszky, B.: Interfacial interactions and reinforcement in thermoplastics/zeolite composites, submitted to Compos Science and Technology
ence of mechanical properties is influenced also by matrix characteristics thus reinforcement is much stronger in a soft than in a hard matrix even at the same level of adhesion [10]. Similarly contradictory and confusing conclusions were published by other groups as well. Upadhyay et al. [11] claim strong adhesion between zeolite and polyamide (PA) based on the simple argument that both are polar. Similarly to Biswas et al. [8, 9], Balkose et al. [6, 12, 13] used the composition dependence of mechanical properties to estimate interactions in polypropylene/zeolite composites and found that they are weak. Other groups [14, 15] used SEM micrographs to evaluate interfacial adhesion and based on the fact that on fracture surfaces the filler is covered by the polymer they claim strong adhesion even when the surface of the zeolite was treated with aliphatic carboxylic acids [14] that are known to decrease surface energy and interactions [16]. Results obtained in a previous part of our work indicated the development of strong interfacial interactions between zeolite and PS polymers (see Chapter 4.)

Available results are clearly contradictory and one of the reasons is that the composition dependence of tensile properties and SEM do not allow the reliable estimation of interfacial adhesion. 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. The desiccant characteristics of the composites have been evaluated and reported in Chapter 3. In this chapter we focus on interfacial interactions in the same composites as in Chapter 3 and try to point out the difficulties in their estimation, show the effect of matrix characteristics and discuss some practical consequences.

5.2. Results and discussion

5.2.1. Properties

As mentioned above, besides desiccant characteristics, i.e. the capacity and rate of water adsorption [17], other properties are also important for the application of polymer/zeolite composites as packaging materials. Usually stiffness, strength and deformability are the mechanical properties to consider. The Young’s modulus of selected composites is plotted against composition in Fig. 5.1. Only a few of the ten polymers is shown in the figure to facilitate viewing; the presentation of all results in a single figure results in a very confusing graph. The continuous lines are drawn only to guide the eye in this and in all other figures, they are not fitted correlations. Accordingly, the number of lines often does not correspond to the number of series in a given figure.

The stiffness of the composites prepared from the four polymers presented in Fig. 5.1 covers a very wide range; it changes from about 0.3 up to around 10 GPa. The values for the composites produced with the other polymers are located between the two correlations bounded by LDPE and SAN. Stiffness increases with increasing zeolite content, as expected, the slope of the increase depends very much on the polymer used as matrix. As a consequence, a product with practically any stiffness can be prepared from the polymers studied in this work, but of course functional characteristics as well as other mechanical properties must be also considered.
Interfacial interactions and reinforcement

Figure 5.1 Young's modulus of selected polymer/desiccant composites plotted against zeolite content. Symbols: (△) LDPE, (◇) PS, (●) HIPS1, (★) SAN

Composite strength is presented in Fig. 5.2 for the same composites as in the previous figure. Composition dependence is different from that shown by stiffness, strength decreases in some matrices, while increases in others. The decrease of strength is often interpreted as a sign of weak interaction between the matrix and the reinforcement, while the increase as strong interfacial adhesion. Such a simplistic explanation is completely misleading, composition dependence and the extent of reinforcement depends on the stiffness of the matrix as well. The filler or reinforcement carries much more load in a weak matrix than in a stiffer one [10]. Similarly to stiffness, strength values measured for the rest of the composites prepared with the remaining polymers as matrix are located within the boundaries set by LDPE and SAN.

The deformability of the composites characterized by their elongation-at-break is plotted as a function of composition in Fig. 5.3 for the composites of the two previous figures. Elongation is plotted in a logarithmic scale because of the very large differences among the composites; ultimate deformation is almost 1000 % for LDPE, while only a few percent at most for stiffer composites. Only two lines are presented here, since the deformability of three of the composites is very similar to each other and very small. In fact most of the composites prepared from the other polymers not shown in the figure have very small deformability, thus one expects also their fracture resistance being quite small. If composites with considerable deformability and impact resistance must be prepared for a certain application, the choice is limited since the desiccant decreases the deformability of the matrix polymers very much.
Figure 5.2 Effect of zeolite content on the tensile strength of composites prepared with various matrices. Symbols: (Δ) LDPE, (◇) PS, (●) HIPS1, (★) SAN

Figure 5.3 Dependence of deformability on zeolite content in polymer/desiccant composites. Symbols: (Δ) LDPE, (◇) PS, (●) HIPS1, (★) SAN
5.2.2. Reinforcement

The strength and deformability of composites depends very much on the strength of interfacial interactions. Reinforcement cannot be judged by the mere observation of the composition dependence of stiffness, yield stress or strength. One must consider the fact that the polymer always wets the high energy surface of mineral fillers and a certain interaction always develops between the components. Reinforcement, i.e. the load-bearing capacity of the second component, can be estimated quantitatively by the use of models; a model was developed earlier to describe the composition dependence of tensile yield stress [18], tensile strength [19] or fracture resistance [20] of particulate filled polymers. The composition dependence of tensile strength is described by Eq. 4.2. If the equation is plotted into a linear form (see Eq. 4.3) the natural logarithm of reduced tensile strength against filler content, we should obtain a linear correlation, the slope of which is proportional to the load-bearing capacity of the reinforcement and under certain conditions to the strength of interaction. The tensile strength of two of the composite series is plotted in this way in Fig. 5.4. The correlations are linear indeed and their slope depends on the properties of the matrix, steep for the soft matrix (LDPE) and small for the stiff polymer (SAN). Accordingly, zeolite reinforces soft polymers much more than stiff materials, as discussed above.

![Figure 5.4](image)

Figure 5.4 Reduced tensile strength of polymer/desiccant composites plotted against zeolite content according to Eq. 4.2. Determination of the extent of reinforcement. Symbols: (△) LDPE, (★) SAN

$B$ values calculated for the composites prepared with all the matrix polymers studied in this part of the research are collected in Table 5.1. We can see that parameter
B covers a wide range from 1.5 to about 6, depending on the polymer in question. The first column of Table 5.1 contains the calculated tensile strength of the composites, $\sigma_0$ (see Eq. 4.2). If we compare these values to parameter $B$, we can see that they are not independent of each other; they express the principles mentioned above, i.e. reinforcement is stronger in weaker, soft matrices.

The model represented by Eq. 4.2 was created using the assumption that in all heterogeneous materials, including polymer composites, an interphase forms spontaneously which considerably influences properties. According to the model parameter $B$ depends on the thickness ($l$) and strength ($\sigma_i$) of the interphase and on the size of the interphase ($A_f$) in the following way

$$B = (1 + A_f \rho_f l) \ln \frac{\sigma_i}{\sigma_0}$$

(5.1)

where $A_f$ is the specific surface area and $\rho_f$ the density of the filler. According to Eq. 5.1, a linear correlation exists between parameter $B$ and the natural logarithm of matrix strength.

Table 5.1 Parameters characterizing reinforcement in polymer/zeolite composites calculated from their tensile strength

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\sigma_0$ (MPa)</th>
<th>$B$</th>
<th>$R^2$</th>
<th>$B\ln\sigma_0$</th>
<th>$W_{AB}$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>13.5</td>
<td>6.08</td>
<td>0.9905</td>
<td>15.8</td>
<td>207.0</td>
</tr>
<tr>
<td>HDPE</td>
<td>30.2</td>
<td>5.09</td>
<td>0.9884</td>
<td>17.3</td>
<td>218.5</td>
</tr>
<tr>
<td>PP</td>
<td>39.6</td>
<td>4.72</td>
<td>0.9773</td>
<td>17.4</td>
<td>220.1</td>
</tr>
<tr>
<td>PS1</td>
<td>38.3</td>
<td>1.80</td>
<td>0.9837</td>
<td>6.6</td>
<td>259.3</td>
</tr>
<tr>
<td>HIPS67</td>
<td>11.9</td>
<td>4.56</td>
<td>0.9926</td>
<td>11.3</td>
<td>256.6</td>
</tr>
<tr>
<td>HIPS86</td>
<td>14.3</td>
<td>3.91</td>
<td>0.9993</td>
<td>10.4</td>
<td>252.3</td>
</tr>
<tr>
<td>SAN</td>
<td>79.9</td>
<td>1.50</td>
<td>0.9951</td>
<td>6.6</td>
<td>260.8</td>
</tr>
<tr>
<td>PC</td>
<td>54.8</td>
<td>1.96</td>
<td>0.9519</td>
<td>7.8</td>
<td>270.1</td>
</tr>
<tr>
<td>PMMA</td>
<td>42.2</td>
<td>1.98</td>
<td>0.9582</td>
<td>7.4</td>
<td>240.0</td>
</tr>
<tr>
<td>PVC</td>
<td>34.7</td>
<td>1.73</td>
<td>0.9342</td>
<td>6.1</td>
<td>276.2</td>
</tr>
</tbody>
</table>

$^a$ matrix strength calculated from the intersection of the linear correlations (see. Eq. 4.2)

$^b$ determination coefficient indicating the goodness of the fit

Parameter $B$ is plotted against matrix strength in Fig. 5.5 and we can see that it corresponds to the prediction; a relatively close linear correlation is obtained with a negative slope for the ten polymers studied. The close relationship clearly proves that reinforcement depends on the characteristics of the matrix and cannot be judged from the composition dependence of tensile yield stress or strength. Fig. 5.5 also proves that although parameter $B$ depends also on interfacial interactions determining the thickness and properties of the interphase [21], it is dominated by matrix properties thus the effect
of interactions is difficult or impossible to deduce from it. Deviations from the linear correlation indicate the effect of experimental error, but also that of interactions. In order to compensate for the effect of the matrix, a quantity taking into consideration matrix strength was calculated and listed in the last but one column of Table 5.1. We can see that the difference is much smaller in this quantity than either in parameter $B$ or matrix strength, but it still does not help much to estimate matrix/filler interaction. Further approaches are needed for this purpose, some of which will be presented in the next sections.

![Figure 5.5](image)

**Figure 5.5**  *Linear correlation between the extent of reinforcement (parameter $B$) and matrix strength for polymer/zeolite composites*

5.2.3. *Cyclic loading, debonding*

If the interaction between the matrix and the filler results from secondary, van der Waals bonds, they are not very strong and under the effect of external load the matrix and the filler may separate at the interface, i.e. debonding occurs. Debonding stress depends on the strength of interaction and can be estimated with the model developed by Vollenberg [22, 23] and Vörös [24], respectively. According to both models initiation stress depends on the strength of interfacial interaction, on the size of the particles and on the stiffness of the matrix [24], as shown by Eq. 4.4. Accordingly, larger initiation stress is needed for debonding with increasing adhesion of the components, with increasing stiffness of the matrix and with decreasing particle size. Debonding experiments were carried out with increasing pre-strains as described in the experimental part and some results are presented in Fig. 5.6. Modulus decreases when debonding starts, thus debonding stress can be determined from the deviation of stiffness from the first, horizontal part of the correlation.
Debonding results in a three-component material consisting of the matrix, particles and voids. The amount of debonded zeolite can be estimated with the help of Hartingsveldt’s approach [25]. The model assumes that bonded particles increase stiffness, while debonded particles do not. The dependence of composite modulus is described by the following expression [26]

\[
E(\varphi) = \left[1 + \frac{\varphi_b}{\beta(1 - \varphi_b)}\right] E_m
\]  

(5.2)

where \( E_m \) is the modulus of the matrix polymer, \( \varphi_b \) is the volume fraction of bonded particles and \( \beta \) is defined as

\[
\beta = \frac{8 - 10 \nu_m}{15(1 - \nu_m)}
\]  

(5.3)

where \( \nu_m \) is the Poisson’s ratio of the matrix. Since debonded particles cannot carry any load, modulus must be corrected by the effective load-bearing cross-section of the matrix, thus composite stiffness becomes

\[
E_c = \left(1 - \varphi_d^{2/3}\right) E(\varphi_b)
\]  

(5.4)

and the amount of bonded particles is defined as
\[ \varphi_b = \varphi_f - \varphi_d \] (5.5)

where \( \varphi_f \) is total filler content, while \( \varphi_d \) is the volume fraction of debonded particles. If we determine the modulus \( (E_c) \) of pre-strained composite samples and know \( \nu_m \), the amount of bonded \( (\varphi_b) \) and debonded \( (\varphi_d) \) particles can be calculated from Eqs. 5.2–5.3. The amount of debonded particles is plotted against pre-strain in Fig. 5.7 for the composites presented in the previous figure. We can see that debonding starts very early, at very small strains for PVC, while only at larger deformations for the two polyolefins presented in the figure, then proceeds almost to completion for all three of them. Practically all the particles are separated from the matrix yielding voids, if the strain is sufficiently large.

![Graph showing debonded particles against prestrain for different matrices](image)

**Figure 5.7** Dependence of the amount of debonded particles on the pre-strain used in the cyclic loading experiment: (\( \nabla \)) PVC, (\( \bigcirc \)) PP, (\( \square \)) HDPE

According to Eq. 4.4, debonding stress depends on the stiffness of the matrix and Fig. 5.8 confirms this effect. Debonding stress determined from cyclic loading \( (\sigma_c^D) \) is plotted against the square root of matrix stiffness as suggested by Eq. 4.4. Although some of the points are grouped together, the correlation agrees well with the prediction of the model. Unfortunately, debonding stress could not be determined for all the matrices, since very stiff materials broke at very small deformations, before debonding started. Since \( \sigma_c^D \) is influenced also by thermal stresses, matrix stiffness and particle size, the determination of the strength of interaction is difficult, requires the knowledge of the parameters of Eq. 4.4.
5.2.4. Interactions

The results presented in the previous sections and the related discussion showed that interfacial interactions play a role in the determination of composite properties, but their estimation is not obvious in the present case. Various methods can be used for the estimation of the strength of interfacial adhesion. One approach used occasionally is the determination of debonding stress from acoustic emission experiments [27], but we could not detect any signals during the tensile testing of the 1 mm thick specimens used in this study. Cyclic experiments could supply information for some of the composites, but debonding stress could not be determined for stiff and especially for brittle polymers.

Occasionally we try to draw conclusions about interfacial interactions from changes in parameter \( B \). Parameter \( B \) is definitely influenced by the strength of interaction, which determines the thickness and properties of the interphase [21]. In the absence of structural effects like the orientation of anisotropic particles or aggregation, parameter \( B \) depends very much on interfacial adhesion and can be estimated from changes in \( B \). In the present case, however, the strong influence of matrix properties on parameter \( B \) makes any estimate of the strength of interaction difficult. Nevertheless, based on the results we can conclude that interfacial interactions are not very strong, since cyclic experiments yielded debonded particles and debonding strength could be determined by the method for some of the polymers. The strength of interaction differs for the polymers used shown by their dissimilar surface tension (Table 5.2), but also by the deviation from the linear correlation in Fig. 5.5.
Table 5.2  The surface tension of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Surface tension (mJ/m$^2$)</th>
<th>$\gamma_s^d$</th>
<th>$\gamma_s^p$</th>
<th>$\gamma_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td></td>
<td>32.5</td>
<td>0.3</td>
<td>32.8</td>
</tr>
<tr>
<td>HDPE</td>
<td></td>
<td>33.2</td>
<td>0.6</td>
<td>33.8</td>
</tr>
<tr>
<td>PP</td>
<td></td>
<td>32.0</td>
<td>0.8</td>
<td>33.0</td>
</tr>
<tr>
<td>PS</td>
<td></td>
<td>40.8</td>
<td>1.6</td>
<td>42.4</td>
</tr>
<tr>
<td>HIPS1</td>
<td></td>
<td>38.5</td>
<td>1.8</td>
<td>40.3</td>
</tr>
<tr>
<td>HIPS2</td>
<td></td>
<td>38.1</td>
<td>1.6</td>
<td>39.7</td>
</tr>
<tr>
<td>SAN</td>
<td></td>
<td>37.3</td>
<td>2.3</td>
<td>39.6</td>
</tr>
<tr>
<td>PC</td>
<td></td>
<td>34.8</td>
<td>3.6</td>
<td>39.7</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td>40.3</td>
<td>0.7</td>
<td>41.0</td>
</tr>
<tr>
<td>PVC</td>
<td></td>
<td>34.7</td>
<td>4.2</td>
<td>38.7</td>
</tr>
</tbody>
</table>

SEM is used quite frequently for the estimation of interfacial adhesion in polymer composites and the results obtained partially support our conclusions presented above. Fig. 5.9 shows micrographs recorded on the fracture surface of selected composites. Debonding and considerable matrix yielding occurs in the LDPE composite (Fig. 5.9a), and clean debonding can be observed in the PP composite (Fig. 5.9b). The danger of using SEM for the estimation of interactions is demonstrated excellently by Fig. 5.9c, showing the micrograph taken from another PP composite at 50 vol% zeolite content. Particles are covered by the matrix thus one could easily draw the conclusion from the micrograph that interaction between the filler and the matrix is strong. However, the conclusion would be wrong and the micrograph is deceiving, since interactions cannot depend on composition, on the one hand, and all evidence (see Fig. 5.6) indicate weak interaction between PP and the zeolite, on the other. Finally the fracture surface of a SAN composite is shown in Fig. 5.9d showing again some debonding, although interpretation is not completely unambiguous and up to opinion in this case as well. Apparently debonding initiated the failure of the composite at very small deformation that resulted also in the failure of the cyclic test for this polymer.

The usual and obvious route of using the reversible work of adhesion for the characterization of the strength of interaction could not be followed directly, because we encountered various problems during the determination of the surface tension of the zeolite. Because of its high surface energy, the apolar component of surface tension could be determined only at 280 °C by IGC and the polar component could not be measured even at this temperature because none of the polar solvents eluted from the column. On the other hand, we could calculate this characteristic from spreading pressure derived from the adsorption isotherm of water on the zeolite. Accordingly, we
obtained 181.9 mJ/m$^2$ for the apolar (IGC) and 440.9 mJ/m$^2$ for the polar (adsorption) component of surface tension. Using these values in further calculations is somewhat questionable because they were determined at different temperatures. However, since the same zeolite was used in all composites, an approximate value is acceptable for comparative purposes. Accordingly, the reversible work of adhesion was calculated for all polymer/zeolite pairs and the results are listed in the last column of Table 5.1. It is obvious that interfacial adhesion is different in the composites, $W_{AB}$ changes from around 200 to 280 mJ/m$^2$. The corrected parameter $B (B\ln\sigma_T)$ used for the estimation of interactions above is plotted against the reversible work of adhesion in Fig. 5.10. A clear correlation exists between the two quantities proving that interfacial interactions influence composite properties and reinforcement indeed. On the other hand, the slope of the correlation is negative, although one would expect an increase in $B$ with increasing interfacial adhesion. The apparent contradiction can be explained, and proves at the same time, that interactions are not very strong and composite properties, as well as reinforcement is determined mainly by matrix characteristics.

![Figure 5.9](image)

**Figure 5.9** SEM micrographs recorded on the fracture surface of polymer/zeolite composites; a) LDPE, 50 vol%, b) PP, 20 vol%, c) PP, 50 vol%, d) SAN, 50 vol%

5.3. Conclusions

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 10 and 80 MPa. The deformability of most composites is small and decreases with increasing zeolite content.
Interfacial adhesion between the matrix polymer and zeolite is not very strong although quantitative determination is hampered by various factors. Most of the composites fail by debonding, thus debonding stress could be determined in cyclic loading and relaxation experiments. Brittle matrices fail by debonding and/or matrix fracture, while considerable shear yielding has been observed in LDPE composites. Composite properties are determined mainly by matrix characteristics and interfacial adhesion plays only a relatively minor role. Accordingly, the matrix of such desiccant composites must be selected mainly according to functional properties and always in view of matrix characteristics.

![Figure 5.10](image)

**Figure 5.10** Correlation between quantities related to interfacial adhesion in polymer/zeolite composites

### 5.4. References


Chapter 6

Effect of matrix characteristics on the properties of HIPS/zeolite composites

6.1. Introduction

Our previous research has shown that the adsorption capacity of desiccant composites depends linearly on the amount of the desiccant present, but it is independent of the type of the polymer used (see Chapter 3). The initial rate of diffusion depends strongly on the specific free volume of the matrix and this factor influences also the overall rate of water adsorption. 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 (see Chapter 4). However, according to our knowledge, a detailed study of these factors has never been carried out before on desiccant composites prepared from zeolite and HIPS.

As a consequence, the goal of our study was to carry out systematic experiments on such composites prepared with a series of high impact polystyrenes as matrix and to determine the effect of their characteristics, especially butadiene content, on the rate and capacity of water adsorption, but also on other composite properties. Two different polystyrene homopolymers were selected as references, and seven HIPS with a wide range of butadiene contents and other characteristics were used as matrix materials. Zeolite 4A was used as desiccant in the experiments.

6.2. Results and discussion

6.2.1. Matrix characteristics and structure

Polystyrene and high impact polystyrene are frequently used as matrix materials for the production of desiccant composites in industrial practice. The actual grade is selected according to processability or mechanical properties; functional characteristics are of secondary importance. In fact very little information is available on the effect of the structure and elastomer content of HIPS on the water adsorption characteristics of the desiccant composite [1]. However, the butadiene content, structure and consequently the properties of HIPS polymers may change in a wide range [2-5]. The most important

---

characteristics of the polymers used in our experiments are listed in Table 2.4. The molecular weight and MFI of the polymer varies considerably, but these characteristics did not prove to be crucial either for functional or application properties. On the other hand, impact resistance is very important for practice, in fact it was one of the aspects of selection; we tried to select grades to cover as wide range of impact strength as possible (see seventh column of Table 2.4). As mentioned above, one of the crucial characteristics of high impact polystyrenes is their butadiene content, which we determined by the measurement of the iodine value. According to the table, butadiene content changes between 4.7 and 12.0 vol%.

![Figure 6.1 Effect of the polybutadiene content of HIPS polymers on their impact resistance](image)

A close correlation exists between impact strength and elastomer content (Fig. 6.1) as expected, but some other factor or factors also play a role as shown by the deviating point of the HIPS120 polymer. The most probable reason is the dissimilar particle size of the butadiene droplets or the amount of embedded polystyrene, which were reported to influence the properties of HIPS considerably [6-10]. The particle size, size distribution and structure of the butadiene particles depends on numerous factors including the molecular weight and amount of the elastomer, the initiator system, stirring, shear stresses, temperature program, monomer and solvent stripping, etc. [11]. The detailed analysis of these factors is out of the scope of this Thesis, but considerable information has been published on the production, structure and properties of HIPS elsewhere [11, 12].
We checked the dispersed structure of our polystyrenes by transmission electron microscopy. Two typical micrographs are presented in Fig. 6.2. The above mentioned characteristics, i.e. size, size distribution and embedded PS differ considerably for the two grades indeed. We determined these characteristics quantitatively and they are listed in Table 2.4 for the HIPS grades used. The width of particle size distributions changes considerably from one polymer to the other. The particle size distribution of the elastomer droplets is presented in Fig. 6.3 for the two grades of Fig. 6.2 to demonstrate this statement.

![Figure 6.2](image1)

*Figure 6.2*  
Heterogeneous structure of two of the HIPS polymers used in the experiments. Typical morphologies; a) HIPS86, b) HIPS65

Besides average size, we determined the most frequent particle size as well and use it in further evaluation. The amount of embedded polystyrene can be deduced from measured moduli with the help of the modified Kerner or Lewis-Nielsen model [13]. We carried out these calculations; the resulting values are compiled in the last column of Table 2.4. One can see that similarly to elastomer content and size, the amount of embedded PS also changes in a wide range and it does not always correlate with butadiene content. As the information presented above shows, the structure of the HIPS grades used in our experiments differs considerably and butadiene content, particle size, embedded polystyrene all might influence both the functional and the application properties of desiccant composites.

The permeation characteristics of polymers depend mainly on their specific free volume as proved by Lee [14] and our own experiments (see Chapter 3). In the case of desiccant composites the diffusion of water is the most important functional characteristic. The water vapor transmission rate of our HIPS samples is listed in the last column of Table 2.3. Although the values are relatively large (a value of 3.6 g 20 μm/m²/24 h was measured for HDPE), they still change considerably. The correlation of WVTR with the elastomer content of the polymers is plotted in Fig. 6.4. The correlation is relatively close, but one value deviates from the general tendency again. We can conclude that the diffusion of water in the polymers is influenced by butadiene content, but other structural parameters may play a role as well, thus we expect them to affect also the desiccant characteristics of the composites.
Figure 6.3  Size distribution of dispersed polybutadiene droplets in the polymers of Figure 2. Symbols: (○) HIPS65, (□) HIPS86

Figure 6.4  Correlation between the water vapor transmission rate of HIPS polymers and their butadiene content
6.2.2. Composite properties

Besides water adsorption desiccant composites should meet other conditions of their specific application as well. Requirements usually include properties related to processing, but also stiffness, strength and toughness. The two main variables in our study are zeolite and butadiene content thus we check their effect on some of the mechanical properties of the composites. We refrain from their detailed discussion and in the next section focus on functional properties instead.

The stiffness of the composites is plotted against zeolite content in Fig. 6.5. Modulus increases with increasing zeolite loading, but the correlations for the composites prepared with HIPS matrices run below that of homopolymers. The elastomer content of the copolymers obviously decreases stiffness, but we obtain two correlations for the seven polymers, and the differences in modulus do not correspond to elastomer content. Composites prepared with HIPS86 and HIPS120 as matrix possess the smallest stiffness. Already the abbreviation of the polymers shows that the first has 8.6, while the second 12.0 vol% butadiene content. HIPS grades with elastomer content smaller and larger than 8.6 vol% equally belong to the other correlation. Besides elastomer content some other factor must also influence modulus and the mechanical properties of our desiccant composites, generally. In order to explain the phenomenon we must assume that besides PS inclusions also zeolite particles are embedded into the elastomer droplets. Embedding was shown to be the thermodynamically preferred structure in multicomponent polymer systems [15], thus we may expect embedding in HIPS/zeolite composites as well. Embedding decreases apparent filler content and increases that of the elastomer thus leading to decreased stiffness.

Obviously not only elastomer content, but some other factor also influences the extent of embedding. This other factor can be the particle size of the dispersed elastomer droplets; HIPS86 and HIPS120 have the average particle size of 2.6, and 2.4 μm respectively, by far the two largest of all the grades used. This result clearly proves that besides elastomer content particle size also influences composites properties. The extent of embedding and its dependence on zeolite content as well as on the characteristics of HIPS composites need further considerations and study.

These conclusions are further corroborated by Fig. 6.6 in which we plotted the Young's modulus of the composites against the butadiene content of the matrix polymer. Stiffness decreases with elastomer and increases with zeolite content as discussed above. Elastomer content dominates at small zeolite content; the deviation from the general tendency is small. However, the deviation of individual values increases with increasing silicate content further confirming our conclusion about the role of embedding in the determination of composite stiffness. Earlier experience with multicomponent materials clearly showed that the extent of embedding increases with increasing filler content [16].
Figure 6.5  Effect of zeolite content on the Young's modulus of desiccant composites. Symbols: (□) PS1, (◇) PS2, (○) HIPS67, (△) HIPS86, (▽) HIPS98, (◁) HIPS47, (▷) HIPS65, (●) HIPS120, (●) HIPS104

Figure 6.6  Influence of zeolite and butadiene content on the stiffness of desiccant composites. Symbols: (□) 10, (○) 30, (△) 50 vol% zeolite
Besides stiffness another important application property of desiccant composites is tensile strength that we plotted against zeolite content in Fig. 6.7. Only selected composites are presented in the figure in order to facilitate viewing. The correlations shown represent typical behavior. The strength of PS composites decreases with increasing zeolite content, while that of HIPS composites increases in smaller or larger extent. The reason for the difference is the dissimilar inherent property of the matrix and its load bearing capacity. Elastomer droplets with small modulus cannot carry much load during deformation thus the tensile strength of HIPS polymers decreases with increasing elastomer content. However, the reinforcing effect of fillers increases with decreasing stiffness of the matrix [17]. The load bearing capacity of the droplets increases also with embedding, since their modulus and strength is increased by the incorporation of the stiff zeolite particles. The combination of HIPS with zeolite is obviously beneficial for the application properties of desiccant composites.

![Tensile strength graph](image)

**Figure 6.7** Tensile strength of the desiccant composites plotted against their zeolite content. Symbols: (□) PS1, (△) HIPS86, (●) HIPS120, (○) HIPS104

6.2.3. Functional properties

The capacity and rate of water adsorption are the most important characteristics of desiccant composites. Capacity depends mainly on zeolite content earlier (Chapter 3 and 4), while rate on the free volume of the polymer (Chapter 3). The question remains, whether butadiene content and the complex structure of HIPS influence these functional properties of desiccant composites. The maximum capacity of water adsorption ($M_\infty$) is plotted against zeolite content for the composites prepared with all PS and HIPS matrices in Fig. 6.8. $M_\infty$ was determined by fitting Eq. 3.1 to experimental water adsorptions.
values just as before (Chapter 3 and 4). The correlation is unambiguous; adsorption capacity is dominated by the amount of zeolite added. The effect of other parameters, if it exists at all, cannot be seen in the figure.

![Graph showing the effect of zeolite content on water adsorption capacity](image)

**Figure 6.8** Effect of zeolite content on the water adsorption capacity ($M_\infty$) of desiccant composites. Symbols are the same as in Figure 6.5

Water adsorption capacity is plotted against the butadiene content of the HIPS matrix in Fig. 6.9 at three different zeolite contents. Quite surprisingly, capacity decreases with increasing elastomer content that is rather difficult to explain. Moreover, the decrease is faster at larger zeolite content and the deviation from the general trend seems to be also larger at larger silicate loading. These correlations indicate the effect of the embedding of the zeolite into the elastomer droplets and probably also that of particle size, but the main reason and mechanism are unclear and need further study and explanation.

The other important characteristic of desiccant composites is the rate of water adsorption. Faster rate is usually more advantageous in all applications. We can determine the overall (see Eq. 3.1) and the initial rate of adsorption (see Eq. 1.3), which depend dissimilarly on desiccant content (Chapters 1, 3 and 4). The overall rate of adsorption is plotted against zeolite content in Fig. 6.10 for selected composites; it decreases with increasing zeolite content, which was explained with the increase of diffusion path (Chapter 3). Fillers were shown to slow down diffusion through composites because of increasing tortuosity of the path [18]. Diffusion proceeds from the edges of the specimen thus particles located there are filled with water fast and water molecules must go around particles already saturated with water. The effect is enhanced for poly-
Effect of matrix characteristics

mers in which diffusion is fast. The deviation from the general tendency is large and it is even larger when all results are plotted. This clearly indicates the role of composition and structure (particle size, embedding) in the determination of the rate of diffusion.

Figure 6.9 Correlation between the butadiene content of HIPS polymers and the water adsorption capacity of desiccant composites. Symbols: (□) 10, (○) 30, (△) 50 vol% zeolite

Figure 6.10 Effect of zeolite content on the overall rate of water adsorption. Symbols: (□) PS1, (▽) HIPS98, (◇) HIPS47, (●) HIPS120, (●) HIPS104
The effect of these factors can be seen somewhat better when we plot the overall rate of diffusion against the elastomer content of the HIPS polymers (Fig. 6.11). Contrary to capacity, elastomer content clearly increases the rate of diffusion independently of zeolite content. The diffusion of small molecular weight substances is always faster in rubbery than in glassy polymers, thus the correlation seems to be evident. On the other hand, deviations from the general tendency indicate again the effect of additional factors, possibly that of particle size, particle structure (see Fig. 6.2) and embedding. The deviations here seem to be independent of zeolite content suggesting that apart from increasing the diffusion path, the desiccant does not influence diffusion much.

The detailed characterization of the HIPS grades used in these experiments showed that they differ considerably in butadiene content, but also in structure. Both the size of the dispersed butadiene droplets and the amount of embedded polystyrene cover wide ranges. The addition of the desiccant to HIPS further modifies its structure; at least a part of the desiccant is also encapsulated into the elastomer droplets. Although zeolite and elastomer content are the variables dominating both the functional and the application properties of our desiccant composites, other factors related to structure also influence them. One possible factor mentioned several times before is the particle size of the butadiene droplets. In order to check this possibility, we plotted all properties and characteristics against particle size as well. The relationship between composite strength and particle size is shown for three different zeolite contents in Fig. 6.12 as an example.

![Figure 6.11](image_url)  
Influence of polybutadiene content on the overall rate of water adsorption. Symbols: () 10, () 30, () 50 vol% zeolite
6.2.4 Discussion

Tensile strength seems to decrease with increasing size of the particles. Unfortunately, elastomer content also influences strength, as it was shown in Fig. 6.7, and the effect of the two factors cannot be separated. Obviously, we cannot confirm or deny the existence of a correlation between particle size and properties. However, in order to obtain some idea about the possible influence of the two factors, i.e. droplet size and elastomer content, we plotted them against each other in Fig. 6.13. A clear tendency exists between particle size and butadiene content, but the correlation is rather loose proving the influence of other parameters, like polymerization conditions, on particle size. Accordingly, also properties must be influenced by structural parameters, but the establishment of exact correlations needs further, more detailed experiments and analysis.

6.3. Conclusions

The experiments carried out with seven high impact polystyrenes and two PS homopolymers as reference showed that efficient desiccant composites can be prepared by using both types of polymers and zeolites. 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 content are the main factors determining 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. However, the determination of exact correlations between these structural parameters and properties needs further experiments and analysis.

Figure 6.13 Correlation between the size of dispersed polybutadiene droplets and butadiene content of HIPS polymers

6.4. References


Chapter 7

HIPS/zeolite hybrid composites: structure and functional properties

7.1. Introduction

HIPS prepared by suspension polymerization has a complicated, salami like structure consisting of a polystyrene matrix with dispersed polybutadiene droplets, which, on the other hand, contain small PS inclusions [1]. Adding a filler, like zeolite, to this material may increase the complexity of structure further. Multicomponent, hybrid materials have been prepared earlier, and in fact they are used extensively in industrial practice today [2-18]. The stiffness of polypropylene (PP), for example, is increased by adding a filler (talc, CaCO₃, short glass fibers), while its impact resistance is improved by the incorporation of an elastomer to produce bumper materials [19, 20]. Two boundary structures may develop in such materials; the components can be dispersed in the PP matrix separately from each other or the filler can be encapsulated by the elastomer to form embedded structure. The actual structure developing depends on the balance of adhesion and shear forces prevailing during the processing of the material [4]. Properties are determined by structure, composites with embedded morphology have smaller stiffness than those with the separate distribution of the components.

Structure development, and the relationship between structure and properties has not been studied much in PS or HIPS composites up to now; very few reports are available in the literature. Siengchin and Karger-Kocsis [17] observed embedded structure in PS/SBR/boehmite composites, while Chang et al. [18] controlled structure by the use of functionalized polymer. They prepared HIPS/elastomer/Mg(OH)₃ composites using SEBS or SEBS-g-MA to achieve separately distributed or embedded structure, respectively. However, no study has been done and results reported on HIPS/zeolite desiccant composites yet. The results obtained in the previous stage of the research (see Chapter 6) indicated the zeolite might be encapsulated in polybutadiene phase in HIPS/zeolite composites and this structure may influence properties. Therefore, the goal of our work was to investigate structure development in such composites, determine the extent of embedding, if it occurs, and find correlations between the structure and functional properties of the composites, if they exist. Seven different HIPS polymers with dissimilar butadiene content and dispersed particle size were used as matrices and a standard 4A type zeolite as desiccant in the study. The results obtained in the previous part (Chapter 6) were analyzed more in detail and the outcome is reported in this chapter.

5 Kenyó, C., Renner, K., Móczó, J., Kröhnke, C., Pukánszky, B.: HIPS/zeolite hybrid composites as active packaging materials: structure and functional properties, submitted to Composite Part A
7.2. Results and discussion

7.2.1. Thermodynamics

As mentioned in the introductory part the structure of multicomponent materials containing an elastomer and a filler is rather complex and two boundary structures, separate dispersion and encapsulation, may form in them during processing. Embedding is the more complicated of the two, since certain conditions must be fulfilled in order to form such an ordered structure. Zeolite particles and elastomer droplets must meet and collide, energy balance must be favorable and the formed structure must be stable and withstand the effect of shear. De-encapsulation was shown to occur in a considerable number of composites [21].

Physicochemical processes occur spontaneously only in cases when the energy balance is advantageous, the change in free energy is negative. Composite preparation and blending results in new surfaces which require surplus energy, thus the change of free energy is positive. The increase in free energy depends on the size of the contact surface and interfacial tension; both are different in the case of separate dispersion and during embedding. At constant volume surface energy can be related to surface tension in the following way

\[ U^S = A^S - T \left( \frac{\partial A^S}{\partial T} \right)_v = \gamma^S - T \frac{d\gamma}{dT} \]  

(7.1)

where \( U^S \) and \( A^S \) are the surface energy and surface free energy of a unit surface, respectively, and \( \gamma^S \) is surface tension. Eq. 7.1 is valid for gases and liquids for which complete reversibility can be assumed [22]. Nevertheless, we can use the equation for qualitative, comparative purposes and neglect the lack of complete reversibility in solids. The change in surface energy during structure formation is proportional to interfacial tension which can be calculated from the geometric mean correlation of Wu [23]

\[ \gamma_{AB} = \gamma_A + \gamma_B - 2\left(\gamma_A^d \gamma_B^d\right)^{1/2} - 2\left(\gamma_A^P \gamma_B^P\right)^{1/2} \]  

(7.2)

where \( \gamma_{AB} \) is interfacial tension, \( \gamma_A \) and \( \gamma_B \) are the surface tensions of the two materials in contact, and \( d \) and \( p \) stand for the dispersion and polar components of surface tension. The surface tension of the components are listed in Table 7.1. We can see that the surface energy of zeolite is much larger than that of the polymers with a significant polar component.

The knowledge of surface tension allows the calculation of interfacial tension according to Eq. 7.2 for both possible cases. In the case of separate dispersion PS/PB and PS/zeolite surfaces must be considered, while PS/PB and PB/zeolite surfaces form when embedding occurs. The calculations were carried out for the composition of 20 vol% zeolite and 10 vol% polybutadiene content. We assumed that in a unit volume of the composite the interface between the matrix and the filler equals to the surface area of the zeolite (average particle size is 4.0 \( \mu \)m) and that the average diameter of the elastomer is 1 \( \mu \)m (see Table 2.4). Furthermore, we assumed that the zeolite is covered only
on its outer surface by the elastomer, it does not penetrate into its pores. Finally, we neglected the PS inclusions inside the elastomer droplets during these model calculations. According to these calculations the surplus energy needed for the creation of new surfaces is 344.7 kJ/m$^3$ in the case of separate dispersion and 323.1 kJ/m$^3$ for embedding. The difference is 21.6 kJ/m$^3$ in favor of embedding, i.e. the embedded structure is energetically favored like in several other cases [4, 24, 25]. Accordingly, we must expect the encapsulation of zeolite within the elastomer thus resulting in a complex morphology, since exclusive structures have never been observed before even when functionalized polymers were used to promote one structure or the other [5-7, 10, 26-29].

The occurrence of embedding and its effect on properties are discussed in the following sections.

Table 7.1  
Surface tension of the components used in the model calculations of structure development

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface tension (mJ/m$^2$)</th>
<th>$\gamma_S^d$</th>
<th>$\gamma_S^b$</th>
<th>$\gamma_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td></td>
<td>40.5</td>
<td>1.1</td>
<td>41.6</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td></td>
<td>32.9</td>
<td>5.0</td>
<td>37.9</td>
</tr>
<tr>
<td>Zeolite</td>
<td></td>
<td>181.9</td>
<td>440.9</td>
<td>622.8</td>
</tr>
</tbody>
</table>

7.2.2. Structure

The main question of structure formation is the occurrence and extent of embedding, as discussed above. Attempts can be made to check encapsulation with the help of electron microscopy [3, 7, 8], but sample preparation and especially interpretation are not straightforward. A much better indication of embedding is the decrease of stiffness. Filler particles embedded into the elastomer extend the volume of the latter, i.e. they act like elastomer droplets and decrease stiffness. The phenomenon is demonstrated in Fig. 7.1 in which the Young's modulus of two series of composites is plotted as a function of zeolite content. Two lines are also added to the figure; the upper one corresponds to the separate dispersion of the components, while the lower one to complete embedding. The stiffness of the two series prepared with the HIPS120 and HIPS104 matrices, respectively, is located between the two boundary lines indicating certain, but not complete embedding.

The extent of embedding can be deduced from deviation from the boundary cases; Fig. 7.1 shows that it is larger for the HIPS120 than for the other material plotted. Obviously, larger butadiene content and larger size of the dispersed elastomer droplets favor embedding (see Table 2.4). The extent of embedding can be calculated with the help of appropriate models. In the case of separate dispersion the composition dependence of Young’s modulus, $E(\phi)$, can be expressed by the extension of the Kerner-Nielsen equation [30]
where $E_m$ is the modulus of the matrix polymer, $\phi_f$ and $\phi_e$ are the volume fraction of the zeolite and the elastomer, respectively. $A_f$ and $A_e$ take the form

$$A_f = \frac{7 - 5 \nu_m}{8 - 10 \nu_m} \quad \text{and} \quad A_e = \frac{8 - 10 \nu_m}{7 - 5 \nu_m}$$

(7.4)

where $\nu_m$ is the Poisson’s ratio of the neat matrix. Parameter $B_f$ and $B_e$ can be calculated as

$$B_f = \frac{E_f / E_m - 1}{E_f / E_m + A_f} \quad \text{and} \quad B_e = \frac{E_m / E_e - 1}{E_m / E_e + A_e}$$

(7.5)

$\Psi$ is a correction factor accounting for the maximum packing fraction ($\phi_{\text{max}}$) of the inclusion and it takes the same form for the filler and the elastomer

$$\Psi_f = 1 + \left( \frac{1 - \phi_{\text{max}}}{\phi_{\text{max}}^2} \right) \phi_f$$

(7.6)

Figure 7.1 Young’s modulus of HIPS desiccant composites plotted as a function of zeolite content. Indication of embedding. Symbols: (○) HIPS120, (□) HIPS104; the upper and lower continuous lines represent the boundary structures of separate dispersion and complete embedding, respectively
Naturally always the appropriate volume fraction and $\varphi_{\text{max}}$ value must be introduced into Eq. 7.6. Deviation of measured stiffness from the one calculated for separate dispersion (see corresponding line in Fig. 7.1) allows the calculation of the volume fraction of embedded particles. The parameters used in the calculations are collected in Table 7.2. The Poisson's ratio of neat PS was taken as 0.34 and its modulus as 3.2 GPa. During the calculation and analysis we ignored the amount of PS particles embedded already within the elastomer droplets, since the actual value of matrix stiffness takes it into account.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Zeolite</th>
<th>Polybutadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus, $E$ (GPa)</td>
<td>25.0</td>
<td>0.002</td>
</tr>
<tr>
<td>Parameter $A$</td>
<td>1.152</td>
<td>0.868</td>
</tr>
<tr>
<td>Parameter $B$</td>
<td>0.760</td>
<td>0.999</td>
</tr>
<tr>
<td>Maximum packing fraction, $\varphi_{\text{max}}$</td>
<td>0.70</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The extent of embedding was calculated for all the composites prepared and it is plotted against butadiene content at three different zeolite contents in Fig. 7.2. The extent of embedding decreases with increasing zeolite content non-linearly as shown by the figure. The compositions plotted were selected accordingly. The tendency shown is easy to understand since the amount of elastomer is limited, it has a certain capacity to embed zeolite particles. At small zeolite and comparatively large polybutadiene content the probability of encapsulation is large. The figure clearly shows also that embedding increases with increasing elastomer content that also seems to be evident. The effect of elastomer content diminishes with increasing zeolite content probably due to the saturation of the droplets by zeolite particles.

However, some other factor or factors also influence the extent of embedding shown by the position of the HIPS67 matrix, in which embedding is relatively small. This other factor might be the particle size of the elastomer droplets. The extent of embedding is plotted against this variable in Fig. 7.3. A tendency exists indeed, but some deviating points can be observed again. HIPS65 has the smallest particle size and relatively small butadiene content, but the extent of embedding is relatively large in it, while HIPS67 has practically the same elastomer content and larger size, still embedding is very small. Further study and analysis is needed to reveal the reason for the deviations from the general tendency and to find the parameters determining the extent of embedding.
Figure 7.2  *Effect of zeolite and polybutadiene content on the extent of embedding in HIPS/zeolite desiccant composites. Symbols: (○) 10, (□) 20, (△) 50 vol% zeolite*

Figure 7.3  *Dependence of the extent of embedding on the size of the dispersed polybutadiene particles. Symbols: (○) 10, (□) 20, (△) 50 vol% zeolite*
7.2.3. Properties

We established in the previous sections that embedding is thermodynamically favored and really occurs in the HIPS/zeolite composites prepared in the study. The questions remains about the effect of structure on the application and functional properties of the composites. Young’s modulus is plotted against the extent of embedding in Fig. 7.4. A clear effect is seen, stiffness decreases considerably with increasing extent of embedding. However, the correlation must be treated with caution, since the extent of embedding depends also on zeolite content (see Figs. 7.2 and 7.3), thus Fig. 7.4 is biased by this dependence. Nevertheless, the effect of embedding exists and can be seen clearly if we compare the various polymers at the same zeolite content; modulus decreases with increasing extent of embedding indeed and the effect is stronger at larger filler content.

![Figure 7.4](image)

**Figure 7.4** Influence of the extent of embedding on the stiffness of HIPS/zeolite desiccant composites. Symbols: (○) 10, (□) 20, (△) 30, (◇) 40, (△) 50 vol% zeolite

A similar, but less strong and clear correlation is obtained if we investigate the dependence of tensile strength on the extent of embedding (Fig. 7.5). Deviations from the general tendency are larger than for stiffness, but tensile strength clearly decreases with increasing extent of embedding. We must also mention here that deformability increases slightly at the same time (not shown), which might be advantageous for several applications since it increases the fracture resistance of the material.
The effect of embedding on application properties is more advantageous than not, but encapsulation may influence functional properties, i.e. the capacity and rate of water adsorption as well. We have shown in previously (Chapter 3, 4 and 6) that the main factor determining the water adsorption capacity of polymer/zeolite composites is their desiccant content; capacity increases linearly with the amount of zeolite used. The capacity of water adsorption is plotted against the extent of embedding in Fig. 7.6. The correlation is strongly biased again by changing zeolite content. A closer scrutiny of values measured at the same zeolite loading reveals that embedding practically does not influence the water adsorption capacity of the desiccant composites studied.

The rate of water adsorption was determined by the measurement of weight as a function of time in an atmosphere of 100 % relative humidity. The results were fitted with models assuming Fickian diffusion (see Eq. 1.3 and Eq. 3.1). The overall rate of adsorption is plotted again the extent of embedding in Fig. 7.7 and it decreases with increasing zeolite content in accordance with earlier observations (Chapter 3, 4 and 6). This composition dependence was explained by the increase of diffusion path with increasing desiccant content. However, if we disregard the effect of zeolite content we do not see any clear tendency as a function of embedding. On the other hand, some factor or factors influence the overall rate of water adsorption significantly, since relatively large scatter is observed within each group of values at the same zeolite content. These factors might be butadiene content, particle size or even the extent of embedded PS.
Figure 7.6  Effect of the extent of embedding on the water adsorption capacity of HIPS/zeolite composites. Symbols: (○) 10, (□) 20, (▽) 30, (◇) 40, (△) 50 vol% zeolite

Figure 7.7  Loose correlation between the overall rate of water adsorption and the extent of embedding in HIPS/zeolite desiccant composites. Symbols: (○) 10, (□) 20, (▽) 30, (◇) 40, (△) 50 vol% zeolite
The initial rate of water adsorption, on the other hand, changes differently, it increases with increasing zeolite content (Fig. 7.8). The effect of embedding is somewhat smaller, but exists, diffusion rate decreases with increasing extent of encapsulation. This can be seen especially well if we follow the tendency at 30 vol% desiccant content (\(\triangle\)). The explanation for the decreased initial rate of water adsorption is not evident at all. Butadiene is an elastomer with low glass transition temperature and large mobility of the molecules at room temperature. The rate of diffusion is large in such materials, since the rate determining process is diffusion through the matrix PS. We might assume that the elastomer molecules penetrate the pores of the zeolite, but this is not very probable and we do not have any evidence for it. A further, more detailed study is needed to reveal the reason for the decrease in the initial rate of water adsorption with increasing extent of embedding.

![Figure 7.8](image)

**Figure 7.8** Influence of the extent of embedding and zeolite content on the initial rate of water adsorption in HIPS/zeolite desiccant composites. Symbols: (○) 10, (□) 20, (\(\triangle\)) 30, (◇) 40, (△) 50 vol% zeolite

### 7.3. Conclusions

Desiccant composites were prepared from seven high impact polystyrenes with different butadiene contents and dispersed droplet sizes and a 4A type zeolite in a wide range of desiccant contents. Thermodynamic analysis of structure development revealed that the embedding of the zeolite into the polybutadiene droplets is the thermodynamically favored process. Comparison of composite stiffness to theoretically predicted values indicated that considerable embedding occurs during composite preparation. The extent of embedding depends on zeolite content, but also on other factors like butadiene
content and the droplet size of the elastomer. Further unidentified factors also influence the extent of embedding. Composite stiffness and strength decreases with increasing extent of embedding. Functional properties are dominated by zeolite content. The water adsorption capacity of HIPS/zeolite desiccant composites depends almost exclusively on zeolite content. The initial rate of water adsorption increases, while the overall rate decreases with increasing desiccant loading. Embedding influences only the initial rate of water adsorption which decreases slightly with increasing extent of encapsulation. The influence of embedding is slightly favorable for application properties, while embedding practically does not affect functional properties thus HIPS is a very advantageous matrix for the production of desiccant composites.

### 7.4. References


Chapter 8

Decreased oxygen permeability of EVOH through molecular interactions

8.1. Introduction

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 N,N’-bis(2,2,6,6-tetramethyl-4-piperidyl)-isophthalamide (Nylostop SEED), which was originally developed for the protection of pigmented polyamides against light induced decomposition. The additive proved to be also 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. EVOH containing the additive in a relatively wide composition range was produced and various properties were determined in the study. A detailed analysis of structure and interactions is presented in this chapter to shed light onto the reason of the observed effects and correlations.

8.2. Results and discussion

8.2.1. Properties

The main hypothesis of the project was that similarly to PA Seed will nucleate also EVOH, increase crystallinity and oxygen permeability decreases as an effect. The OTR of films is plotted against additive content in Fig. 8.1. Permeability decreases at small Seed concentrations as expected, but increases considerably at larger additive contents. The initial decrease seems to be small, but it is approximately 30 %, which is more than any effect achieved by blending and only slightly smaller than the decrease resulting from the use of layered silicates (~50 %), but without the disadvantageous effect of the latter. We may conclude as a result that the additive influences oxygen permeability indeed, but the reason for the effect must be identified with further study. Changes in other properties and the analysis of structure should offer more information about the mechanism and origin of the effect. The increase in permeability at large additive content merits further considerations as well. If nucleation and changes in crystalline structure result in the improvement observed, one would expect a saturation effect, OTR remaining constant at large SEED contents. Obviously, some other, probably

---

structural changes lead to the minimum in the OTR vs. additive content correlation resulting from the superposition of two different effects.

![Graph showing the effect of additive content on OTR](image)

**Figure 8.1  Effect of Seed content on the oxygen permeation of EVOH films**

The influence of the additive on the Young’s modulus of the polymer is presented in **Fig. 8.2**. The results strongly corroborate our preliminary assumption, stiffness increases with increasing additive content presumably because of increasing crystallinity and probably larger lamella thickness [5]. Similarly to OTR, two stages can be observed in the composition dependence of Young’s modulus as well. Stiffness increases quite steeply at small and somewhat more moderately at larger additive contents, above 1.5–2.0 wt%.

Ultimate tensile properties are presented as a function of additive content in **Fig. 8.3**. The changes in tensile strength agree more or less with the results presented in **Figs. 8.1 and 8.2**, i.e. strength increases considerably at small additive contents. On the other hand, the composition dependence of deformability seems to contradict our initial assumption. Changing crystallinity leading to larger stiffness usually results in decreased deformability and not to increased elongation-at-break. Simultaneous increase of strength and deformability often indicates changing structure, like physical or chemical cross-linking or decreased crystallinity. Moreover, the maximum in both quantities hints also to further structural changes, to the probability of phase separation caused by the limited solubility of the additive in the polymer. A heterogeneous, two-phase structure with weak interfacial interaction of the phases could result in the decrease of strength and deformability at large additive content.
Figure 8.2  Dependence of the stiffness of EVOH plates on additive content.

Figure 8.3  Ultimate tensile properties of EVOH plotted against Seed content. Symbols: (○) tensile strength, (□) elongation-at-break.
8.2.2. Structure

The modulus of crystalline polymers is determined mainly by crystallinity and the thickness of the lamella grown during crystallization [5]; lamella thickness increases with increasing crystallization temperature, thus also with nucleation [6, 7]. The heat of fusion proportional to crystallinity is plotted against additive content in Fig. 8.4. Rather surprisingly crystallinity does not increase, but decreases with increasing additive content. The detailed analysis of the DSC traces recorded in the two heating and the cooling run indicated that Seed does not nucleate EVOH. All quantities related to crystallinity (heat of fusion, heat of crystallization) decreased with increasing additive content, the melting temperature was constant in both heating runs and the temperature of crystallization also decreased as Seed content increased. These results clearly indicate that the decrease in OTR as an effect of the additive is not caused by changing crystalline structure, but by some other factor or factors.

Figure 8.4  Effect of additive content on the crystallinity ($\Delta H_{m1}$) of EVOH

XRD spectra were also recorded and analyzed in order to confirm the modification of crystalline structure. The traces are presented in Fig. 8.5 for selected compositions. Crystal form does not change at small additive content, but new peaks appear on the traces above 2.5 wt% Seed content. Possible changes in crystallinity cannot be deduced from the traces in this form, but their quantitative analysis by the approach of Brückner [2] allowed the determination of crystallinity, which is plotted against additive content in Fig. 8.6.
The correlation is practically identical to the one presented in Fig. 8.4, and plotting the two quantities, i.e. the heat of fusion and crystallinity determined by XRD, against each other yielded a straight line with negligible scatter (not shown). These results further confirm that crystallinity does not increase, but decreases as an effect of the additive, this latter does not nucleate EVOH and the changes observed in properties are caused by another factor, probably by interactions.

Figure 8.5 XRD traces of EVOH containing various amounts of Seed additive
8.2.3. Solubility

The extremes in Figs. 8.1 and 8.3 indicated the modification of structure, which cannot result from changing crystallinity, since it decreases monotonously with increasing additive content. A possible reason might be phase separation, the limited solubility of the additive in the polymer. A further indication for the existence of separate phases was supplied by the XRD traces presented in Fig. 8.5. Above 2.5 wt% Seed content new peaks appear in the traces, which correspond to certain reflections of the additive. Obviously, the additive is present as a separate phase in crystalline form at these concentrations.

Changes in the optical properties of polymers may also reveal phase changes. Crystalline units as well as dispersed particles are often large enough to interfere with visible light and this interference results in considerable haze that is often used for the characterization of the optical properties of plastic products. Haze is the total flux of light scattered within the angular range between 2.5 and 90° and normalized to the total transmitted flux [8]. Haze indicates changes in optical properties more sensitively than transparency, which is the fraction of incident light that passes through an object. The haze value of the plates containing different amounts of Seed is plotted as a function of composition in Fig. 8.7. The correlation is very interesting and clearly reveals all structural changes in the polymer as an effect of increasing additive content. Haze decreases at small additive concentrations due to decreasing crystallinity. At around 2 wt% Seed content haze starts to increase and reaches practically 100 % at the largest additive con-
tent because of phase separation and the presence of large dispersed particles. These changes agree well both with the XRD results (Fig. 8.5), but also with the changes in mechanical properties (Figs. 8.2 and 8.3).

![Figure 8.7](image)

**Figure 8.7**  *Effect of additive content on the haze of 1 mm thick EVOH plates*

8.2.4. Interactions

The functional groups of the additive and the hydroxyl groups of the polymer may develop relatively strong interactions. Molecular modeling by using the DFT approach showed that hydrogen bonds can form between the two substances indeed (see Fig. 8.8). The two compounds are in the lowest energy state when the hydroxyl group of the polymer and the carbonyl of the additive are at about 2 Å distance from each other which corresponds to the distance of hydrogen bonds. The energy of the interaction is 28 kJ/mol, which is relatively strong. The interaction should result in a shift of the corresponding absorptions bands in the infrared spectrum of the material.

The spectra are presented in Fig. 8.9 for selected additive contents in the range of the carbonyl vibration of the amide group (around 1650 cm\(^{-1}\)). A considerable shift can be observed at small additive contents, which seems to level out at larger amounts of Seed, but the spectra in Fig. 8.9 do not allow a more precise determination of band shifts. The results of quantitative analysis are shown in Fig. 8.10, in which the position of the carbonyl absorption is plotted against additive content. The absorption band shifts more than 10 cm\(^{-1}\) wavelength in the range of 0-2 wt% additive content and remains constant afterwards. The strong shift corroborates previous results and further justifies
the changes in structure and properties presented in previous sections. The results clearly prove that not crystalline structure, but interactions determine properties in the EVOH/additive system studied.

Figure 8.8  Formation of hydrogen bonds between EVOH and Seed; DFT modeling

8.2.5. Discussion

The control of oxygen permeation has strong practical relevance. EVOH is one of the polymers with the smallest oxygen permeation, but many attempts are made to improve barrier properties even further [9-12]. Most of these approaches failed to result in sufficient improvement in this property. Instead of blending or using fillers, we added a small molecular weight additive to EVOH to decrease oxygen permeation with positive results. Although the change in the targeted property is relatively small, it is significant. Contrary to our original assumption the additive, i.e. Seed, does not act as a nucleating agent, but the effect observed can be assigned to molecular interactions.

Both molecular modeling and FTIR spectroscopy proved that the –OH groups of the polymer and the amide groups of the additive strongly interact with each other and this interaction results in all the observed changes in properties. Because of interactions, crystallinity decreases somewhat, but the decrease does not result in smaller stiffness and strength. At small concentrations the additive dissolves in the amorphous phase of the polymer decreasing molecular mobility. Decreased mobility results in increased stiffness and strength, but also increased overall deformability due to the physical cross-link points created by hydrogen bonds. Smaller mobility and hydrogen bonds decrease also oxygen diffusion, the direct effect of which is clearly shown by Fig. 8.11.
Up to the solubility level a very close linear correlation exists between oxygen permeability and the shift in the position of the carbonyl absorption of the amide groups. Above the solubility limit, which is around 2.0 wt% the additive forms a separate phase. Phase separation leads to a maximum in ultimate tensile properties (Fig. 8.3), the appearance of new reflections in the XRD spectra (Fig. 8.5) and the deviation from the straight line in Fig. 8.11. The results prove strongly the effect of the additive on the structure and properties of EVOH and show a novel way to control oxygen permeation in such polymers.

Figure 8.9  Shift in the position of the carbonyl absorption of amide groups with increasing additive content
Figure 8.10  Effect of additive content on the position of the carbonyl absorption of amide groups

Figure 8.11  Direct correlation between oxygen permeation and molecular interactions (carbonyl shift); full symbols: below solubility level, empty symbols: separate additive phase
8.3. Conclusions

Poly(ethylene-co-vinyl alcohol) of 48 mol% ethylene content was modified with N,N’-bis(2,2,6,6-tetramethyl-4-piperidyl)-isophthalamide to decrease the oxygen permeability of the polymer even further. The results showed that oxygen transmission decreased considerably when the additive was added at less than 2.0 wt% concentration. The decrease resulted 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. Stiffness and strength, but also deformability increased as a result. 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.

8.4. References

Chapter 9

Summary

Functional and smart packaging materials develop with surprising rate and they represent the future of packaging in every respect. They meet the demand of industry and the public and make the packaging of certain wares safer or better. Although the use of active packaging is industrial practice already, relative limited information is available on basic correlations, on the factors determining the desired functions. Such correlations would make possible the improvement of efficiency and/or the decrease of price. Süd Chemie and its affiliate AirSec SAS are involved in the production of active packaging materials for the pharmaceutical and the electronic industry. Their profound interest is to obtain as much basic knowledge about these materials as possible in order to improve the quality of their existing products or to develop new ones. Since many of the functional packaging materials are based on heterogeneous polymer systems, four factors determine their properties: component characteristics, composition, structure and interfacial interactions. Our laboratory has extensive experience in this area and did considerable basic research on correlations related to these factors in the past. The four factors had to be upended only with the study of characteristics related to the given function. In this project, most of the research was done on desiccant composites controlling the humidity of the packaged ware, but experiments were carried out also on materials with good oxygen barrier characteristics. The combined experience of the two partners in the practical and theoretical side of the problem led to interesting results most of which are presented in this Thesis. Although we summarized the most important results at the end of each chapter, we briefly repeat them here to give a concise overview. At the end of this chapter we compile our most important new findings in a few thesis points.

The study of polymer/zeolite desiccant composites prepared with ten different matrices showed that the desiccant can adsorb considerable water in its free pores. 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. 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. 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. Fast adsorption can be achieved only with polymers having large free volume.

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 10 and 80 MPa. The deformability of most composites is small and decreases with increasing zeolite content. Interfacial adhesion between the matrix polymer and zeolite is not excessively strong.
although quantitative determination is hampered by various factors. Most of the composites fail by debonding thus debonding stress could be determined in cyclic loading and relaxation experiments. Brittle matrices fail 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.

The systematic study of five zeolites and their desiccant PS composites 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, zeolite characteristics influence the moisture adsorption of the polymer only marginally; adsorption capacity is determined by zeolite content, while the rate of adsorption 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. The dispersion of the zeolite is very good both in PS and in HIPS composites. Mechanical properties are excellent mainly because of the reasonable interfacial adhesion between the components. Because of their larger surface energy, composites containing X type zeolites have larger viscosity and they reinforce the polymer more than the A type desiccants. Matrix properties influence mainly application related properties, reinforcement and ductility is better in HIPS than in PS composites.

The experiments carried out with seven high impact polystyrenes and two PS homopolymers as reference showed that efficient desiccant composites can be prepared by using both types of polymers and zeolites. 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 content are the main factors determining 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.

Desiccant composites were prepared from seven high impact polystyrenes with different butadiene contents and dispersed droplet sizes and a 4A type zeolite in a wide range of desiccant contents. Thermodynamic analysis of structure development revealed that the embedding of the zeolite into the polybutadiene droplets is the thermodynamically favored process. Comparison of composite stiffness to theoretically predicted values indicated that considerable embedding occurs during composite preparation. The extent of embedding depends on zeolite content, but also on other factors like butadiene content and the droplet size of the elastomer. Composite stiffness and strength decreases with increasing extent of embedding. Functional properties are dominated by zeolite content. The water adsorption capacity of HIPS/zeolite desiccant composites depends almost exclusively on zeolite content. The initial rate of water adsorption increases, while the overall rate decreases with increasing desiccant loading. Embedding influences only the initial rate of water adsorption which decreases slightly with increasing
extent of encapsulation. The influence of embedding is slightly favorable for application properties, while embedding practically does not affect functional properties, thus HIPS is a very advantageous matrix for the production of desiccant composites.

Poly(ethylene-co-vinyl alcohol) of 48 mol% ethylene content was modified with N,N’-bis(2,2,6,6-tetramethyl-4-piperidyl)-isophthalamide to decrease the oxygen permeability of the polymer even further. The results showed that oxygen permeation decreased considerably when the additive was added at less than 2.0 wt% concentration. The decrease resulted 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. Stiffness and strength, but also deformability increased as a result. 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.

The most important conclusions of this Thesis can be summarized briefly in the following main points:

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 (3).

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 (3).

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 (4, 6).

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 (5).

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 (6).

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 fa-
vored 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 (7).

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 (8).
### List of symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>elongation-at-break (%)</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>correction factor accounting for the maximum packing fraction</td>
</tr>
<tr>
<td>$\gamma_A$, $\gamma_B$</td>
<td>surface tension (mJ/m$^2$)</td>
</tr>
<tr>
<td>$\gamma_{AB}$</td>
<td>interfacial tension (mJ/m$^2$)</td>
</tr>
<tr>
<td>$\gamma_S$</td>
<td>surface tension (mJ/m$^2$)</td>
</tr>
<tr>
<td>$\gamma_S^d$</td>
<td>dispersion component of the surface tension (mJ/m$^2$)</td>
</tr>
<tr>
<td>$\gamma_S^p$</td>
<td>polar component of the surface tension (mJ/m$^2$)</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>volume fraction of the filler in the composite</td>
</tr>
<tr>
<td>$\varphi_b$</td>
<td>volume fraction of bonded particles</td>
</tr>
<tr>
<td>$\varphi_e$</td>
<td>volume fraction of elastomer</td>
</tr>
<tr>
<td>$\varphi_{max}$</td>
<td>maximum packing fraction</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>relative elongation</td>
</tr>
<tr>
<td>$\nu_m$</td>
<td>Poisson’s ratio of the matrix</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>density of the filler (g/cm$^3$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>tensile strength (MPa)</td>
</tr>
<tr>
<td>$\sigma^D$</td>
<td>debonding stress (MPa)</td>
</tr>
<tr>
<td>$\sigma^D_C$</td>
<td>debonding stress (MPa) determined from cyclic loading</td>
</tr>
<tr>
<td>$\sigma^T$</td>
<td>thermal stress (MPa)</td>
</tr>
<tr>
<td>$\sigma_T$</td>
<td>true tensile strength of the composite (MPa)</td>
</tr>
<tr>
<td>$\sigma_{T0}$</td>
<td>true tensile strength of the matrix (MPa)</td>
</tr>
<tr>
<td>$\sigma_{red}$</td>
<td>reduced tensile strength</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>yield stress of the composite</td>
</tr>
<tr>
<td>$\sigma_{y0}$</td>
<td>yield stress of the matrix</td>
</tr>
<tr>
<td>$\sigma_{yi}$</td>
<td>yield stress of the interphase</td>
</tr>
<tr>
<td>$\sigma_{yred}$</td>
<td>reduced yield stress of the composite</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>free enthalpy of adsorption</td>
</tr>
<tr>
<td>$\Delta H_m$</td>
<td>heat of fusion (J/g)</td>
</tr>
<tr>
<td>a</td>
<td>overall rate of water adsorption (s$^{-1}$)</td>
</tr>
<tr>
<td>b</td>
<td>initial rate of water adsorption (s$^{-1/2}$)</td>
</tr>
<tr>
<td>c</td>
<td>concentration of the diffusing substance (mol/cm$^3$)</td>
</tr>
<tr>
<td>l</td>
<td>thickness of the interphase</td>
</tr>
</tbody>
</table>
List of symbols

n parameter characterizing the strain hardening of the matrix
r radius of particle (µm)
t time of adsorption (s)
v molar volume of the polymer (cm³)
v* free volume needed for diffusion (cm³)
v₀ occupied volume of the polymer (cm³)
v.sf free volume of the polymer (cm³)
x space co-ordinate measured normal to the surface
A, B independents of the concentration of the diffusing gas
Aᵣ specific surface area of fillers (m²/g)
AMP antimicrobial packaging
Aₛ surface free energy of a unit surface
ATR attenuated total reflection
B load bearing capacity of the dispersed phase
BHT butylated hydroxy-toluene
C₁, C₂ constant for the determination of debonding stress
CaCl₂ calcium chloride
CaCO₃ calcium carbonate
CaO calcium oxide
CaSO₄ calcium sulfate
CED cohesive energy density
CoPP poly(propylene-co-ethylene)
D diffusion coefficient (cm²/s)
DFT density functional theory
DMA dynamic mechanical analysis
DSC differential scanning calorimetry
E Young's modulus (GPa)
Eₑ Young's modulus of the composite
Eᵣ Young's modulus of the filler
Eₘ Young's modulus of the matrix polymer
EVOH ethylene-vinylalcohol copolymer
F rate of transfer per unit cross section (mol/cm²·s)
Fₐ adhesion strength (mJ/m²)
FTIR Fourier transform infrared spectroscopy
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALS</td>
<td>sterically hindered amine</td>
</tr>
<tr>
<td>HDPE</td>
<td>high-density polyethylene</td>
</tr>
<tr>
<td>HIPS</td>
<td>high impact polystyrene</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>IGC</td>
<td>inverse gas chromatography</td>
</tr>
<tr>
<td>K</td>
<td>equilibrium constant of adsorption</td>
</tr>
<tr>
<td>L</td>
<td>thickness of the sample (mm)</td>
</tr>
<tr>
<td>LDPE</td>
<td>low-density polyethylene</td>
</tr>
<tr>
<td>LLDPE</td>
<td>linear low-density polyethylene</td>
</tr>
<tr>
<td>M$_\infty$</td>
<td>water uptake reached after infinite time (%)</td>
</tr>
<tr>
<td>MFI</td>
<td>melt flow index (g/10 min)</td>
</tr>
<tr>
<td>Mg(OH)$_3$</td>
<td>magnesium hydroxide</td>
</tr>
<tr>
<td>MgA</td>
<td>Linde A type zeolite containing Mg$^{2+}$ cations</td>
</tr>
<tr>
<td>MgX</td>
<td>Linde X type zeolite containing Mg$^{2+}$ cations</td>
</tr>
<tr>
<td>MgY</td>
<td>Linde Y type zeolite containing Mg$^{2+}$ cations</td>
</tr>
<tr>
<td>M$_n$</td>
<td>number average molecular weight (mol/g)</td>
</tr>
<tr>
<td>M$_t$</td>
<td>time dependent weight increase (%)</td>
</tr>
<tr>
<td>M$_w$</td>
<td>weight average molecular weight (mol/g)</td>
</tr>
<tr>
<td>NaA</td>
<td>Linde A type zeolite containing Na$^+$ cations</td>
</tr>
<tr>
<td>NaX</td>
<td>Linde X type zeolite containing Na$^+$ cations</td>
</tr>
<tr>
<td>NaY</td>
<td>Linde Y type zeolite containing Na$^+$ cations</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>polyamide 6</td>
</tr>
<tr>
<td>Nylostab SEED</td>
<td>N,N’-bis(2,2,6,6-tetramethyl-4-piperidyl)-isophthalamide</td>
</tr>
<tr>
<td>OTR</td>
<td>oxygen transmission rate (cm$^3$/m$^2$/day)</td>
</tr>
<tr>
<td>P</td>
<td>permeability (cm$^3$ mm/m$^2$/24 h/bar)</td>
</tr>
<tr>
<td>PA</td>
<td>polyamide</td>
</tr>
<tr>
<td>PA 6</td>
<td>polyamide 6</td>
</tr>
<tr>
<td>PAN</td>
<td>polyacrylonitrile</td>
</tr>
<tr>
<td>PC</td>
<td>polycarbonate</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PEG</td>
<td>polyethylene glycol</td>
</tr>
<tr>
<td>PET</td>
<td>poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PETG</td>
<td>polyethylene-terephthalate glycol modified</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>PIPN-PS</td>
<td>polymer interpenetrating network – polystyrene</td>
</tr>
<tr>
<td>PLA</td>
<td>poly(lactic acid)</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl-methacrylate)</td>
</tr>
<tr>
<td>PMP</td>
<td>polymethylpentene</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
</tr>
<tr>
<td>PPO</td>
<td>polypropylene-oxide</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PVAc</td>
<td>polyvinyl-acetate</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinyl-chloride</td>
</tr>
<tr>
<td>PVDC</td>
<td>polyvinylidene-dichloride</td>
</tr>
<tr>
<td>R</td>
<td>universal gas constant (J/mol K)</td>
</tr>
<tr>
<td>Rh</td>
<td>relative humidity (%)</td>
</tr>
<tr>
<td>S</td>
<td>solubility (cm-mm/m²/bar)</td>
</tr>
<tr>
<td>SAN</td>
<td>styrene-acrylnitrile copolymer</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TerPP</td>
<td>poly(propylene-co-ethylene-co-1-butene)</td>
</tr>
<tr>
<td>T_g</td>
<td>glass transition temperature (°C)</td>
</tr>
<tr>
<td>TGA</td>
<td>thermal gravimetry</td>
</tr>
<tr>
<td>U_s</td>
<td>surface energy of a unit surface</td>
</tr>
<tr>
<td>V_t</td>
<td>volume of the pores</td>
</tr>
<tr>
<td>W_AB</td>
<td>reversible work of adhesion (mJ/m²)</td>
</tr>
<tr>
<td>WVTR</td>
<td>water vapor transmission rate (g 20 μm/m²/24 h)</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
I would like to express my sincere gratitude to my supervisor, Béla Pukánszky for his patience, guidance and support provided throughout this study. I should also thank to my friend and colleague, Károly Renner for his immeasurable endurance that gave me the strength to go along this long road and also to Christoph Kröhnke, who initiated all the research from this Thesis was built up. I would like to thank all my friends and colleagues at the Laboratory of Plastics and Rubber Technology at Budapest University of Technology and Economics and the associated Polymer Physics Research Group at the Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, HAS for creating a friendly, creative atmosphere, it was always a pleasure to work there with them. I am grateful for my students: Dóra Andrea Kajtár, Zsófia Péter, Petra Rácz, Sándor Zsolt Somogyi and Ádám Gyürki for the work we had done and the great time we had spent together. I highly appreciate the financial support of the National Scientific Research Fund of Hungary (OTKA Grant No. K 101124 and K 108934) and also to the former Süd-Chemie AG, today Clariant, Business Unit Masterbatches on functional packaging materials. Most profound thanks to my family and my closest friends: it would be very hard to accomplish my PhD work without their encouragement and love.
List of publications

Papers used for the preparation of the Thesis


Other publications


**Conference presentations**


Nyilatkozat

Alulírott Kenyó Csaba kijelentem, hogy ezt a doktori értekezést magam készítettem és abban csak a megadott forrásokat használtam fel. Minden olyan részt, amelyet szó szerint, vagy azonos tartalmban, de átfogalmazva más forrásból átvettem, egyértelműen, a forrás megadásával megjelöltem.


Kenyó Csaba