Doctoral Thesis

Polyethylene-layered silicate nanocomposites

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Polyethylene-Layered Silicate Nanocomposites

Dissertation
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Eidgenössische Technische Hochschule Zürich
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Doctor of Sciences

presented by
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Dr. Maged A. Osman, co-examiner

2004
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Publications

Results based on this study are about to be published or were already presented:

Poster:

Polymer Clay Nanocomposites, with H.-R. Lusti and V. Mittal, presented at the NanoConference 2003, St. Gallen

Articles:

Tensile Properties of Polyethylene-Layered Silicate Nanocomposites, with M.A. Osman and U.W. Suter; in preparation

Barrier Properties of Polyethylene-Layered Silicate Nanocomposites, with M.A. Osman and U.W. Suter; in preparation

Oxygen barrier and mechanical properties of polyethylene layered silicate nanocomposites containing additives at low concentrations, with M.A. Osman and U.W. Suter; in preparation

Influence of the chemical constitution of the SAM on montmorillonite on the properties of polyethylene clay nanocomposites, with M.A. Osman and U.W. Suter; in preparation
Abstract

The focus of this thesis is nanocomposites of high-density polyethylene and layered silicates. The surface of montmorillonite was modified to improve its dispersion in HDPE using different approaches. The barrier and tensile properties of the new materials was analyzed. The results were compared with those reported in the literature. In order to explain the macroscopic behavior, the morphology was examined using SEM, TEM and WAXD.

The properties of nanocomposites presented in this thesis surpass those reported in the literature. The largest improvement was obtained for composites with densely packed monolayers on the surface of the filler and for those containing small amounts of polyethylene-block-polyethylene glycol. We found that the pretreatment of the filler before compounding has a strong influence on its state of dispersion in the polymer matrix. The crystallinity of the polymer did not change significantly in the composites compared to neat HDPE. The mineral was aligned in the composite on micrometer scale, but had no preferential orientation on nanometer scale. Coexistence of delaminated silicate layers and stacks was observed for the composites without copolymer additive. Intercalated and exfoliated clay was noticed when copolymers were used as additive.

In each of the four sections of chapter 4 (Results and Discussion), one synthesis approach is discussed. In section 4.1 the packing density of the alkyl chains in the monolayer on the montmorillonite and the surface coverage was varied. Layered silicates with different cation exchange capacities were used and modified with organic cations containing one to four octadecyl chains. The tensile modulus and oxygen permeability coefficient were improved by up to 40% at a mineral volume fraction of 0.028. A correlation between the basal-plane spacing of the filler and the material properties was found. The tensile modulus and oxygen barrier for the synthesized systems were related to each other. The filler concentration dependence of the oxygen permeability was as predicted by theory, although the absolute values did not reach the improvement anticipated by theory, probably due to misalignment and incomplete delamination.

The influence of chemically different surface modifications of the filler was studied in section 4.2. It was found that aromatic groups have a negative influence on the barrier properties. With 2.8 vol% inorganic filler content, the best enhancement achieved was 30% and 35% for tensile modulus and oxygen permeability, respectively.

The approach in section 4.3 was to attach macromolecules to the filler surface via polymerization reaction. Layered silicates carrying vinyl groups on the surface
were used for *polymerization to the surface*. For *polymerization from the surface*, an initiator was attached to the mineral surface. Polymerization reactions of ethylene, octene and styrene were carried out in the presence of the modified montmorillonite. The properties of the nanocomposites containing these fillers did not exceed those with layered silicates modified by cation exchange.

In the last section of *Results and Discussion*, the influence of the addition of small amounts of copolymers was studied. Random copolymers generally improved the gas barrier but the tensile properties deteriorated, compared to the corresponding composite without copolymer. However, the addition of polyethylene-*block*-polyethylene glycol improved both the gas barrier and the tensile modulus. For 6.9 wt% copolymer and 2.8 vol% mineral, the enhancement was close to 60% for both properties. A higher degree of delamination compared to the composite without polymer additive could be observed.
Zusammenfassung


Der Einfluss von chemisch verschiedener Oberflächenmodifikation des Füllstoffs wurde in Abschnitt 4.2 untersucht. Ein negativer Einfluss von aromatischen Gruppen auf die Barriereeigenschaften wurde beobachtet. Bei 2.8 vol% an-
organischen Füllstoffanteil war die maximale Verbesserung für das E-Modul 30% und für die Sauerstoffbarriere 35%.


1 Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>area of different components</td>
<td>$[m^2]$</td>
</tr>
<tr>
<td>BenzC16</td>
<td>benzylhexadecyldimethylammonium</td>
<td></td>
</tr>
<tr>
<td>BenzVinyl</td>
<td>(ar-vinylbenzyl)trimethylammonium</td>
<td></td>
</tr>
<tr>
<td>$c$</td>
<td>concentration</td>
<td>$[mol \cdot m^{-3}]$</td>
</tr>
<tr>
<td>$d$</td>
<td>thickness of the membrane</td>
<td>$[m]$</td>
</tr>
<tr>
<td>C18</td>
<td>trimethyloctadecylammonium</td>
<td></td>
</tr>
<tr>
<td>2C10</td>
<td>dimethylolodecylammonium</td>
<td></td>
</tr>
<tr>
<td>2C18</td>
<td>dimethyldioctadecylammonium</td>
<td></td>
</tr>
<tr>
<td>3C18</td>
<td>methyltrioctadecylammonium</td>
<td></td>
</tr>
<tr>
<td>3C8</td>
<td>methyltrioctylammonium</td>
<td></td>
</tr>
<tr>
<td>4C18</td>
<td>tetraoctadecylammonium</td>
<td></td>
</tr>
<tr>
<td>CEC</td>
<td>cation exchange capacity</td>
<td>$[\mu mol \cdot g^{-1}]$</td>
</tr>
<tr>
<td>$d$</td>
<td>membrane thickness</td>
<td>$[\mu m]$</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
<td>$[m^2 \cdot s^{-1}]$</td>
</tr>
<tr>
<td>$d_{001}$</td>
<td>basal-plane spacing</td>
<td>$[nm]$</td>
</tr>
<tr>
<td>DSC</td>
<td>dynamic scanning calorimetry</td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>tensile modulus</td>
<td>$[MPa]$</td>
</tr>
<tr>
<td>$E_c$</td>
<td>tensile modulus of different components</td>
<td>$[MPa]$</td>
</tr>
<tr>
<td>$F_i$</td>
<td>force acting on different components</td>
<td>$[N]$</td>
</tr>
<tr>
<td>HDPE</td>
<td>high density polyethylene</td>
<td></td>
</tr>
<tr>
<td>Im6</td>
<td>[4-(tert-butyldioxy)hexyl]trimethylammonium</td>
<td></td>
</tr>
<tr>
<td>$J$</td>
<td>flux</td>
<td></td>
</tr>
<tr>
<td>$\delta l_i$</td>
<td>deformation of different components</td>
<td>$[m]$</td>
</tr>
<tr>
<td>M680</td>
<td>montmorillonite Nanofil 757</td>
<td></td>
</tr>
<tr>
<td>M880</td>
<td>montmorillonite CloisiteNa$^+$</td>
<td></td>
</tr>
<tr>
<td>M900</td>
<td>montmorillonite Optigel CK</td>
<td></td>
</tr>
<tr>
<td>M1000</td>
<td>montmorillonite Optigel CMO</td>
<td></td>
</tr>
<tr>
<td>$m_i$</td>
<td>mass</td>
<td>$[g]$</td>
</tr>
<tr>
<td>$M_i$</td>
<td>molecular weight of compound $i$</td>
<td>$[g \cdot mol^{-1}]$</td>
</tr>
<tr>
<td>Mn</td>
<td>number molecular weight</td>
<td>$[g \cdot mol^{-1}]$</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
<td></td>
</tr>
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</table>
1 Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OM</td>
<td>organically modified montmorillonite</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
</tr>
<tr>
<td>P</td>
<td>permeability coefficient</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PE-MA</td>
<td>polyethylene-graft-(maleic anhydride)</td>
</tr>
<tr>
<td>P(E-MAA)</td>
<td>poly[ethylene-co-(methacrylic acid)]</td>
</tr>
<tr>
<td>P(E-VOH)</td>
<td>poly[ethylene-co-(vinyl alcohol)]</td>
</tr>
<tr>
<td>PE-PEG</td>
<td>polyethylene-block-polyethylene glycol</td>
</tr>
<tr>
<td>P from S</td>
<td>polymerization from the surface</td>
</tr>
<tr>
<td>4PhenyI</td>
<td>tetraphenylphosphonium</td>
</tr>
<tr>
<td>2Phytly</td>
<td>dimethylphytylammonium</td>
</tr>
<tr>
<td>$pO_2$</td>
<td>oxygen permeability coefficient</td>
</tr>
<tr>
<td>$P_{toS}$</td>
<td>polymerization to the surface</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$S$</td>
<td>solubility coefficient</td>
</tr>
<tr>
<td>$r_T$</td>
<td>transmission rate</td>
</tr>
<tr>
<td>SAM</td>
<td>self assembled monolayer</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>$t_L$</td>
<td>time-lag value</td>
</tr>
<tr>
<td>$\phi_i$</td>
<td>volume fraction</td>
</tr>
<tr>
<td>$\Phi_i$</td>
<td>weight fraction</td>
</tr>
<tr>
<td>$\psi_I$</td>
<td>amount of initiator on the surface</td>
</tr>
<tr>
<td>$\psi_V$</td>
<td>initial amount of vinyl groups on the surface</td>
</tr>
<tr>
<td>WAXD</td>
<td>wide-angle x-ray diffraction</td>
</tr>
<tr>
<td>x</td>
<td>distance</td>
</tr>
<tr>
<td>$\varepsilon_B$</td>
<td>strain at break</td>
</tr>
<tr>
<td>$\varepsilon_Y$</td>
<td>yield strain</td>
</tr>
<tr>
<td>$\sigma_B$</td>
<td>stress at break</td>
</tr>
<tr>
<td>$\sigma_Y$</td>
<td>yield stress</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>stress on different components</td>
</tr>
<tr>
<td>VDAC</td>
<td>vinylbenzyldimethyldecylammonium</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
</tr>
</tbody>
</table>
2 Introduction

2.1 General

Inorganic-organic hybrid materials have been the object of scientific research over decades [1, 2]. Montmorillonite filled polymers are enjoying renewed interest, following publications of Toyota on nylon clay nanocomposites [3–5]. By using modified organophilic layered silicate, they could delaminate the mineral into single sheets of one nanometer thickness. Within a short period of time, enhanced moduli [4, 6–8], strength [4, 6, 7], thermal stability [9–11], flame retardancy [12] and decreased gas permeability [13–15] of polymer layered silicate nanocomposites, which exceed those of conventional composites and unfilled polymers, have been reported. These improvements were achieved at low filler loading, due to the small interparticle distance, the high percentage of surface polymer and the high aspect ratio of the delaminated montmorillonite sheets.

![Diagram of layered silicate polymer composites](image)

Figure 2.1: Illustrations of the three model cases of nanocomposites.

In Figure 2.1 three simple, idealized model cases of clay composites are shown. On the right side, all sheets of the layered silicate are delaminated, also called exfoliated. This is the desirable case, where the maximum aspect ratio
is achieved and the highest improvement of the properties is expected. For completely exfoliated nanocomposites, no peak in wide angle x-ray diffraction (WAXD) can be observed, because ordered structure is no longer present and the distances between the single layers are too large. Certain conditions, particularly poor sample preparation and measuring techniques as well as low filler fractions, may also result in the absence of x-ray reflections, which may then be misinterpreted as complete exfoliation [14,16].

The drawing in the middle depicts the structure of an intercalated composite. The distance between the single sheets increases, but a short-range order survives. For this case an increase of the basal-plane spacing may be observed using WAXD. X-ray diffraction signals for basal-plane spacing greater than 5 nm are beyond the detection threshold of WAXD. In this case, small angle x-ray diffraction is an alternative.

On the left of Figure 2.1, a conventional composite is shown. The layers are neither delaminated nor intercalated and the filler is in the same state as it was before compounding.

In reality a hybrid of at least two of the model cases almost always is observed. Depending on which structure dominates, the properties are more or less enhanced.

2.2 Layered Silicates

The layered silicate used for this study, montmorillonite, is a 2:1 phyllosilicate. The structure of a 2:1 phyllosilicate is shown in Figure 2.2: it consists of two tetrahedral layers, with an octahedral layer in between. The base unit consists of two Si tetrahedrons, three Al octahedrons and again two Si tetrahedrons. The tetrahedrons and octahedrons, respectively, are connected with their edges, consisting of oxygen atoms. The oxygen can belong to the tetrahedrons as well as to the octahedrons. In montmorillonite, some aluminum Al$^{3+}$ cations in octahedron positions are substituted by magnesium cations Mg$^{2+}$ [17,18]. The charge is compensated by a counterion, usually alkali or alkali earth cations.

The thickness of a mineral layer is approximately 10 Å. The diameter of a single mineral crystal varies, between few nanometers and up to several micrometers. The number of exchangeable cations per formula unit is between 0.3-0.4 eq.. The cations of the layered silicates can be exchanged against other inorganic cations [19,20] or organic cations [20–22]. The cation exchange capacity (CEC) can be quantitatively determined via exchange with organic cations [23]. The area per cation varies between around 100 to 200 Å$^2$ for clay minerals with high and low CEC, respectively [21].
Montmorillonite in a pristine state consists of stacks of sheets with counterions in between. In water the mineral can be dispersed, separating the sheets completely, thus leading to high aspect ratio platelets of 1 nm thickness and diameters up to several hundred nanometers. In order to do so in an organic solvent or a polymer, the counterions are exchanged against organic cations, often ammonium derivatives. Such, the surface of the silicate is covered with a self-assembled monolayer (SAM). As the organic cations occupy more space than the sodium ion, the interlayer distance increases and the attraction forces between the sheets are reduced. Because the chemistry of the organic tails of the cations can be used to match the polarity of the matrix, the originally hydrophilic silicon oxide surfaces may change to hydrophobic [25,26]. The successful polymerization from the surface of mica via ionically bound initiators has been reported by Suter and coworkers [27–31]. In Figure 2.3 a scheme of a cation exchange with an ammonium derivative is shown. Several reports on the structure and morphology of such SAM’s have been published recently [24,26,32–36].

Due to their low prize, not only from the scientific, but also from the economical point of view, clay minerals as filler are interesting.
2.3 Polyethylene

Polyethylene is, with one third of the world plastic production, by far the most commonly employed polymer [37]. The world production of LDPE and LLDPE was 30 million tons in 2001 and is expected to increase till 2010 up to 45 million tons. For HDPE the world production was 23 million tons in 2001 and will reach 38 million tons in 2010 [38]. Polyethylene is not soluble in any solvent up to 60°C. Nevertheless it swells in aliphatic and aromatic hydrocarbons as well as in the halogenated derivates. In polar solvents on the other hand, like alcohols, ester and ketons, it does not swell. Polyethylene is inert against water, bases and acids, except strongly oxidizing acids.

High density polyethylene exhibits good thermal stability, water vapor barrier and a low glass-transition temperature, which makes it, in contrast to polypropylene, applicable for packaging frozen foods. HDPE is used mainly in packaging, besides some applications in construction [39]. In packaging
2 Introduction

Applications often laminates of different polymers are used. Each layer has a certain function, e.g. oxygen barrier, water vapor barrier, mechanical property or adhesion [37]. The different layers are bonded together via adhesion, coextrusion or extrusion coating [40]. Polyolefins act normally as water vapor or carrier layer. Improving the oxygen barrier and mechanical properties of polyolefins can save expensive processing as well as additional functional layers. Hence, HDPE is very attractive as a matrix for studying the barrier and mechanical properties of polymer layered silicate nanocomposites.

In general PE is synthesized with two fundamentally different methods. One is the polymerization under high pressure and the other under low pressure. The products differ in the degree of branching and as a consequence in crystallinity and density.

Low density polyethylene (LDPE) is obtained with the high pressure polymerization process. Because of strong branching of the main chain, the density is low: between 0.915-0.935 g/cm³ with a crystallinity between 40-50%. If ethylene is copolymerized with other olefins, in particular with butene and octene, the backbone branching of polyethylene synthesized under high pressure can be reduced significantly. Those copolymers are named LLDPE (Linear Low Density Polyethylene). The polymerization reaction for LDPE is carried out at 1400-3500 bar and 150-350°C and is initiated with oxygen or peroxides. Under these conditions ethylene is in its overcritical state and forms a homogeneous phase with polyethylene. The reaction is done continuously in a pipe reactor or in a stirring autoclave.

Polymerizing ethylene under low pressure leads to linear unbranched chains. The material has a crystallinity of 60-80% and a density of 0.95-0.965%, hence the name high-density polyethylene (HDPE). High molecular weight (HMW) HDPE has a molecular weight between 200 000 and 500 000 g·mol⁻¹, ultra high molecular weight (UHMW) HDPE has molecular weights of 300 000 to 20 000 000 g·mol⁻¹. The polymerization is carried out under a pressure of less than 60 bar and temperatures between 60 and 250 °C, using transition metal catalysts.

The method for polymerizing ethylene under high pressure was discovered in 1933 at ICI in England. The low pressure polymerization was patented in 1953 independently by Phillips Petroleum Co, Standard Oil of Indiana and K. Ziegler. For his research on polyethylene K. Ziegler received the Nobel prize in 1963 together with G. Natta for his work on polypropylene.
2.4 State of the Art

Since the Toyota publications [3–5] the field of layered silicate-polymer nanocomposites has received much attention in the literature [6,7,9–15]. Many synthesis strategies and names for the synthesis strategies have been proposed. Of these, the synthesis of clay polymer nanocomposites can be classified into four main processes [41]:

*Template synthesis*: This method is only applicable for water-soluble polymers, as the inorganic crystals are grown in an aqueous polymer solution. It is by far the method which is used fewest. The economic potential is rather small.

*Exfoliation-adsorption technique*: An organically modified clay is exfoliated to single layers in a solvent, in which the polymer is also soluble. The composite material is obtained by evaporation of the solvent or by precipitation of polymer and mineral. This technique has the advantage, that it is easier to obtain a homogeneous dispersion of polymer and layered silicate in solution. One big disadvantage, though is the excessive amount of solvent required. Water soluble polymers address this issue, but the water solubility criteria restricts the choice of polymer and the associated material properties as a result. Furthermore, the *exfoliation-adsorption technique* needs more processing steps compared to other preparation methods.

*In situ polymerization*: The layered silicate is swollen in the liquid monomer or a solution of it. The polymerization is carried out between and around the layers and can be initiated using common techniques. This method is only useful if the clay can be dispersed well in the reaction mixture. Two frequent problems with this method are, insufficient molecular weight of the polymer and small yield. It has also been reported, that exfoliated mineral layers of PE-nanocomposites synthesized by *in situ polymerization* collapsed during processing [42].

*Melt intercalation*: This requires no solvent, the polymer melt is mixed with the mineral in the molten state. The advantage of this method is that it can be implemented in common polymer processing, e.g. injection molding. In order to obtain reasonable results, positive interactions between polymer and mineral surface are necessary in addition to the usual control over process parameters such as shear field and temperature.

Polyethylene-layered silicate nanocomposites have been synthesized so far with all methods, except of the first one.

The first report on HDPE clay nanocomposites prepared with the *exfoliation-adsorption technique* was given by Jeon et al. [43]. Organically modified clay
was dissolved with HDPE in hot xylene and benzonitrile. The composite was obtained via precipitation in THF. Unfortunately, they didn't report the properties of the HDPE clay nanocomposite. Other work was carried out with toluene as a solvent at 170°C in an autoclave [44] and in pure xylene [45]. For the latter ZnAl hydroxide was used as inorganic filler, the tensile modulus improved by 50% at 10 wt% filler loading.

More work was done using in situ polymerization for OM-PE nanocomposites. Bergmann et al. [46] gave the first report, where the polymerization was carried out with a palladium catalysts. A weakening of the x-ray signal was observed, but the material properties were not examined. Alexandre et al. [42] reported, that composites obtained by ethylene polymerization with methylaluminoxanes intercalated in montmorillonite could improve the stress at break by more then 50% at 4 wt% filler, but the tensile modulus decreased by 10% at the same time. It was noted, that the system was not in structural equilibrium, as the mineral layers collapsed during processing. Similar results were published later once more from the same research group [47]. Subsequently, more work was published with this technique using different catalysts and clay minerals [48–58]. Using a Ziegler-Natta catalyst and palygorskite as clay, Rong et al. [50] obtained a nanocomposite with a tensile modulus of 850 MPa and yield strength of 31.8 MPa for 10 wt% filler loading. Unfortunately the value for the pure polyethylene was not given. Using a similar system Due et al. [51] could improve the impact strength by a factor of 2.5 and the tensile strength by 10% for 1.4 wt% mineral loading. When ethylene was polymerized in the presence of silica and montmorillonite, the tensile modulus could be improved by up to 60% and the tensile strength by up to 25% for 5.4 wt% filler loading, but not reproducibly [58].

By far, most of the work to date on polyethylene clay nanocomposites, is based on melt compounding [59–93], with most of the synthesis done using copolymers as matrix or additive [72–93]. Reports given on nanocomposites based on pure HDPE as matrix and modified filler can be compared with the results of section 4.1 and 4.2 of this thesis. Heinemann et al. [60] reported a direct comparison between melt compounding and in situ polymerization. The results were not clear, as in one case tensile modulus increased by over 60% for the composite prepared by melt compounding while the polymerized composite exhibited no reinforcement. In other systems the opposite was observed. It was concluded, that the number of branchings per chain is the key factor for the properties, because “the interaction between polymer and clay is enhanced. With 7.5 wt% modified montmorillonite Truss and Lee [67] reported an enhanced tensile modulus of 10%, whereas yield strength did not change. Arroyo et al. [65] could improve the stiffness and strength of a PP/LDPE blend by 35-50% with 10 wt% filler. But, the amount of PP in the blend was changed at the same time, so that the improvement can not
be ascribed unambiguously to the filler. Kim and White [71] observed that montmorillonite in a LLDPE matrix improved the tensile modulus by 25% and decreased the yield strength by 15% at 7 wt% filler loading. The same group found earlier an increase of 30 and 50% of the tensile modulus and 30 and 20% of the tensile strength for 5 and 10 wt% filler in a chlorinated PE matrix [62].

Other properties of nanocomposites containing only HDPE and clay, like reduced photo-oxidative degradation [63], flammability properties [64, 66] and thermal degradation [68] were also explored.

Su, Jiang and Wilkie [69] used an approach similar to that explored in section 4.1 Ionically Bound Polymers. The matrix was pure PE, but the filler was modified before melt compounding with oligo- respectively polymers. With a filler loading of 15 wt%, containing oligomers, the enhancement was 30% and 25% for tensile modulus while the yield stress deteriorated 15% and 25% for styrene and methacrylate oligomers, respectively.

Many of the publications on polyethylene nanocomposites with copolymer added to the PE matrix, used additives containing maleic anhydride [73, 77-88, 91]. The advantage is enhancement of the interaction between polymer and filler, which leads to improved dispersion and delamination of the filler. Therefore copolymer additives are also named compatibilizers. In some works reported on polyethylene-layered silicates nanocomposites the whole matrix consisted of maleic anhydride grafted polyethylene. Wang et al. [79] gave an account of a composite with 5 vol% filler in a matrix of maleated LLDPE with an increased yield strength of 40%. In a report published by Gopakumar et al. [81], the tensile modulus rose with 5 wt% clay in polyethylene and maleated PE by 10% and 20%, respectively, compared to the pure PE. Mehrabzadeh and Kamal [83] reported an increase of the tensile modulus of 30% in HDPE as well as in a blend of HDPE and maleated HDPE at 5 wt% filler loading. Using a blend of PE and maleated PE, Wang, Koo and Chung [88] observed an improvement of the tensile modulus up to 40% at 1.5 vol% filler loading.

Several papers were published, in which poly[ethylene-co-(vinyl acetate)] was employed as additive or matrix [72, 74, 75, 89, 90, 92, 93]. Alexandre et al. [72, 74] reported an increase of the tensile modulus of 70% at 3.4 wt% filler loading for a nanocomposite with ethylene-vinyl acetate copolymer which contained 27 wt% vinyl acetate. Using 5 wt% filler and an ethylene-vinyl acetate copolymer with 10.8 mol% vinyl acetate, the same author reported the enhancement of the tensile modulus by 100%. Jeon, Ryu and Chang [89] presented a work where the tensile modulus increased by 30% for 2.5 wt% filler loading in a PE matrix containing 15 wt% vinyl acetate. Note that the copolymers of ethylene and vinyl acetate are mutagenic, which makes their use for instant in food packaging.
questionable.

Lia et al. [91] reported the mixing of PE with a montmorillonite/(polyethylene-block-polyethylene glycol) master batch. The tensile strength was improved compared to the OM-PE composite. However, neither values for comparison with the pure PE nor other tensile properties were given.

In the publications listed above dealing with additives, large amounts of copolymers were added - sometimes the whole matrix consisted of copolymer. The influence of copolymer additives at low concentrations was studied in section 4.4 Effect of Copolymer as Additives of this thesis.

Only few studies on the permeation-barrier properties of polyethylene layered mineral composites can be found in the literature. Siddarmaiah et al. [59] reported, that LDPE composite containing 2 wt% mica showed a water vapor transmission reduced by 65% and an oxygen transmission reduced by 35% compared to the pure LDPE. At the same time the tensile strength went down by 50%. Kato et. al [84] observed that the nitrogen gas permeability coefficient for a composite containing 5.4 wt% modified montmorillonite and 30 wt% maleic-anhydride grafted low density polyethylene in a PE matrix was reduced by 28%. At the same time tensile modulus increased 1.8 times compared to neat PE, whereas the tensile strength deteriorated by 86% compared to pure PE, but improved 40% compared to the matrix mixture. Both reports did not normalize the results to the actual thickness of the examined sample, leaving some uncertainty.
2.5 Scope of the thesis

Although great progress has already been achieved with the new developed materials, their properties are not yet optimal and the upper limits for their properties has not been explored. Especially the combination of enhanced properties, such as stiffness and toughness or gas barrier properties has not been reached yet. Furthermore, most advances have been achieved only on a laboratory scale, since the optimal synthetic route for these composites has not been reached. A correlation between the particulate dimensional parameters or the composite structure and the material properties is still missing. All kinds of polymer matrices have been used to synthesize nanocomposites. However, the results with thermoplastic polymers like polyolefins, due to their nonpolar character, are rather meager.

The aim of this project was to synthesize layered silicate nanocomposites with high density polyethylene (HDPE) via melt intercalation. The project focused on improving the gas barrier properties as well as on obtaining materials with better mechanical properties. Further goal of this study has been to establish a correlation between the microstructure and the properties of the nanocomposite.
3 Background

3.1 Permeation of Gases Through Materials

Polymer clay nanocomposites exhibit improved barrier properties compared to their polymer matrix. In Figure 3.1, the random pathway of a gas molecule through a composite filled with high aspect ratio particles is shown, the pathway becomes much larger due to the presence of filler.

3.1.1 Isotropic Materials

The first step of a permeant gas molecule on the path through a barrier membrane is the sorption of the gas by the barrier material. The solubility of the permeant can be described by the solubility coefficient $S$. In the simplest case the solubility coefficient is a contribution coefficient which describes the resulting difference in concentration $\Delta c$ at a given pressure difference $\Delta p$. This correlation is known as Henry’s law for gases:

$$\Delta c = S \cdot \Delta p$$  \hspace{1cm} (3.1)

One-dimensional flux $J$ through isotropic media is described by Fick’s first law (First Law of Diffusion):
3 Background

\[ J(x, t) = -D \cdot \frac{\delta c(x, t)}{\delta x} \]  \hspace{1cm} (3.2)

where \( c \) is the concentration of the permeant, \( D \) is the diffusion coefficient, \( x \) is the distance into the substrate, and \( t \) is the diffusion time. The diffusion coefficient depends on the gas as well as on the matrix. The negative sign indicates that the diffusing molecule flows in the direction of decreasing concentration.

From the conservation of mass, we also know that

\[ \frac{\delta c(x, t)}{\delta t} = -\frac{\delta J(x, t)}{\delta x} \] \hspace{1cm} (3.3)

Combining Eq. 3.3 with Eq. 3.2 leads to Fick’s Second Law(Second Law of Diffusion):

\[ \frac{\delta c(x, t)}{\delta t} = D \cdot \frac{\delta^2 c(x, t)}{\delta x^2} \] \hspace{1cm} (3.4)

With time independent concentrations on both sides of a membrane with a thickness \( d \) and at equilibrium we obtain:

\[ \frac{\delta c(x, t)}{\delta t} = 0 \] \hspace{1cm} (3.5)

The concentration gradient is constant. Hence, the equation for one dimensional diffusion under these conditions, with \( D \) assumed to be constant, is:

\[ \frac{\delta c(x)}{\delta x} = D \cdot \frac{\delta^2 c(x)}{\delta x^2} \] \hspace{1cm} (3.6)

Using the boundary conditions,

\[ c(x = 0) = c_0 \] \hspace{1cm} (3.7)

and

\[ c(x = d) = c_d \] \hspace{1cm} (3.8)

we obtain:

\[ \frac{\delta c(x)}{\delta x} = \frac{c_d - c_0}{L} = constant \] \hspace{1cm} (3.9)

The concentration decreases linearly from \( c_0 \) to \( c_d \) as shown in Figure 3.2, the flux \( J \) is equal over the cross section and can be described with:

\[ J = -D \cdot \frac{\delta c(x)}{\delta x} = D \cdot \frac{c_d - c_0}{d} \] \hspace{1cm} (3.10)
For gases, the concentration is expressed in terms of partial pressure and we obtain:

\[
J = P \cdot \frac{P_d - P_0}{d}
\]  \hspace{1cm} (3.11)

where the permeability coefficient \( P \) is constant. The correlation between the partial pressure \( p \) and the concentration at the surface \( c_s \) is given by

\[
c_s = S \cdot p
\]  \hspace{1cm} (3.12)

with \( S \) being the solubility coefficient. With constant diffusion coefficient \( D \) we obtain

\[
P = S \cdot D
\]  \hspace{1cm} (3.13)

This means that with known solubility coefficient, the diffusion coefficient can be described with permeability and constant flux respectively.

In dynamic measurements first the sample is conditioned \((c_0 = c_d)\). Then the concentration is step changed \((c_0 \neq c_d)\), keeping \( c_0 \) and \( c_d \) at a constant value. If we time-integrate the amount of gas passing the membrane we observe that after a certain time the integrated curve, which describes the amount of gas per unit time, becomes linear. Extending the linear part of the curve (constant flow) with the time axis, one gets the \textit{time-lag} value \((t_L)\) \[97\]. Mathematically \( t_L \) is obtained by integrating Eq. 3.6, resulting in:

\[
t_L = \frac{d^2}{6 \cdot D}
\]  \hspace{1cm} (3.14)

Hence, with the experimentally determined time-lag and a known thickness of the sample foil the diffusion coefficient can be determined, as shown in Figure 3.3. For mineral polymer composites diffusion takes place only in the polymer.
Figure 3.3: Schematic illustration of the time-dependence of the integrated flux $J$, i.e. the amount of gas passing through the membrane.

phase (the diffusion through the mineral is orders of magnitude smaller). Measuring $D$ and $S$ is error-prone, resulting in comparatively high values. Normally, the permeability coefficient is measured directly as a material property. In general the transmission rate $r_T$ is determined, which is a measure for the volume of gas passing through a membrane of known area per unit time. With the thickness $d$ of the sample and the pressure $p$ one obtains the permeability coefficient $P$, which is independent from the sample geometry, pressure and time:

$$P = \frac{r_T \cdot d}{p} = \frac{\text{quantity of permeant} \cdot \text{film thickness}}{\text{area} \cdot \text{time} \cdot \text{pressure}}$$

(3.15)

The permeability coefficient $P$ is reported with a variety of different units in literature. We chose to present $P$ in units of $[\text{cm}^3 \cdot \mu\text{m}/\text{m}^2 \cdot \text{day} \cdot \text{mmHg}]$. It can be converted to the SI unit $[\text{cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}]$ by multiplying with $8.68 \cdot 10^{-16}$.

### 3.1.2 Materials with Plate-like Inclusions

One of the first models to describe the permeation of gases through mineral filled polymers was given by Nielsen [98]. The model predicts the reduction of the permeability coefficient which is expected. The theory is based on the increase of the pathway of a gas molecule through a composite, caused by the filler, as shown in Fig. 3.4. The model does not take into account Brownian motion and assumes impermeability of the filler for the gas as well as perfect alignment of the mineral inclusions. The ratio of the permeability coefficient of the composite $P_c$ to the one of the polymer matrix $P_m$, is given by:

$$\frac{P_c}{P_m} = \frac{\phi_m}{\tau}$$

(3.16)
where $\phi_m$ is the polymer volume fraction and $\tau$ is the increase of the pathway length of the diffusing particle which is given by

$$\tau = \frac{d'}{d}$$

$d'$ describes the path length of the diffusing particle and $d$ the thickness of the membrane. With perfect alignment and a rectangular shape of the filler, $d'$ can be described with

$$d' = d + d \cdot \frac{L}{2 \cdot W} \cdot \phi_f$$

where $L$ is the length of the inclusion and $W$, its width. $\phi_f$ describes the filler volume fraction. Combining Eq. 3.17 and 3.18, $\tau$ can be written as

$$\tau = 1 + \frac{L}{2 \cdot W} \cdot \phi_f$$

where $L/W$ equals the aspect ratio $\alpha$ of the Filler. Using this and Eq. 3.19 in Eq. 3.16 we obtain an expression for the decrease of the permeability, depending on the filler volume fraction and the aspect ratio.

$$\frac{P_c}{P_m} = \frac{\phi_m}{1 + \frac{\alpha \cdot \phi_f}{2}}$$

With $\phi_m = 1 - \phi_f$ and $x = \alpha \cdot \phi_f$, Eq. 3.20 can be transformed into the following equation:
In contrast to the analytic solution provided by Nielsen in 1967, current research methods entail using powerful simulation techniques. Gusev et al. [99] found, based on finite element analysis, an exponential decay of the permeability of composites with disk-shaped filler particles depending on the filler volume fraction and aspect ratio, as shown in Fig. 3.5:

$$\frac{P_c}{P_m} = \exp \left[ -\left( \frac{x}{x_0} \right)^\beta \right]$$  \hspace{1cm} (3.22)

where $x = \alpha \cdot \phi_f$ is the product of the aspect ratio $\alpha$ and the filler volume fraction $\phi_f$. The least square parameters for the fit presented in Figure 3.5 are $\beta=0.71$ and $x_0=3.47$.

The ratio of the permeability coefficient for randomly orientated platelets and perfect aligned platelets as a function of the aspect ratio appears in Figure 3.6. The filler fraction was kept constant at 0.03. With increasing aspect ratio, the effect of misalignment becomes larger. The decrease in permeability due to misalignment approaches a constant value above an aspect ratio of 20. The gas barrier

*Figure 3.5:* Dependence of the permeability of composites on the product of aspect ratio and filler volume fraction, obtained by finite element simulations by Gusev et al. [99].
3 Background

Platelet aspect ratio

Figure 3.6: The ordinate shows the ratio between the permeability for randomly oriented disk-shaped particles and the permeability for perfectly aligned ones. The graph depicts the dependence of the permeability of composites with disks of random orientation on the aspect ratio at a fixed volume fraction of 0.03, simulated by Lusti [100].

Figure 3.7: Dependence of the permeability of composites on maximum angle of misalignment of the filler with aspect ratio = 50 and a volume fraction of 0.03, as simulated by Lusti [100].
Figure 3.7 presents the dependence of the permeability on the alignment. The x-axis represents the maximum angle of misalignment, the y-axis the ratio of $P$ of misaligned and aligned composites. The aspect ratio and volume fraction were kept constant.

Other theoretical approaches for predicting barrier properties have been discussed in literature [101–103].
3 Background

3.2 Mechanical Properties of Laminated Composites

The simplest models for predicting the upper and lower bound of the tensile modulus of composite materials are based on the ideal case of lamellar composites, consisting of alternating layers with high and low moduli.

First we shall consider the Voigt [104] model. In this model the maximum stiffness is obtained with an uniaxial stress applied parallel to the layers. The strain has to be the same for each layer. Figure 3.8 shows a schematic sketch of a Voigt composite. The force on the composite is the sum of the forces on filler $F_f$ and matrix $F_m$:

$$F_c = F_f + F_m$$  \hspace{1cm} (3.23)

Figure 3.8: Isostrain conditions for layered composite after Voigt [104].

and matrix $F_m$:

$$F_c = F_f + F_m$$  \hspace{1cm} (3.23)

since force is equal to stress times area, one arrives at

$$\sigma_c \cdot A_c = \sigma_f \cdot A_f + \sigma_m \cdot A_m$$  \hspace{1cm} (3.24)

$A_f$ and $A_m$ are the areas of each layer which face the applied stress. Both are of the same length, so they can be represented by their volumes or volume fractions $\phi_f$ and $\phi_f$, with the volume fraction of the composite $\phi_c$ equal to unity. Hence,

$$\sigma_c \cdot \phi_c = \sigma_f \cdot \phi_f + \sigma_m \cdot \phi_m$$  \hspace{1cm} (3.25)

The last equation can be rewritten in terms of tensile modulus $E$ under isostrain conditions.
3 Background

\[ E_c = E_f \cdot \phi_f + E_m \cdot \phi_m \]  
\[ (3.26) \]

\( E_c \) is in this case a Voigt average modulus. For systems with more than two components it can be rewritten as the sum over the volume fraction times tensile modulus of each component.

\[ E_c = \sum \phi_i \cdot E_i \]  
\[ (3.27) \]

Eq. 3.27 describes the theoretical upper bound for the tensile modulus of composite materials. Actual measured moduli lie well below this theoretical limit.

The modulus can be also calculated for the force applied transverse to the layers. These calculations were first done by Reuss [105]. As shown in Figure 3.9 the same force acts on each layer, so the same stress exists if each layer has the same area. This form of loading is referred to as isostress or homogeneous stress condition.

![Figure 3.9: Isostress conditions for layered composite after Reuss [105].](image)

The total deformation \( \delta l_c \) is equal to the sum of the deformations in each component:

\[ \delta l_c = \delta l_f + \delta l_m \]  
\[ (3.28) \]

With \( \varepsilon = \delta l/l \) we can convert the length change to strain, leading to:

\[ \varepsilon_c \cdot l_c = \varepsilon_f \cdot l_f + \varepsilon_m \cdot l_m \]  
\[ (3.29) \]
In the next step we substitute the tensile modulus $E$ as the ratio of uniform stress to strain $\varepsilon = \frac{\sigma}{E}$ and obtain:

$$\frac{\sigma \cdot l_c}{E_c} = \frac{\sigma \cdot l_f}{E_f} + \frac{\sigma \cdot l_m}{E_m}$$  \hspace{1cm} (3.30)

In our model system the cross-section of the composite is uniform. Hence, the length of a component is proportional to its volume fraction. With $\phi_c$ taken as unity we come to

$$\frac{1}{E_c} = \frac{\phi_f}{E_f} + \frac{\phi_m}{E_m}$$  \hspace{1cm} (3.31)

Rewriting Equation 3.31 we obtain

$$E_c = \frac{E_f \cdot E_m}{E_m \cdot \phi_f + E_f \cdot \phi_m}$$  \hspace{1cm} (3.32)

The general case for multi-component materials is given by:

$$E_c^{-1} = \sum_i \phi_i \cdot E_i^{-1}$$  \hspace{1cm} (3.33)

Equation 3.32 predicts the theoretical lower bound for two-component composite materials. The tensile modulus of a composite can not drop below this value, unless, for instance, for polymers, the matrix suffered from degradation during sample preparation. Note, the moduli predicted by the theories of Voigt and Reuss can be different by dimensions. This is in particular the case, when the modulus of the filler is much larger than the one of the matrix.
4 Results and Discussion

4.1 Octadecyl modified clays

4.1.1 Varying the Packing Density & Surface Coverage

The surface of a pristine montmorillonite sheet is hydrophilic. It is covered with hydrated cations, which act as counterions to the negative charges on the surface. It is clear, that in order to separate the stacks of those layers in a polyethylene matrix, the surface has to be modified. This should be done in such a way, that the surface energy of the modification comes close to the one of polyethylene. Intuitively one would think of a surface covered completely with alkyl chains, where the chains of the polyethylene only “see” chemically identical neighbors. We used melt compounding for the sample preparation. During compounding shear forces are applied to the melt. By covering the surface completely with alkyl chains, we sought to reduce the attractive force between the sheets. This force is reduced due to the increased distance between the mineral sheets and because the surface becomes hydrophobic. We thought that this way the modified silicate sheets can slide off under shear force in the melt, which are hindered from collapsing due to the high viscosity of the matrix. Nevertheless, this does not necessarily lead to thermodynamically stable systems. An optimum grafting density for achieving this stability was proposed by Hasegawa et al. [106]. For this reason the grafting density, in this study named packing density, was also varied. In this section the influence of surface coverage and the packing of octadecyl chains on the surface was studied. In order to vary the packing density two parameters were altered. One was the cation exchange capacity (CEC) of the montmorillonite. Although it is a unit per gram, it is also correlated to the number of charges per unit area [18]. Hence the packing density can be varied using the same surface modification on montmorillonites with different CEC. The montmorillonites we used have CEC of 680, 880, 900 and 1000 μmol/g, the abbreviations used for this study are M680, M880, M900 and M1000, respectively. The other parameter we changed was the number of octadecyl chains per exchanged cation. The four cations we used for this are shown in Figure 4.1.

The surface-modification was carried out in a water/alcohol dispersion of the clay. After cation exchange, the organophilic clay was washed several times in
order to remove excess ions from the surface. In the next step it was freeze-dried and sieved. The nanocomposite was obtained by adding the mineral powder to the HDPE melt in a compounding chamber. The mixture was kneaded under shear for 20 minutes and afterwards pressed to sheets for analysis of the polymer composite. The results are discussed below.

**Preliminary Experiments**

At the beginning of this study the question emerged how the, sometimes very coarse, montmorillonite can be brought into a state which makes its dispersion in the polymer melt easier. Milling and sieving still led to particles large in size. Besides, milling always is accompanied by filler contamination. We decided to freeze-dry and sieve the filler before compounding. After several attempts we chose dioxane for the OM and water for the pristine clay as solvents, for technical reasons as well as for good dispersion. The result was convincing, as shown in Figure 4.2. On the left image the filler was only milled and sieved, on the right side the filler was freeze-dried out of dioxane before compounding. The particles become smaller with freeze-drying due to their fine dispersion in the solvent, which is retained during drying.

**Crystallinity**

The degree of crystallinity influences most properties [107] of polymers, the tensile [108,109] and barrier properties [110] are most important in this study. Fillers can act as nucleating agent, and different properties of a polymer and its composites can not be attributed directly to the filler, without paying attention to the crystallinity.
Figure 4.2: SEM images, showing the influence of freeze-drying on the particle size of OM in the composites. On the left side a large agglomerate in a composite of 2C18-M900 at 1.8vol% mineral fraction without freeze-drying before compounding is shown. On the right side an image of a composite containing the same filler, but freeze-dried before compounding is displayed.

In our system the crystallinity could not be determined by WAXD, as the reflection of the clay appears in the amorphous halo of the HDPE. Determining the density as a measurement of the crystallinity for a system containing surface treated filler is too inaccurate. Therefore we chose thermal analysis to determine the degree of crystallinity.

The results are displayed in Table 4.1. Note that the crystallinity does not change markedly with the filler or the modification, except for the systems containing unmodified montmorillonite, where a slight increase is evident. As there is no significant difference between the melting enthalpy of the nanocomposites

Table 4.1: Melt enthalpy $\Delta H_m [J/g]$ and crystallinity of HDPE and its 2.8 vol% composites.

<table>
<thead>
<tr>
<th></th>
<th>untreated</th>
<th>C18</th>
<th>2C18</th>
<th>3C18</th>
<th>4C18</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pure HDPE</strong></td>
<td>202 (0.69)</td>
<td>-</td>
<td>210 (0.72)</td>
<td>210 (0.72)</td>
<td>-</td>
</tr>
<tr>
<td>M680</td>
<td>210 (0.72)</td>
<td>209 (0.71)</td>
<td>210 (0.72)</td>
<td>210 (0.72)</td>
<td>-</td>
</tr>
<tr>
<td>M880</td>
<td>215 (0.73)</td>
<td>-</td>
<td>203 (0.70)</td>
<td>204 (0.70)</td>
<td>-</td>
</tr>
<tr>
<td>M900</td>
<td>219 (0.75)</td>
<td>207 (0.71)</td>
<td>204 (0.70)</td>
<td>203 (0.70)</td>
<td>207 (0.71)</td>
</tr>
<tr>
<td>M1000</td>
<td>211 (0.72)</td>
<td>207 (0.71)</td>
<td>205 (0.70)</td>
<td>208 (0.71)</td>
<td>-</td>
</tr>
</tbody>
</table>
and the matrix, the changes of the barrier and tensile properties can be directly correlated with the filler.

**Morphology**

WAXD characterization of the pristine and modified clay as well as the composites are shown in Table 4.2. The composites exhibit the same basal-plane spacing as the filler powder. Nanocomposites of M900-2C18 with different loading showed the same interlayer distance. The interlayer distance increases for a mineral with increasing number of octadecyl chains per cation, in agreement with TGA measurements, of Table 4.3. In other words, the area being available on the surface becomes smaller for a single chain, with an increasing number of long tails per ammonium. Hence, the surface coverage increases and the area which exhibits the polar silicon oxide decreases. The octadecyl chains cannot align parallel to the surface any longer. They are forced in an orientation more perpendicular to the surface. As a result, the sheets become more separated. An indicator for the surface coverage is the amount of organic material on the surface. It was determined by TGA and is displayed in Table 4.3. Figure 4.3 illustrates the correlation of the organic matter on the surface of the layered silicate with the basal-plane spacing. The more organic matter is added with cation exchange, the further the silicate sheets become separated.

**Table 4.2:** Basal-plane spacing of OM in nanometers.

<table>
<thead>
<tr>
<th></th>
<th>C18</th>
<th>2C18</th>
<th>3C18</th>
<th>4C18</th>
</tr>
</thead>
<tbody>
<tr>
<td>M680</td>
<td>1.82</td>
<td>2.45</td>
<td>3.25</td>
<td>-</td>
</tr>
<tr>
<td>M880</td>
<td>-</td>
<td>2.51</td>
<td>3.48</td>
<td>-</td>
</tr>
<tr>
<td>M900</td>
<td>1.85</td>
<td>2.66</td>
<td>3.58</td>
<td>3.94</td>
</tr>
<tr>
<td>M1000</td>
<td>2.14</td>
<td>3.28</td>
<td>3.84</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 4.3:** Amount of organic matter in grams per gram clay. Determined with TGA after cation exchange.

<table>
<thead>
<tr>
<th></th>
<th>C18</th>
<th>2C18</th>
<th>3C18</th>
<th>4C18</th>
</tr>
</thead>
<tbody>
<tr>
<td>M680</td>
<td>0.202</td>
<td>0.430</td>
<td>0.504</td>
<td>-</td>
</tr>
<tr>
<td>M880</td>
<td>-</td>
<td>0.492</td>
<td>0.639</td>
<td>-</td>
</tr>
<tr>
<td>M900</td>
<td>0.304</td>
<td>0.504</td>
<td>0.767</td>
<td>0.862</td>
</tr>
<tr>
<td>M1000</td>
<td>0.364</td>
<td>0.649</td>
<td>0.855</td>
<td>-</td>
</tr>
</tbody>
</table>
4 Results and Discussion

Figure 4.3: Dependence of the interlayer distance of OM on the amount of organic matter on the surface.

For 2C18 and 3C18, the basal-plane spacing increases with the CEC of the clay. With increasing CEC the charge density becomes higher, hence the ammonium cations are closer together, the octadecyl chains are forced into a more vertical position. The packing of the chains as well as the surface coverage increases.

Although the interlayer distance measured with WAXD in the composites did not increase, we observed delaminated sheets in coexistence with stacks of silicate sheets using TEM. Figure 4.4 provides TEM images with features characteristic of the nanocomposite of 2C18-M880. In the left image, taken at low magnification, the filler is well oriented parallel to the surface. At this magnification one cannot see single layers, the darker areas which can be seen are areas rich in silicate layers. At high magnification (right image), single disordered sheets are clearly distinguishable. Stacks of mineral sheets are also evident. These are the origin of the x-ray reflection, and exhibit the same basal-plane spacing as the filler before compounding. It is very interesting to notice, that the degree of orientation changes with the length scale.

Previous studies assumed one orientational parameter for composites [87, 94, 111]. However barrier properties and tensile modulus depend strongly on the orientation [111], so their dependence on the length scale is clearly significant. Considering the sample preparation provides a possible explanation. When preparing the foils for permeability measurements and TEM, pieces of the nanocomposite are pressed in the melt to form foils. The particles,
which are larger in diameter and thickness, orient in the flow, so they offer less resistance to the polymer melt. Single layers and stacks consisting of only a few layers are extremely flexible [112] and flow with the matrix, following turbulences. Therefore they can be found in all orientations, as well as in a wrapped state. Real-time scattering experiments during sample preparation would be a good test for this hypothesis. However, this is a rather difficult task, which needs specialized equipment, and clearly lies beyond the scope of this thesis.

It is also remarkable, that only single clay sheets and stack of layers, but no intercalated structure, can be observed. We suggest that the attraction between alkyl chains on the surface and high-density polyethylene are not strong enough to force the polymer in between the layers, but the shear stress imposed on the system during compounding leads to separation of single sheets from the larger clay particles. This argument is supported by the Flory-Huggins parameter $\chi$, which describes the interaction between polymer and solvents. $\chi$ at 149°C is 0.28 for HDPE and n-dodecane, which is similar to that of the octadecyl chains on the surface [113]. Simulations have shown, that for such a modification, which is considered a short chain modification, $\chi$ has to be largely negative in order to obtain a completely exfoliated composite [114,115]. This is consistent with our observations and explanations. Hence the single clay sheets we observe in TEM are not in thermodynamic equilibrium but kinetically trapped. In order to delaminate the stacks further, a higher shear field has to be applied or compounding time extended, both having a negative influence on the molecular weight of the polymer.
4 Results and Discussion

**Tensile Properties**

Table 4.4 lists the tensile properties of the composites with different fillers. Tensile modulus $E$ as well as yield strength $\sigma_Y$ increase with growing number of alkyl chains in the ammonium salt. In the same manner, the yield strain $\varepsilon_Y$ decreases. Stress at break $\sigma_B$ tend to decrease with increasing number of alkyl chains, but the trend is not very pronounced. Strain at break $\varepsilon_B$ was reduced, but the nanocomposites are still ductile.

The highest reinforcement was obtained for nanocomposites filled using 3C18-M880. The same material evinces the highest yield stress of 28 MPa and a very low yield strain of 6.2 %. Compared to 10% increase of tensile modulus and no change of yield reported by Truss et al. [67], the improvement reached with 3C18-M880 is superior. The enhancement is also greater than an increase of 25% and reduction of 15% tensile strength reported Kim et al. [71].

Composites containing untreated filler do not follow the overall trend. This can have several reasons. The treatment of the filler before compounding should be considered first. The OM is freeze dried from dioxane, while the pristine clay is freeze dried from water. The dispersion of the clay in the solvent for freeze drying determines the grain size of the OM after freeze drying. The swelling in dioxane improves with increasing hydrophobicity of the surface of the clay sheets. Accordingly the grains of the clay with a higher surface coverage are smaller in size, than those with lower surface coverage. Water, on the other hand is the best solvent in order to disperse pristine clay, so that its particles are probably the smallest before compounding, which explains the exceptional behavior.

Moreover, untreated filler has a positive influence on the crystallinity, as discussed above, and on the tensile properties as well. Furthermore the stick-slip behavior plays an important role. The mechanical properties are influenced by the interaction between matrix and filler [116–118]. The adsorption of PE chains on pristine montmorillonite is higher than on modified montmorillonite, thus influencing the mechanical properties.

In Figure 4.5 the correlation between interlayer distance of modified filler, independent of the clay, and the reduced tensile properties at 2.8 vol% is shown. The dependence of the mechanical properties on the interlayer distance is clear. Tensile modulus and yield stress increase with larger basal-plane spacing, whereas yield strain decreases and the stress at break decreases little. The reinforcement is up to 40% for the composites containing filler with the largest basal-plane spacing. As discussed in Section Morphology the orientation is length scale dependent and the filler in the composite is polydisperse. Comparison
Figure 4.5: Correlation between basal-plane spacing and tensile properties of the nanocomposites at 0.028 mineral volume fraction. The lines represent linear fits of the data displayed.
4 Results and Discussion

Table 4.4: Tensile properties of HDPE and its OM-nanocomposites at 2.8% inorganic volume fraction.

<table>
<thead>
<tr>
<th></th>
<th>$E^a$</th>
<th>$\sigma_Y^b$</th>
<th>$\varepsilon_Y^c$</th>
<th>$\sigma_B^d$</th>
<th>$\varepsilon_B^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[MPa]</td>
<td>[MPa]</td>
<td>[%]</td>
<td>[MPa]</td>
<td>[%]</td>
</tr>
<tr>
<td>pure HDPE</td>
<td>1020</td>
<td>26</td>
<td>9.6</td>
<td>36</td>
<td>1180-1750</td>
</tr>
<tr>
<td>M680</td>
<td>1200</td>
<td>26</td>
<td>8.2</td>
<td>22</td>
<td>910-1060</td>
</tr>
<tr>
<td>C18-M680</td>
<td>1090</td>
<td>25</td>
<td>8.4</td>
<td>25</td>
<td>70-1330</td>
</tr>
<tr>
<td>2C18-M680</td>
<td>1280</td>
<td>25</td>
<td>7.5</td>
<td>23</td>
<td>70-1330</td>
</tr>
<tr>
<td>3C18-M680</td>
<td>1270</td>
<td>25</td>
<td>6.3</td>
<td>19</td>
<td>10-600</td>
</tr>
<tr>
<td>M880</td>
<td>1330</td>
<td>26</td>
<td>7.8</td>
<td>22</td>
<td>960-1080</td>
</tr>
<tr>
<td>2C18-M880</td>
<td>1270</td>
<td>25</td>
<td>7.6</td>
<td>23</td>
<td>780-1230</td>
</tr>
<tr>
<td>3C18-M880</td>
<td>1420</td>
<td>28</td>
<td>6.2</td>
<td>20</td>
<td>170-970</td>
</tr>
<tr>
<td>M900</td>
<td>1250</td>
<td>25</td>
<td>8.4</td>
<td>23</td>
<td>840-1100</td>
</tr>
<tr>
<td>C18-M900</td>
<td>1180</td>
<td>25</td>
<td>8.8</td>
<td>21</td>
<td>130-1100</td>
</tr>
<tr>
<td>2C18-M900</td>
<td>1320</td>
<td>26</td>
<td>6.7</td>
<td>14</td>
<td>20-320</td>
</tr>
<tr>
<td>3C18-M900</td>
<td>1320</td>
<td>28</td>
<td>6.3</td>
<td>20</td>
<td>80-1020</td>
</tr>
<tr>
<td>4C18-M900</td>
<td>1410</td>
<td>28</td>
<td>5.9</td>
<td>20</td>
<td>60-980</td>
</tr>
<tr>
<td>M1000</td>
<td>1340</td>
<td>27</td>
<td>7.8</td>
<td>23</td>
<td>660-1190</td>
</tr>
<tr>
<td>C18-M1000</td>
<td>1190</td>
<td>25</td>
<td>8.7</td>
<td>26</td>
<td>920-1180</td>
</tr>
<tr>
<td>2C18-M1000</td>
<td>1260</td>
<td>26</td>
<td>7.3</td>
<td>20</td>
<td>50-1200</td>
</tr>
<tr>
<td>3C18-M1000</td>
<td>1310</td>
<td>28</td>
<td>6.6</td>
<td>22</td>
<td>780-1520</td>
</tr>
</tbody>
</table>

$^a$Relative probable error 5%.
$^b$Relative probable error 2%.
$^c$Relative probable error 4%.
$^d$Relative probable error 10%.
$^e$The range of measured values is given.

of results with theoretical predictions are therefore of questionable value. A comparison with the simple cases of Voigt and Reuss is discussed in the Section Concentration Dependence.

The basal-plane spacing, which correlates with the tensile properties, is determined by packing density, surface coverage and length of the alkyl chains of the cation. Its coupling with the amount of organic material, and consequently the packing density, can be seen in Table 4.2 and Figure 4.3. Surface coverage also
correlates with the packing density of the chains. With increasing numbers of octadecyl chains as well as with increasing CEC the surface is covered more.

**Barrier properties**

The results of the oxygen permeability studies for 2.8 vol% filler are presented in Table 4.5. The oxygen permeability coefficient decreases over 40% for the composite containing 3C18-M880. With increasing numbers of alkyl chains the permeability coefficient decreases.

The average aspect ratio of the filler, apart from the volume fraction, is the key factor for the barrier properties. The aspect ratio depends on the degree of filler delamination. With increasing surface coverage, packing density and basal-plane spacing, the filler delaminate more easily. The correlation between basal-plane spacing and oxygen permeability is presented in Figure 4.5. The gas barrier is improved with increasing interlayer distance, independent of clay and modification.

Kato et al. [84] reported nearly 30% lower permeability, with 5.4 wt% filler, and 30% maleic anhydride grafted PE as additive. In this study we improved the barrier by 40% without copolymer additive and an inorganic volume fraction of 0.028. Siddaramaiah et al. reported a decrease of the oxygen permeability by 35% at 2 wt% mica in LDPE. However, the measurements were not normalized to the thickness and the tensile strength dropped by 50%.

In Figure 4.6, the reduced tensile modulus is plotted against reduced oxygen permeability coefficient. The two properties correlate, because both depend on the degree of delamination as well as the orientation.

**Summary**

Polyethylene clay nanocomposites, containing fillers with different packing densities of the self-assembled monolayer on the surface, were synthesized. The crystallinity of the composites is similar to the one of pure HDPE, suggesting that the OM does not act as nucleating agent. The fineness of the OM before compounding strongly influences its state in the composite.

The synthesized materials are stronger and more rigid than HDPE. Tensile modulus increased by up to 40% and yield strength by 10%, whereas yield strain decreased by 25% and stress at break by 50%. The maximum elongation, went down for most systems between 20 and 80%. The oxygen barrier was improved by over 40% for 2.8 vol% inorganic filler content. The improvement of the tensile properties as well as the barrier property exceed those reported in literature.
4 Results and Discussion

Figure 4.6: Properties of nanocomposites with a inorganic filler fraction of 2.8%. Upper graph: Basal-plane spacing plotted against reduced oxygen permeability coefficient of OM nanocomposites. The line is only a guide to the eye. Lower Graph: Correlation between barrier properties and tensile modulus. The straight line presents a linear fit of the data.
Table 4.5: Oxygen permeability coefficient of HDPE and its OM nanocomposites at 2.8% inorganic volume fraction.

<table>
<thead>
<tr>
<th></th>
<th>$p_{O_2}$ $^a$ [cm$^3 \cdot \mu m/(m^2 \cdot day \cdot mmHg]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>54</td>
</tr>
<tr>
<td>M680</td>
<td>38</td>
</tr>
<tr>
<td>C18-M680</td>
<td>40</td>
</tr>
<tr>
<td>2C18-M680</td>
<td>38</td>
</tr>
<tr>
<td>3C18-M680</td>
<td>35</td>
</tr>
<tr>
<td>M880</td>
<td>37</td>
</tr>
<tr>
<td>2C18-M880</td>
<td>37</td>
</tr>
<tr>
<td>3C18-M880</td>
<td>31</td>
</tr>
<tr>
<td>M900</td>
<td>41</td>
</tr>
<tr>
<td>C18-M900</td>
<td>42</td>
</tr>
<tr>
<td>2C18-M900</td>
<td>33</td>
</tr>
<tr>
<td>3C18-M900</td>
<td>34</td>
</tr>
<tr>
<td>4C18-M900</td>
<td>32</td>
</tr>
<tr>
<td>M1000</td>
<td>36</td>
</tr>
<tr>
<td>C18-M1000</td>
<td>46</td>
</tr>
<tr>
<td>2C18-M1000</td>
<td>36</td>
</tr>
<tr>
<td>3C18-M1000</td>
<td>33</td>
</tr>
</tbody>
</table>

$^a$Relative probable error 8%.

with PE matrices.

The tensile properties as well as the barrier properties correlate with the basal-plane spacing of the filler. Enlarging the interlayer distance leads, for systems similar to those studied in this section, to improved material properties.

A correlation between the oxygen permeability coefficient and the tensile modulus was observed, indicating that both depend in the same way on the microstructure, i.e., delamination of the filler and orientation.

TEM investigations showed stacks of layers, which caused the reflection for
WAXD, as well as delaminated sheets, whereas intercalated stacks were not seen. This indicates that the attractive force between filler and matrix is small and the sheets become separated by the shear force during compounding. The orientation of the filler does change with the length scale. Larger particles oriented parallel to the surface, whereas on the nanometer scale no preferential orientation could be observed.
4.1.2 Filler Concentration Dependence

A concentration series was synthesized to study the dependence of the composite properties on the filler content. A comparison of results and theoretical predictions is presented below.

Tensile Properties

The results of the tensile testing are shown in Table 4.6. With increasing filler content the tensile modulus increased over 30%, while yield strain dropped over 30%. The yield stress does not change and stress at break is reduced by 50%. Strain at break is reduced with increasing amount of filler; the material becomes less ductile. With increasing filler content the maximum elongation is reduced, as the material becomes more brittle. The reduced tensile properties are plotted in Figure 4.7. One can see that the properties change linearly up to a filler content of 2.8 vol%. Towards higher concentration the change of the properties levels off.

In Figure 4.8 the experimentally determined concentration dependence of the reinforcement is plotted together with theoretical predictions. The Voigt [104] and the Reuss [105] model were used for the prediction, as they represent the upper and lower bounds for the reinforcement, respectively. One key parameter in order to determine those bounds is the tensile modulus of the filler. This value is difficult to determine for layered minerals. The values reported for mica lie between 137 and 205 GPa [119], for kaolin 20 GPA [120] and for montmorillonite

Table 4.6: Tensile properties of HDPE and its 2C18-M900 nanocomposites with different filler loading.

<table>
<thead>
<tr>
<th>Mineral fraction [vol %]</th>
<th>$E$ $^a$ [MPa]</th>
<th>$\sigma_Y$ $^b$ [MPa]</th>
<th>$\varepsilon_Y$ $^c$ [%]</th>
<th>$\sigma_B$ $^d$ [MPa]</th>
<th>$\varepsilon_B$ $^e$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1020</td>
<td>26</td>
<td>9.6</td>
<td>36</td>
<td>1180-1750</td>
</tr>
<tr>
<td>0.9</td>
<td>1060</td>
<td>26</td>
<td>9.3</td>
<td>27</td>
<td>1290-1860</td>
</tr>
<tr>
<td>1.8</td>
<td>1250</td>
<td>26</td>
<td>8.2</td>
<td>27</td>
<td>620-1240</td>
</tr>
<tr>
<td>2.8</td>
<td>1330</td>
<td>26</td>
<td>6.7</td>
<td>14</td>
<td>20-320</td>
</tr>
<tr>
<td>4.0</td>
<td>1360</td>
<td>25</td>
<td>6.3</td>
<td>18</td>
<td>30-1080</td>
</tr>
</tbody>
</table>

$^a$Relative probable error 5%.

$^b$Relative probable error 2%.

$^c$Relative probable error 4%.

$^d$Relative probable error 10%.

$^e$The range of measured values is given.
Figure 4.7: Concentration dependence of the tensile properties on the inorganic volume fraction of 2C18-M900 nanocomposites.
4 Results and Discussion

Figure 4.8: Reinforcement of 2C18-M900 nanocomposites compared with bounds given by the Voigt and Reuss model for laminated composites. The model predictions are given for three different tensile modules of the filler. The various curves predicted using the Reuss model are practically indistinguishable and are below the experimental data points.

the estimated values are between 140 and 170 GPa [121, 122]. We found no experimentally determined values for montmorillonite. Hence, in the Figure 4.8 the predictions are plotted for the upper and lower value reported for mica, as well as the one for kaolin. The experimental values are higher then the lower bound, given by the Reuss model, but much lower than the ones predicted by the Voigt model. It was shown in the last section, that the orientation is scale dependent. One assumption of both models is that the filler is perfectly oriented, where in the Reuss model the stress is applied parallel to the sheets and in the Voigt model, perpendicular. In order to improve the tensile modulus, the alignment of the filler must be enhanced. This also would have a positive influence on
the barrier properties. The influence of incomplete delamination and imperfect alignment on the tensile modulus was discussed at full length in a report given by Brune et al. [111]. More appropriate models which predict the bounds for the tensile modulus for real systems need, apart from the modulus of the filler, the morphology of the composite as an input [123, 124]. As discussed above, the orientation of the filler depends on the scale, making such calculations very difficult. Alternatively, the modulus can be simulated using the finite element approach as reported by Gusev [125, 126].

**Barrier properties**

In Table 4.7 the values of the oxygen permeability coefficient for different concentrations of 2C18-M900 is given. The oxygen barrier increases up to 40% for a mineral filler fraction of 0.04. In Figure 4.9 the relative oxygen permeability coefficient is plotted against the filler fraction together with a theoretical prediction calculated following the equations given by Nielsen [98] based on geometric considerations and Gusev et al. [99] found with finite element simulations. Both models assume perfect alignment of the filler and monodisperse particles. The input parameters were the volume fraction and an aspect ratio of 110 similar to the one of M880, which was determined as described in the next section. In the examined range of filler volume fraction both predictions lie close together. The maximum improvement predicted could not be reached, but the experimental values flatten off, as predicted for higher filler content. The less-than-maximum improvement is due in part to the misalignment on the small scale, as discussed for the tensile properties. Due to misalignment, the barrier properties of nanocomposites with randomly disk-shaped particles oriented may have values as low as half the value of perfectly aligned systems [100], also shown in Figures 3.6 and 3.7.

**Table 4.7:** Barrier properties of HDPE and its 2C18-M900 nanocomposites with different filler loading.

<table>
<thead>
<tr>
<th>Mineral fraction [vol %]</th>
<th>$p_{O_2}^a$ [cm$^3$ μm/(m$^2$ day mmHg)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>54</td>
</tr>
<tr>
<td>0.9</td>
<td>49</td>
</tr>
<tr>
<td>1.8</td>
<td>35</td>
</tr>
<tr>
<td>2.8</td>
<td>33</td>
</tr>
<tr>
<td>4.0</td>
<td>31</td>
</tr>
</tbody>
</table>

$^a$Relative probable error 8%.

---

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4 Results and Discussion

Figure 4.9: Correlation between inorganic filler fraction and barrier properties of 2C18-M900 nanocomposites, with a theoretical prediction. The aspect ratio for the calculation was 110.

An additional reason is that the clay was only partially delaminated as shown in Figure 4.4. Hence, the maximum aspect ratio could not be achieved. The two effects have already been discussed in a report given by Osman et al. [15].

Summary

A concentration series of 2C18-M900 was prepared and the results were compared with theoretical predictions. The tensile modulus is higher than calculated using the Reuss model, but much smaller than the upper theoretical bound given by the Voigt model. The tensile modulus changes approximately linear at very low filler loading and levels off at higher filler loading, in contrast to the models which predict linear dependence.

The oxygen permeability coefficient did not reach the theoretical limits pre-
4 Results and Discussion

dicted by Gusev et al. and Nielsen, due to misorientation and incomplete delamination. Nevertheless, the concentration dependence followed the basic trend of the predictions. In order to improve the tensile modulus and barrier properties further, the clay has to be delaminated to a higher degree and the alignment has to be enhanced.
4.2 Influence of the Chemical Structure of the Surface Modification of Fillers

In the last section the influence of the packing density of octadecyl chains and the surface coverage on the composite properties was studied. The CEC of the layered silicate and the number of C18 chains per ammonium was varied. There, we tried to cover the surface completely and increase the interlayer distance significantly before compounding in order to reduce the attraction between silicate sheets. In this chapter the influence of the chemical structure on the nanocomposite properties, i.e., the chemistry of the alkyl chains of the organic cation, is examined. A structure which allows complete mixing with the PE chains was aspired. The organic cations used for the modification of the surface are shown

![Cationic compounds and their abbreviation used in this chapter. From the left to the right: dimethyldioctadecylammonium, didecyldimethylammonium, methyltrioctylammonium, dimethyldiphytanylammonium, benzylhexadecyldimethylammonium and tetraphenylphosphonium](image)

in Figure 4.10. In order to perturb the crystallinity of the octadecyl chains, a mixture of 2C18 and 2C10 (1:1) was used. In order to obtain an isotropic monolayer and a high surface coverage, while preventing crystallization, 3C8 was used, as C8 chains are too short to crystallize. For the same reason, 2Phytal was used; here the crystallization maybe prevented as the phytanyl chains are a mixture of isomers. To examine the influence of aromatic groups in the monolayer on the properties of the nanocomposite, BenzC16 as well as 4Phenyl were used. Organic cations with polar groups were not examined, as there were no indications that they could improve the delamination of the mineral sheets. In contrast, polar groups reduce the miscibility with HDPE.
4 Results and Discussion

Preliminary Studies

Figure 4.11: Diminution of the TGA intercalation peak of excess ammonium salt of dimethyldioctadecylammonium on M880.

We chose M880 CloisiteNa+, to perform the studies in this and the following sections for several reasons: M880 has an average CEC, which is between M680 and M1000 and most publications on polymer clay nanocomposites use CloisiteNa+ as a clay source. We favored M880 over M900, because it was easier to disperse than M900. This made it easier to remove excess ammonium ions on the surface. Figure 4.11 illustrates, how the excess ammonium was removed from the clay. The peak at around 250°C is that of intercalated salt. After washing the clay once, it vanished almost completely. The removal of excess ammonium salt was much more difficult with M900. The aspect ratio of the filler in the composites determines many of the material properties [111, 127]. The maximum aspect ratio of an exfoliated silicate layer is given by diameter, which determines the upper bound for the improvement of the barrier properties. In order to estimate the particle diameter, the clay was examined by TEM. Water dispersions were vitrified, so that single clay sheets of 1 nm thickness and different diameter could be observed. A series of pictures was made, and the length of approximately 1500 particles was measured. Analyzing this data, an average diameter was obtained, which provides the upper theoretical limit of the aspect ratio. The distribution of the radii is shown in Figure 4.12 on the top; on the bottom typical TEM images are shown. The distribution is not symmetric. There are many more small than large particles. A small difference was noted, when a hydrophilic instead of a hydrophobic mesh was used for the sample preparation. However, both meth-
4 Results and Discussion

Figure 4.12: Analysis of M880. Distribution of the radii of single clay sheets are displayed on the top. On the top left the sample was prepared with a hydrophilic mesh, on the top right with a hydrophobic mesh. On the bottom a typical TEM image with single clay sheets of 1 nm thickness and different lengths are shown.

ods led to the same average diameter of the sheets, which was found to be 110 nm. With a thickness of 1 nm of a single silicate sheet, the maximum average aspect ratio is 110. Using the findings of Gusev and Lusti [99] and predictions of Nielsen [98] the improvement of the gas barrier was calculated to be 0.4 times the value of the matrix at a inorganic filler fraction of 0.028.

DSC

In Table 4.8 the melting enthalpy and the crystallinity of the nanocomposites are shown. The melting enthalpy did not increase significantly for any compound. With these findings the improvements of the properties can be attributed to the filler and not to a change in crystallinity of HDPE.
Table 4.8: Melt enthalpy $\Delta H_m$ and crystallinity of HDPE and its OM 2.8 vol% composites.

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>2C18</th>
<th>2C10/2C18</th>
<th>3C8</th>
<th>2Phytyl</th>
<th>BenzC16</th>
<th>4Phenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>[J/g]</td>
<td>202</td>
<td>203</td>
<td>207</td>
<td>203</td>
<td>214</td>
<td>208</td>
<td>204</td>
</tr>
<tr>
<td>cryst.</td>
<td>0.69</td>
<td>0.69</td>
<td>0.71</td>
<td>0.70</td>
<td>0.73</td>
<td>0.71</td>
<td>0.70</td>
</tr>
</tbody>
</table>

**Morphology**

Table 4.9: Amount of organic matter on the mineral surface after cation exchange, percentage of exchanged cations and the effect on the basal-plane spacing of M880.

<table>
<thead>
<tr>
<th>Modification</th>
<th>organic matter per gram mineral [g/g]</th>
<th>exchanged cations [% of CEC]</th>
<th>$d_{001}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2C18</td>
<td>0.492</td>
<td>92</td>
<td>2.51</td>
</tr>
<tr>
<td>2C10/2C18</td>
<td>0.353</td>
<td>95</td>
<td>1.88</td>
</tr>
<tr>
<td>3C8</td>
<td>0.316</td>
<td>85</td>
<td>1.89</td>
</tr>
<tr>
<td>2Phytyl</td>
<td>0.398</td>
<td>68</td>
<td>2.79</td>
</tr>
<tr>
<td>BenzC16</td>
<td>0.315</td>
<td>91</td>
<td>1.84</td>
</tr>
<tr>
<td>4Phenyl</td>
<td>0.247</td>
<td>100</td>
<td>1.87</td>
</tr>
</tbody>
</table>

The effect of the surface modification on the interlayer distance is reported in Table 4.9. The nanocomposites showed x-ray reflections at the same positions as the clay, indicating that the polymer was not intercalated.

With decreasing number of carbon atoms per cation, the basal-plane spacing decreases. Note that all modifications, except 2C18 and 2Phytyl, are close together. The large interlayer distance for 2Phytyl stems from the 20 carbon atoms per phytanyl chain.

The amount of organic matter per gram mineral, also shown in Table 4.9, is plotted against the basal-plane spacing in Figure 4.13. There is no linear dependence as observed in the last section (Figure 4.3). 4Phenyl-M880 has a relatively high basal-plane spacing for the amount of organic material. This can be understood by considering the tetrahedral structure of the molecule as shown in Figure 4.10. The phenyl groups, which are not flexible, are pointing in the corners of the tetrahedron. In contrast to cations with alkyl groups, the phenyl
4 Results and Discussion

1. Phytyl 
2. C18
3. C8
4. Phenyl
5. Benz

Figure 4.13: Interlayer distance versus organic matter on the surface of OM.

Groups are fixed in their position as discussed by Meier [128]. Thus, the interlayer distance deviates from the expected behavior. Phytyl also shows a rather large basal-plane spacing corresponding to the chain length.

Tensile properties

In Table 4.10 the tensile properties of the nanocomposites are displayed. The reinforcement was between 15 and 30 % for 2.8 vol% inorganic loading. For all samples, the yield stress did not change significantly, whereas the yield strain decreased by up to 20% and the stress at break by up to 60%. The differences between the composites are quiet small which make the interpretation of the results difficult.

Still, the increase in tensile modulus is superior to the improvement of 10% reported by Truss et al. [67] at similar loading. The tensile modulus was enhanced by 25%, the same as reported by Kim et al. [71] at the same filler loading, but they observed a decrease of the tensile strength whereas our system showed no change. The maximum elongation was reduced for all composites, it varies strongly. Hence, it is very difficult make any conclusions from these data. Only for 2C10/2C18-M880 is significant decrease is observed, as this sample is brittle.

In Figure 4.14 the tensile properties are plotted vs. the interlayer distance of the clay. In contrast to the last section, no correlation between the basa-
plane spacing and the tensile properties is apparent. No other parameter which correlates with the tensile properties could be found. In the last section, where we
4 Results and Discussion

Table 4.10: Tensile properties of HDPE and its 2.8 vol% OM nanocomposites.

<table>
<thead>
<tr>
<th></th>
<th>$E_T^a$ [MPa]</th>
<th>$\sigma_Y^b$ [MPa]</th>
<th>$\varepsilon_Y^c$ [%]</th>
<th>$\sigma_B^d$ [MPa]</th>
<th>$\varepsilon_B^e$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>1020</td>
<td>26</td>
<td>9.6</td>
<td>36</td>
<td>1180-1750</td>
</tr>
<tr>
<td>2C18</td>
<td>1270</td>
<td>26</td>
<td>7.6</td>
<td>21</td>
<td>780-1230</td>
</tr>
<tr>
<td>2C10/2C18</td>
<td>1320</td>
<td>26</td>
<td>8.2</td>
<td>13</td>
<td>80-220</td>
</tr>
<tr>
<td>3C8</td>
<td>1260</td>
<td>26</td>
<td>7.8</td>
<td>23</td>
<td>510-1430</td>
</tr>
<tr>
<td>2Phytol</td>
<td>1150</td>
<td>25</td>
<td>8.1</td>
<td>17</td>
<td>140-1330</td>
</tr>
<tr>
<td>BenzylC16</td>
<td>1310</td>
<td>27</td>
<td>7.5</td>
<td>15</td>
<td>860-1190</td>
</tr>
<tr>
<td>4Phenyl</td>
<td>1250</td>
<td>25</td>
<td>7.7</td>
<td>18</td>
<td>650-930</td>
</tr>
</tbody>
</table>

$^a$Relative probable error 5%.
$^b$Relative probable error 2%.
$^c$Relative probable error 4%.
$^d$Relative probable error 10%.
$^e$The range of measured values is given.

observed a correlation, only the packing density was changed, while the chemistry of the tails of the cations was the same. In this section, we changed the chemistry and the packing of the organic tails on the surface.

Barrier Properties

Table 4.11: Oxygen permeability coefficient for OM-HDPE nanocomposites at 2.8% inorganic volume fraction and different surface modifications.

<table>
<thead>
<tr>
<th>Surface modification</th>
<th>$p_{O_2}^a$ $[cm^3 \cdot \mu m / (m^2 \cdot day \cdot mmHg)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>54</td>
</tr>
<tr>
<td>2C18</td>
<td>37</td>
</tr>
<tr>
<td>2C10/2C18</td>
<td>34</td>
</tr>
<tr>
<td>3C8</td>
<td>37</td>
</tr>
<tr>
<td>2Phytol</td>
<td>36</td>
</tr>
<tr>
<td>BenzylC16</td>
<td>40</td>
</tr>
<tr>
<td>4Phenyl</td>
<td>40</td>
</tr>
</tbody>
</table>

$^a$Relative probable error 8%.

The oxygen permeability coefficient is displayed in Table 4.11. It could be
reduced by 35% for the composite containing 2C10/2C18-M880 compared to pure HDPE. The nanocomposites containing montmorillonite modified with BenzC16 and 4Phenyl improved the barrier properties less than those with alkyl chains. This suggest that aromatic groups have a negative influence on the oxygen barrier of the composites. Nevertheless, such influence was not observed for the tensile properties.

**Summary**

Fillers with chemically different surface modifications were incorporated in a polyethylene matrix. The melt enthalpy did not change significantly for the composites compared to pure polyethylene.

For nanocomposites with 2.8 vol% mineral loading the tensile modulus went up by 30%, while the yield stress stayed constant and the yield strain, stress at break and strain at break decreased.

The oxygen barrier was improved by more than 35%. The results of the preceding section could not be surpassed. Still, the tensile properties are similar or exceed those reported in literature.

Clays modified with alkylammonium ions, improved the barrier properties of the composites more than those modified with aromatic moieties.

In contrast to the last section, no correlation between the basal-plane spacing and the material properties was found, probably due the different chemical structure of the cations.
4.3 Ionically Bound Polymers

4.3.1 Polymerization to the Surface

In order to improve the miscibility of the polymer chains with the modified clay surface, it was suggested to modify the surface with polydisperse chains [129] or long chains [114]. In this way the effects of autophobicity and depletion, i.e., the repulsion and demixing of polymer chains with a chemically identical monolayer, can be reduced. For the purpose of improving the mixing of polymer chains and filler modification, we wanted to attach long alkyl chains to the surface. Geke et al. [22] reported the cation exchange of ammonium terminated poly(ethylene oxide) on mica.

In this section we describe the polymerization to the surface, in the next section the polymerization from the surface is described. In principle ethylene can be polymerized following two different mechanisms. The low pressure polymerization with Ziegler-Natta catalysts leads to mostly unbranched, long linear chains, i.e., high-density polyethylene (HDPE). The catalysts are highly active and each catalyst molecule leads to several polymer chains. With radical polymerization, ethylene is polymerized under high pressures (more than 1000 bar), leading to branched chains which are shorter than the chains of HDPE. The product, low-density polyethylene (LDPE), is less crystalline than HDPE because of the chain branching. The initiation is normally done with peroxide compounds, which stay as an endgroup of the polymer chain. If the pressure is less high for the radical polymerization, polyethylene wax is obtained, i.e., the chains are shorter. Nevertheless, in the presence of other polymerizable groups, ethylene can be radically copolymerized at low pressure [130]. The goal of the experiments in this section was to attach polymerizable groups to the surface of the clay, which can be radically copolymerized with ethylene, as shown in Figure 4.15. The surface modification was done via cation exchange with different ratios of polymerizable groups and alkyl ammonium salts. Consequently the polymerization was carried out in toluene or dioxane with ethylene under a pressure of 50 to 100 bar. Polymerization with styrene and octene was done under ambient pressure. Polymerization was initiated with a radical initiator, which stays as an end group at the propagating chain. A white paste was obtained, consisting of polymer, solvent and OM. Excess polymer was removed from the mineral via extraction and the OM was freeze-dried and sieved as usual. Then the composites were prepared via melt compounding as in the preceding sections. Polymerization reactions with similar filler modification but with a different monomer have been described in literature [131]. There, the surface was modified completely with a vinyl group containing cation. For this work different ratios of reactive and unreactive ammonium compounds were used in order to avoid that radicals, formed on the surface, react with the neighbor molecules attached to the surface.
Figure 4.15: Proposed mechanism of propagation to the surface, which leads to polyethylene chains attached to the surface. On the left the propagating ethylene chain with a phenyl end group and an active radical together with the vinyl ammonium on the mineral surface is shown. In the middle the propagating chain has reacted with the vinyl group, where the radical is located now. The propagation can then go on, following radical polymerization mechanism. The radical can react with another ethylene molecule, as shown on the right side, or with a neighbor vinyl group.

Nomenclature

The different systems studied are listed in Table 4.12. The number behind the first letter tells what fraction of the surface was covered with the vinyl compound with regard to the CEC of the mineral. The second letter is the first letter of the solvent, in which the reaction was carried out. The third letter is the first letter of the monomer and the following number gives the mineral volume percent in the composite.

Vinylbenzyldimethyldodecylammonium was used as vinyl group for the polymerization with ethylene and octene together with dimethyldiocatadecylammonium. For the polymerization of styrene, (ar-vinylbenzyl)trimethylammonium was used together with benzylhexadecyldimethylammonium. Dioxane and toluene were used as solvents.

Some of the nanocomposites contained large agglomerates, which could be observed by the naked eye. Those composites could not always be used for examination of the barrier properties, since foils of such materials contained holes. Furthermore, the composites with big agglomerates were very brittle. The two composites with mineral containing polystyrene, as well as the one with 50% vinyl groups on the surface, had agglomerates. As discussed already in the last section, montmorillonite containing aromatic groups on the surface does not disperse well in HDPE. This observation is confirmed here. The polystyrene chains decrease
4 Results and Discussion

Table 4.12: Nomenclature of the M880 composites. $\psi_V$ is the original vinyl content at the surface, $\phi_f$ is the filler volume fraction

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>$\psi_V$ [% of CEC]</th>
<th>Solvent</th>
<th>Monomer</th>
<th>$\phi_f$ [vol%]</th>
<th>Agglomerates</th>
</tr>
</thead>
<tbody>
<tr>
<td>V50-D-E-2.8(A)</td>
<td>50</td>
<td>Dioxane</td>
<td>Ethylene</td>
<td>2.8</td>
<td>Yes</td>
</tr>
<tr>
<td>V30-D-E-2.7</td>
<td>30</td>
<td>Dioxane</td>
<td>Ethylene</td>
<td>2.7</td>
<td>No</td>
</tr>
<tr>
<td>V10-D-E-2.0</td>
<td>10</td>
<td>Dioxane</td>
<td>Ethylene</td>
<td>2.0</td>
<td>No</td>
</tr>
<tr>
<td>V30-T-E-2.8</td>
<td>30</td>
<td>Toluene</td>
<td>Ethylene</td>
<td>2.8</td>
<td>No</td>
</tr>
<tr>
<td>V30-D-O-2.8</td>
<td>30</td>
<td>Dioxane</td>
<td>Octene</td>
<td>2.8</td>
<td>No</td>
</tr>
<tr>
<td>VB20-T-S-3.0(A)</td>
<td>20</td>
<td>Toluene</td>
<td>Styrene</td>
<td>3.0</td>
<td>Yes</td>
</tr>
<tr>
<td>VB10-T-S-3.0(A)</td>
<td>10</td>
<td>Toluene</td>
<td>Styrene</td>
<td>3.0</td>
<td>Yes</td>
</tr>
</tbody>
</table>

the compatibility between surface and matrix further, so that agglomeration of the filler takes place. The other composite with agglomerates was the one, with 50% vinyl groups on the surface. Since the surface was highly covered with vinyl groups, the vinyl groups of different layers may have reacted with each other. In this manner neighboring layers are chemically bound to each other, hence separation of the layers becomes hampered.

DSC

Table 4.13: Melt enthalpy $\Delta H_m$ and crystallinity of HDPE and its OM nanocomposites.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_m$ [J/g]</th>
<th>Cryst.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>202</td>
<td>0.69</td>
</tr>
<tr>
<td>2C18-M880 2.8vol %</td>
<td>203</td>
<td>0.69</td>
</tr>
<tr>
<td>V50-D-E-2.8(A)</td>
<td>213</td>
<td>0.73</td>
</tr>
<tr>
<td>V30-D-E-2.7</td>
<td>214</td>
<td>0.73</td>
</tr>
<tr>
<td>V10-D-E-2.0</td>
<td>210</td>
<td>0.72</td>
</tr>
<tr>
<td>V30-T-E-2.8</td>
<td>214</td>
<td>0.73</td>
</tr>
<tr>
<td>V30-D-O-2.8</td>
<td>210</td>
<td>0.72</td>
</tr>
<tr>
<td>VB20-T-S-3.0(A)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VB10-T-S-3.0(A)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4 Results and Discussion

In Table 4.13 the melting enthalpies and crystallinity of the nanocomposites is shown. Compared to the pure HDPE only a small increase is evident, which could be due to experimental errors. For the discussions of the properties in this section, we shall neglect the differences.

Morphology

Table 4.14: Amount of organic matter on the mineral after polymerization reaction and washing and the effect on the basal-plane spacing of M880.

<table>
<thead>
<tr>
<th></th>
<th>org. matter per gram mineral [g/g]</th>
<th>d$_{001}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V50-D-E-2.8(A)</td>
<td>0.466</td>
<td>2.31</td>
</tr>
<tr>
<td>V30-D-E-2.7</td>
<td>0.649</td>
<td>2.46</td>
</tr>
<tr>
<td>V10-D-E-2.0</td>
<td>0.579</td>
<td>2.38</td>
</tr>
<tr>
<td>V30-T-E-2.8</td>
<td>0.610</td>
<td>2.32</td>
</tr>
<tr>
<td>V30-D-O-2.8</td>
<td>0.506</td>
<td>2.34</td>
</tr>
<tr>
<td>VB20-T-S-3.0(A)</td>
<td>0.309</td>
<td>1.75</td>
</tr>
<tr>
<td>VB10-T-S-3.0(A)</td>
<td>0.288</td>
<td>1.71</td>
</tr>
</tbody>
</table>

Table 4.14 presents the basal-plane spacing and the amount of organic matter on the clay. The clay and the associated nanocomposite had x-ray reflections at the same positions, indicating that ordered stacks are still existent in the composite. The amount of organic material on the surface varies independent of the amount of reactive groups. This is probably due to different amounts of polymer on the filler surface. Nevertheless, it could not be determined how much polymer was attached to the surface and how much was intercalated. The basal-plane spacing of the unreacted clay of V50-D-E-2.8 was similar to the corresponding OM after polymerization and extraction.

Tensile properties

The tensile properties of the nanocomposites are displayed in Table 4.15. Tensile modulus increased by up to 35% for VB20-T-S-3.0(A), while the other systems exhibited an increase of around 20%. Yield strain decreased by 15% on average and stress at break by 50%. Yield stress went down between 1 and 2 MPa for all systems. The enhancement of the tensile properties exceed those reported by Su et al. [69]. They could improve the tensile modulus by 30% and 25%,
whereas yield stress deteriorated 15% and 25% for fillers modified with styrene and methacrylate oligomers, respectively. The filler loading was 15 wt%, and was modified with oligomers before compounding.

A closer inspection of the montmorillonite modification via polymerization reveals no clear influence of the polymerization conditions. The highest reinforcement was obtained with the montmorillonite with styrene as monomer for the polymerization, i.e., VB20-T-S-3.0(A), exceeding those of 2C18-M880. Nevertheless, the other nanocomposite containing filler polymerized in the presence of styrene, did not evidence such properties. Hence the large improvement of VB20-T-S-3.0(A) can not be assigned unambiguously to using a different monomer. Both composites with styrene as monomer for the polymerization contained large agglomerates, which could be observed by the naked eye. The influence of the solvent could not be clearly determined.

### Barrier properties

In Table 4.16 the oxygen permeability coefficient of the composites is shown. The composite containing filler polymerized in presence of octene, V30-D-O-2.8, showed the best improvement. Nevertheless, the differences are small and only tendencies can be seen. Remarkably, the nanocomposite with only 2 wt% filler

<table>
<thead>
<tr>
<th>Table 4.15: Tensile properties of HDPE and its OM nanocomposites.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>V30-D-E-2.8(A)</td>
</tr>
<tr>
<td>V10-D-E-2.0</td>
</tr>
<tr>
<td>V30-T-E-2.8</td>
</tr>
<tr>
<td>V30-D-O-2.8</td>
</tr>
<tr>
<td>VB20-T-S-3.0(A)</td>
</tr>
<tr>
<td>VB10-T-S-3.0(A)</td>
</tr>
</tbody>
</table>

*a*Relative probable error 5%.

*b*Relative probable error 2%.

*c*Relative probable error 4%.

*d*Relative probable error 10%.

*e*The range of measured values is given.
## Results and Discussion

### Table 4.16: Oxygen permeability coefficient of HDPE and its OM nanocomposites.

The composites with no data listed, had holes in the foils for permeation measurements.

<table>
<thead>
<tr>
<th></th>
<th>$p_{O_2}$ [^{a}]</th>
<th>[cm$^3$ (\mu\text{m}/(m^2 \cdot \text{day} \cdot \text{mmHg})]]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>2C18-M880 2.8vol%</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>V50-D-E-2.8(A)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>V30-D-E-2.7</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>V10-D-E-2.0</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>V30-T-E-2.8</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>V30-D-O-2.8</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>VB20-T-S-3.0(A)</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>VB10-T-S-3.0(A)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Relative probable error 8%.

had similar barrier properties like the composites with 2.8 wt%.

The composites with holes in the foils for permeation measurements were those with large agglomerates, except VB20-T-S-3.0(A), which also exhibited the highest tensile modulus.

### Summary

Polymerization reactions have been carried out in the presence of montmorillonite carrying polymerizable groups. Systems with fillers polymerized in the presence of styrene, as well as the one with 50% vinyl groups polymerized in the presence of ethylene, contained large agglomerates. Nevertheless, the montmorillonite containing 30% vinyl groups and polymerized in the presence of styrene led to the nanocomposite with highest elastic modulus, although it contained large agglomerates.

The properties of materials presented here exceed those reported in the literature for composites prepared with a similar approach.

No dependence or correlation between the reaction conditions, the monomer and the nanocomposites could be found.
4.3.2 Polymerization from the Surface

In this section we attempted to attach polymer chains to the silicate surface via polymerization from the surface. A scheme of the polymerization reaction is shown in Figure 4.16. A monocationic peroxide initiator was attached to the surface, whereas in the last section the initiator was dissolved in the solvent. Fan et al. [132] discussed the advantage of monocationic initiator compared to bicationic initiators. The initiator is thermally activated and two radicals are formed, one of which is attached to the silicate layer surface. Hence, after initiation of the polymerization reaction with this radical, the chain stays attached to the mineral. Similar reactions but with different monomers have been described in the literature [27–31,132]. In the experiments presented here, the ethylene pressure used for the polymerization was between 50 and 200 bars. Under these conditions no long polyethylene chains can be obtained. This is not undesirable, as it was not our goal to attach chains with very high molecular weight to the surface. After polymerization the reaction slurry was extracted with xylene in order to remove the unbound polymer. The OM obtained was then suspended in dioxane and freeze-dried as described in the sections before.

![Figure 4.16: Proposed initiation which leads to polyethylene chains attached to the surface. On the left the initiator attached to the silicate surface via cation exchange is displayed. Through thermal activation, the initiator decomposes and two radicals are formed as shown in the middle left. The radical which is attached to the silicate leads to polymers attached to the surface. The proposed propagation is drawn on the right side of the figure.](image)

**Nomenclature**

The nomenclature of the composites is shown in table 4.17. It follows the same scheme as in last section. Comparable to the compound which contained 50% vinyl groups on the surface in the last section, the composite with the filler with 50% initiator contained agglomerates.
Table 4.17: Nomenclature of the M880 composites. \( \psi_I \) is the initiator content, \( \phi_f \) is the mineral filler fraction

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>( \psi_I ) [% CEC]</th>
<th>Solvent</th>
<th>Monomer</th>
<th>( \phi_f ) [vol%]</th>
<th>Agglomerates</th>
</tr>
</thead>
<tbody>
<tr>
<td>I50-D-E-2.8(A)</td>
<td>50</td>
<td>Dioxane</td>
<td>Ethylene</td>
<td>2.8</td>
<td>Yes</td>
</tr>
<tr>
<td>I30-T-E-2.8</td>
<td>30</td>
<td>Toluene</td>
<td>Ethylene</td>
<td>2.8</td>
<td>No</td>
</tr>
<tr>
<td>I30-D-O-2.8</td>
<td>30</td>
<td>Dioxane</td>
<td>Octene</td>
<td>2.8</td>
<td>No</td>
</tr>
</tbody>
</table>

DSC

Table 4.18: Melt enthalpy \( \Delta H_m \) and crystallinity of HDPE and its OM nanocomposites.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H_m ) [J/g]</th>
<th>cryst.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>202</td>
<td>0.69</td>
</tr>
<tr>
<td>2C18-M880 2.8vol%</td>
<td>203</td>
<td>0.69</td>
</tr>
<tr>
<td>I50-D-E-2.8(A)</td>
<td>211</td>
<td>0.72</td>
</tr>
<tr>
<td>I30-T-E-2.8</td>
<td>216</td>
<td>0.74</td>
</tr>
<tr>
<td>I30-D-O-2.8</td>
<td>216</td>
<td>0.74</td>
</tr>
</tbody>
</table>

The melting enthalpy and crystallinity of the compounds are presented in Table 4.18. As before, it did not change significantly, so that the different properties can be attributed to the filler.

Morphology

X-ray diffraction data appear in Table 4.19. The basal-plane spacing of the modified clay before compounding and in the composite did not change. Hence, in the composite we can still observe ordered structures of non-delaminated silicate sheets.

In the same table the amount of organic matter is presented. It is highest for the nanocomposite with the clay polymerized in the presence of octene. The same material also has the highest basal-plane spacing. Still, the differences are too small to make any conclusions. It is also unclear from the results to which degree the polymerization reaction took place on the surface.
Table 4.19: Amount of organic matter on the mineral after polymerization reaction and washing and the effect on the basal-plane spacing of M880.

<table>
<thead>
<tr>
<th></th>
<th>org. matter per gram mineral [g/g]</th>
<th>$d_{001}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I50-D-E-2.8(A)</td>
<td>0.355</td>
<td>2.41</td>
</tr>
<tr>
<td>I30-T-E-2.8</td>
<td>0.451</td>
<td>2.21</td>
</tr>
<tr>
<td>I30-D-O-2.8</td>
<td>0.474</td>
<td>2.48</td>
</tr>
</tbody>
</table>

Mechanical Properties

The tensile properties of the composites are shown in table 4.20. The nanocomposite with the filler polymerized using ethylene demonstrated a higher tensile modulus than to the one polymerized with octene. The increase was about 25% compared to the pure HDPE. The yield strain decreased by 15% and stress at break by up to 60%. The properties are similar to those of the nanocomposite with 2C18-M880 at a filler fraction of 0.028 (provided in the same table for comparison). Taking this into account, it is questionable if the attachment of PE chains to the silicate surface was successful. For a large number of long chains attached to the surface, further improvement of the tensile properties can be expected.

Nevertheless, we found our results comparable to those reported using an analogue approach [69].

Table 4.20: Tensile properties of HDPE and its OM nanocomposites.

<table>
<thead>
<tr>
<th></th>
<th>$E$ [MPa]</th>
<th>$\sigma_Y$ [MPa]</th>
<th>$\varepsilon_Y$ [%]</th>
<th>$\sigma_B$ [MPa]</th>
<th>$\varepsilon_B$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>1020</td>
<td>26</td>
<td>9.6</td>
<td>36</td>
<td>1180-1750</td>
</tr>
<tr>
<td>2C18-M880 2.8vol %</td>
<td>1270</td>
<td>26</td>
<td>7.6</td>
<td>21</td>
<td>780-1230</td>
</tr>
<tr>
<td>I50-D-E-2.8(A)</td>
<td>1140</td>
<td>26</td>
<td>7.6</td>
<td>14</td>
<td>70-890</td>
</tr>
<tr>
<td>I30-T-E-2.8</td>
<td>1270</td>
<td>25</td>
<td>8.1</td>
<td>13</td>
<td>70-840</td>
</tr>
<tr>
<td>I30-D-O-2.8</td>
<td>1160</td>
<td>26</td>
<td>8.1</td>
<td>16</td>
<td>120-980</td>
</tr>
</tbody>
</table>

-aRelative probable error 5%.
bRelative probable error 2%.
cRelative probable error 4%.
dRelative probable error 10%.
eThe range of measured values is given.
Barrier Properties

The oxygen permeability coefficient of the composites is shown in table 4.16, the improvement was similar to the one of 2C18-M880 at a filler fraction of 0.028. With a decrease of around 35% I30-D-O-2.8 had the lowest (best) permeability. As discussed for the tensile properties, the success of the polymerization reaction is unclear, as we expected further improvement.

Table 4.21: Oxygen permeability coefficient of HDPE and its M880 nanocomposites. The foils of the composite without a value contained holes.

<table>
<thead>
<tr>
<th></th>
<th>$p_{O_2}$ $[cm^3 \cdot \mu m/(m^2 \cdot day \cdot mm Hg)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>54</td>
</tr>
<tr>
<td>2C18-M880 2.8vol%</td>
<td>37</td>
</tr>
<tr>
<td>I50-D-E-2.8(A)</td>
<td>-</td>
</tr>
<tr>
<td>I30-T-E-2.8</td>
<td>37</td>
</tr>
<tr>
<td>I30-D-O-2.8</td>
<td>35</td>
</tr>
</tbody>
</table>

$a$Relative probable error 8%.

Comparable to the last section, the material with filler containing 50% functionalization, contained agglomerates and led to foils for the permeation measurements with holes.

Note the barrier of these nanocomposites is higher, than those with Polymerization to the surface.

Summary

Polymerization reactions were carried out, initiated with an initiator ionically bound to the surface of silicate layers. For composites with fillers covered with 30% initiator, the barrier properties were improved by around 35% and the tensile modulus around 25%. As in the last section, no correlation with the reaction conditions was noticed.
4.4 Effect of Copolymers as Additives

4.4.1 Influence of the Chemical Structure

In this last section of Results and Discussion we focus not on the influence of the surface modification of the layered silicate, but on the influence of copolymers as additives to a system described earlier, i.e. a nanocomposite with 2C18-M880. It is known, that polymers do not mix easily with surface-attached chains, even if they are chemically identical [133, 134]. The miscibility can be enhanced when the packing density of the alkyl chains is reduced, or when chains with different lengths are attached to the surface. Long chains can be attached to the surface in the form of copolymers. The polar part of the copolymer can be adsorbed on the surface via physisorption, while the nonpolar part serves to match the free energy of polymer. In this chapter the influence of copolymers on the properties of polyethylene nanocomposites is reported. In a first step nanocomposites were synthesized with an already commercially treated montmorillonite using a series of copolymers. Of those we chose four copolymers for further investigation, based on the basal-plane spacing and reports in literature. These compounds were synthesized with a home surface modified montmorillonite, 2C18·M880.
Results and Discussion

PE-block-PEG Random PE Copolymer modified montmorillonite

Figure 4.18: Proposed adsorption of block-copolymers and random-copolymers at the surface of OM in the polymer melt. The polar block of the block copolymer PE-PEG MN 575 is adsorbed on the surface. It consists of 3-5 repeat units of ethylene oxide. The alkyl block, containing approximately 32 CH$_2$ groups, dangles from the surface. Whereas the random copolymer has some polar groups that may be adsorbed to the surface of several mineral sheets, due to the high molecular weight of the polymer.

Preliminary Experiments

The basal-plane spacing determined using WAXD measurements of the nanocomposites with additives containing a commercially treated montmorillonite, Tixogel VP, are shown in Table 4.22. The structures of the copolymers appear in Figure 4.17. The compounds were synthesized with a OM to copolymer ratio of 1:1 in order to have a pronounced effect on the basal-plane spacing. The copolymers are sorted by increasing basal-plane spacing of the corresponding nanocomposite. The highest increase was observed for polyethylene-block-polyethylene glycol, the lowest one for polyethylene-graft-(maleic anhydride). In Section 4.1 we observed a correlation between interlayer distance and material properties of the composites. For this reason we selected the copolymers for a more detailed study on a basis of the interlayer distance in the nanocomposite.

Polyethylene-block-polyethylene glycol was the only block copolymer used for in study. We tested it with two different molecular weights. The blockcopolymer with the lower molecular weight showed a stronger influence on the basal-plane spacing. Accordingly, we investigated it more closely. Besides block copolymers, with a short polar block and a long nonpolar block, like the PE-block-PEG used for this study, were proposed by Balazs et al. [135] as optimal exfoliating agent. Poly[ethylene-co-(methacrylic acid)] was also chosen for its influence on the interlayer distance. Since much work has been published with polyethylene-graft-
Table 4.22: Effect of different copolymers on the basal-plane spacing of VP at 1.8 vol% additive and 1.8 vol% inorganic filler loading.

<table>
<thead>
<tr>
<th>copolymer</th>
<th>(d_{001} \text{ [nm]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>no copolymer</td>
<td>2.50</td>
</tr>
<tr>
<td>Polyethylene-block-polyethylene glycol, Mn 575</td>
<td>3.83</td>
</tr>
<tr>
<td>Polyethylene-block-polyethylene glycol, Mn 875</td>
<td>3.64</td>
</tr>
<tr>
<td>Poly[ethylene-co-(methacrylic acid)],</td>
<td>3.55</td>
</tr>
<tr>
<td>Poly[ethylene-co-(acrylic acid)] (10% acrylic acid)</td>
<td>3.54</td>
</tr>
<tr>
<td>Poly[ethylene-co-(acrylic acid)] (5% acrylic acid)</td>
<td>3.41</td>
</tr>
<tr>
<td>Polyethylene oxidized</td>
<td>3.52</td>
</tr>
<tr>
<td>Poly(ethylene-co-butylene) mono-ol</td>
<td>3.25</td>
</tr>
<tr>
<td>Poly(ethylene-co-octene)-graft-(maleic anhydride)</td>
<td>3.32</td>
</tr>
<tr>
<td>Poly[ethylene-co-(vinyl alcohol)]</td>
<td>3.21</td>
</tr>
<tr>
<td>Poly(ethylene-co-trialkoxyvinylsilane)</td>
<td>3.18</td>
</tr>
<tr>
<td>Polyethylene-\textit{graft}-(maleic anhydride)</td>
<td>3.10</td>
</tr>
</tbody>
</table>

(maleic anhydride) as additive or even as matrix, it was an obvious choice despite the poor widening of the basal-plane spacing. A fourth copolymer, poly[ethylene-co-(vinyl alcohol)], also often used in the literature, was included. Nanocomposites with 2C18-M880 as filler were prepared using the four chosen copolymers. We adjusted the amount of filler to make the results comparable with the findings of the last sections. The results of these four nanocomposites are presented below.

**WAXD**

Table 4.23 shows the interlayer distances of the HDPE nanocomposites containing the selected copolymers and 2C18-M880, as well as the abbreviations used in the following text. As the nanocomposites contain more inorganic filler, compared to the ones in the Preliminary Studies, the ratio between copolymer and montmorillonite is shifted towards montmorillonite. The amount of copolymer which is available to intercalate between the mineral sheets decreases relatively. Hence, the increase in basal-plane spacing is less than for the composites shown in Table 4.22. The nanocomposite containing P(E-VOH), show a relatively high increase of the interlayer distance compared to the other composites. A similar basal-plane spacing was reported using P(E-VOH) as matrix by Artzi et al. [76]. The reason may be the large amount of OH groups in the copolymer (see Table...
Table 4.23: Effect of selected copolymers on the basal-plane spacing of 2C18-M880 nanocomposites at 1.7 wt% copolymer and 2.8 vol% inorganic filler loading and the abbreviation of the copolymers.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>d_{001} [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>no copolymer</td>
<td>2.51</td>
</tr>
<tr>
<td>Polyethylene-block-polyethylene glycol, Mn 575</td>
<td>2.86</td>
</tr>
<tr>
<td>Poly[ethylene-co-(methacrylic acid)]</td>
<td>2.71</td>
</tr>
<tr>
<td>Poly[ethylene-co-(vinyl alcohol)]</td>
<td>3.05</td>
</tr>
<tr>
<td>Polyethylene-graft-(maleic anhydride)</td>
<td>2.43</td>
</tr>
</tbody>
</table>

The OH group is polar and adsorbs on the silicate surface, hence, the interlayer distance is increased.

DSC

Table 4.24: Melt enthalpy $\Delta H_m$ and crystallinity of HDPE and its 2.8 vol% 2C18-M880 nanocomposites with 1.7 wt% copolymer additive.

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>no copolymer</th>
<th>PE-PEG</th>
<th>P(E-MAA)</th>
<th>P(E-VOH)</th>
<th>PE-MA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_m$ [J/g]</td>
<td>202</td>
<td>203</td>
<td>207</td>
<td>218</td>
<td>216</td>
<td>212</td>
</tr>
<tr>
<td>Cryst.</td>
<td>0.69</td>
<td>0.69</td>
<td>0.71</td>
<td>0.74</td>
<td>0.74</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Looking at the melting enthalpies in Table 4.24, a small increase is apparent for all nanocomposites containing copolymer. Still, it is hard to conclude anything from this data, as all copolymers have thermal transitions at different temperatures and with different $\Delta H$. Hence, the data in Table 4.24 represent a rough estimation of the real melt enthalpy of the polyethylene in the nanocomposites.

Tensile properties

The tensile properties of the nanocomposites with different copolymers are reported in Table 4.25. For all systems containing copolymers the stress at break decreased significantly, whereas yield strain and yield stress exhibited only a small decrease. The tensile modulus of the nanocomposites with copolymer additive showed a decrease, compared to the one containing only mineral filler and became close to the value of pure HDPE. An exception was the one containing PE-PEG with an improvement of 30%, more reinforced than the one without copolymer. This means that all copolymers act as plasticizer in the composite, except for
the blockcopolymer PE-PEG. We suggest that the PEG block of PE-PEG is adsorbed completely to the surface of the mineral, whereas the random copolymers still have polar groups exposed to the polyethylene matrix, as proposed in Figure 4.18.

Table 4.25: Tensile properties for 2C18-M880 nanocomposites at 2.8 vol% inorganic and 1.7 wt% copolymer fraction.

<table>
<thead>
<tr>
<th></th>
<th>$E^{a}$ [MPa]</th>
<th>$\sigma_{Y}^{b}$ [MPa]</th>
<th>$\varepsilon_{Y}^{c}$ [%]</th>
<th>$\sigma_{B}^{d}$ [MPa]</th>
<th>$\varepsilon_{B}^{e}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>1020</td>
<td>26</td>
<td>9.6</td>
<td>36</td>
<td>1180-1750</td>
</tr>
<tr>
<td>no copolymer</td>
<td>1270</td>
<td>26</td>
<td>7.6</td>
<td>21</td>
<td>780-1230</td>
</tr>
<tr>
<td>PE-PEG</td>
<td>1320</td>
<td>25</td>
<td>8.1</td>
<td>17</td>
<td>250-1100</td>
</tr>
<tr>
<td>P(E-MAA)</td>
<td>1080</td>
<td>25</td>
<td>8.4</td>
<td>14</td>
<td>70-1230</td>
</tr>
<tr>
<td>P(E-VOH)</td>
<td>1080</td>
<td>23</td>
<td>7.9</td>
<td>15</td>
<td>20-990</td>
</tr>
<tr>
<td>PE-MA</td>
<td>1030</td>
<td>25</td>
<td>8.9</td>
<td>15</td>
<td>920-1520</td>
</tr>
</tbody>
</table>

$^{a}$Relative probable error 5%.

$^{b}$Relative probable error 2%.

$^{c}$Relative probable error 4%.

$^{d}$Relative probable error 10%.

$^{e}$The range of measured values is given.

Except for the nanocomposite with PE-PEG our samples did not achieve the tensile property enhancement reported by other groups [72, 74, 81, 83, 89]. The discrepancy probably arises because we used only small amounts of copolymers, whereas the authors of [72, 74, 89] used, for instance polyethylene-co-(vinyl acetate), containing up to 15 to 27 wt% vinyl acetate, as a matrix. The composite with PE-MA contained only 1.8 wt% polyethylene-graft-(maleic anhydride), compared to materials with the whole matrix consisting of PE-MA, enhancing the tensile modulus by 10-30% [81, 83].
Figure 4.19: Basal-plane spacing plotted against the tensile properties of 2.8 vol% 2C18-M880 nanocomposites containing 1.7 wt% of different copolymers. The dotted lines are only a guide to the eyes.
In Figure 4.19, the tensile properties of the composites are plotted versus the basal-plane spacing. The yield strain correlates clearly with the interlayer distance. The graphs of the other tensile properties emphasize the different influence of PE-PEG on the material. It exhibited an improvement which is not consistent with the behavior of the other copolymers. For the systems incorporating random copolymers the tensile properties correlate with the basal-plane spacing. PE-PEG as blockcopolymer does not follow this rule, as its chemistry of the polymer chain is different. In contrast to the random copolymers, all polar groups are located at one end of the macromolecule. This causes a different adsorption behavior as discussed above and presented in Figure 4.18.

**Barrier Properties**

**Table 4.26:** Oxygen permeability coefficient for 2C18-M880 nanocomposites at 2.8 vol% inorganic and 1.7 wt% copolymer fraction.

<table>
<thead>
<tr>
<th></th>
<th>$pO_2$ [cm$^3$ $\cdot$ $\mu$m/(m$^2$) $\cdot$ day $\cdot$ mmHg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>54</td>
</tr>
<tr>
<td>no copolymer</td>
<td>37</td>
</tr>
<tr>
<td>PE-PEG</td>
<td>31</td>
</tr>
<tr>
<td>P(E-MAA)</td>
<td>32</td>
</tr>
<tr>
<td>P(E-VOH)</td>
<td>36</td>
</tr>
<tr>
<td>PE-MA</td>
<td>33</td>
</tr>
</tbody>
</table>

$^a$Relative probable error 8%.

The oxygen permeability coefficients are displayed in Table 4.26. All nanocomposites with copolymers exhibit improved barrier properties compared to PE as well as to the nanocomposite with the same filler but without copolymer additive. For the material containing PE-PEG the improvement is more than 40% compared to pure HDPE and close to 20% compared to the nanocomposite containing the same filler but no copolymer. These results are, except for PE-PEG, in strong contrast to the tensile properties which deteriorated. Apparently the copolymers help to disperse and delaminate the clay sheets in the HDPE matrix, but act at the same time as a plasticizer. P(E-VOH) has the weakest influence on the oxygen permeability coefficient, although its influence on the interlayer distance is the strongest of all copolymers. There is no evidence of a correlation between the oxygen permeability coefficient and the basal-plane
spacing for the different copolymers, as seen for the mechanical properties.

In a report presented by Kato et al. [84], the nitrogen permeability with a nanocomposite containing 30 wt% PE-MA and 5.4 wt% inorganic filler loading decreased by 30% compared to PE. All nanocomposites with copolymer additives used in this study improved the barrier properties by 40%, except the one with P(E-VOH) showing an enhancement of 30%. Moreover these superior results were reached at a copolymer weight fraction of only 0.017.

**Summary**

A series of polyethylene clay nanocomposites with copolymers as additives was prepared and their basal-plane spacing measured. Of those, four systems were investigated more closely.

As for the composites described in the previous sections, the crystallinity did not change significantly compared to pure HDPE, nor for the one without copolymer additive.

All nanocomposites showed an increase of the interlayer distance compared to the composite without copolymer. The tensile properties deteriorated for all nanocomposites with copolymer except of the one with PE-PEG. In contrast all systems had better barrier properties in comparison to the composite without additive. The improvement was up to 40% compared to HDPE and 20% with respect to the composite without copolymer. The barrier properties exceeded those reported in literature, although the concentration of copolymer additive was sixteen times lower.

PE-PEG has a positive influence on the barrier as well as on the elastic modulus, it was the clear choice for further experiments. The positive influence of block copolymers on the exfoliation, proposed by Balazs, Singh and Zhulina [136] could be confirmed.
4.4.2 Polyethylene-block-Polyethylene Glycol

In the preceding section we looked at the influence of different copolymers on the properties of clay nanocomposites. Out of the examined copolymers, PE-PEG led to the best results. Here the influence of PE-PEG was studied further.

In addition to the nanocomposites shown in tables, one composite with PE-PEG as copolymer and BenzC16-M880 as filler was synthesized. The experiment was repeated three times, but each time agglomerates were observed. Hence, these composites were not examined further. This is consistent with the results of the Section 4.2 and 4.3. It was shown there, that surface modification containing aromatic groups have a negative influence on the barrier properties. In Section 4.3 the composites with fillers containing polystyrene on the surface had agglomerates.

**Morphology**

A concentration series with 2.8 vol% 2C18 · M880 and different amounts of PE-PEG, as well as a polymer blend of PE-PEG and HDPE without filler was synthesized. The influence of different PE-PEG content on the basal-plane spacing appears in Table 4.27. With increasing PE-PEG content, the interlayer distance increases. The dependence in the range examined is nearly linear, as Figure 4.22 reveals. The increase of basal-plane spacing indicates, that with increasing amount of PE-PEG, more copolymer is incorporated between the silicate sheets.

<table>
<thead>
<tr>
<th>PE-PEG \ [wt%]</th>
<th>(d_{001}) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.51</td>
</tr>
<tr>
<td>1.7</td>
<td>2.86</td>
</tr>
<tr>
<td>3.4</td>
<td>3.12</td>
</tr>
<tr>
<td>6.9</td>
<td>3.63</td>
</tr>
</tbody>
</table>

In Figure 4.20, TEM images of a composite with and without 3.4 wt% PE-PEG are shown. The image on the left, with PE-PEG, shows many more delaminated layers than the picture on the right (without copolymer). Stacks of layers were also observed in the TEM micrographs of nanocomposites with PE-PEG, which are not displayed here. Those are responsible for the signal in...
4 Results and Discussion

Figure 4.20: The TEM image on the left was taken from a composite containing 3.4 wt% PE-PEG and 2.8 vol% M800 modified with 2C18. The composite of the right image contained the same amount of 2C18-M880, but no PE-PEG.

WAXD listed in Table 4.27. However, delamination of the layered silicate was much less in those nanocomposites without copolymer additive.

The images clearly show, that the PE-PEG directly influences the delamination of the clay and that this improved delamination, and not the copolymer itself, alter the properties of the composite.

The silicate sheets were not aligned in the composite with PE-PEG on the nanometer scale, as observed for nanocomposites without copolymer additives in section 4.1.1. On a larger scale, we could observe a preferential orientation, similar to those shown in Figure 4.4. We conclude that the copolymer improves the delamination, but does not influence the orientation.

Tensile Properties

The results of the tensile testing are given in Table 4.28. With increasing amount of PE-PEG the tensile modulus and the yield stress increase, while the yield strain decreases. Stress at break goes down with addition of PE-PEG, but then increases with further addition above 1.7 wt%. In comparison to pure HDPE, the tensile modulus could be improved by 60% at 6.9 wt% PE-PEG content, this is an increase of 35%, compared to the nanocomposite without copolymer. Nevertheless, the material with 6.9 wt% PE-PEG is very brittle, and the ultimate elongation is very small. The transition from rigid and still ductile and rigid to brittle can be observed between 3.4 and 6.9 wt% PE-PEG.
Table 4.28: Tensile properties of HDPE and its 2.8 vol% 2C18-M880 nanocomposites with different PE-PEG content.

<table>
<thead>
<tr>
<th>PE-PEG [wt%]</th>
<th>$E^{a}$ [MPa]</th>
<th>$\sigma_{Y}^{b}$ [MPa]</th>
<th>$\varepsilon_{Y}^{c}$ [%]</th>
<th>$\sigma_{B}^{d}$ [MPa]</th>
<th>$\varepsilon_{B}^{e}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>1020</td>
<td>26</td>
<td>9.6</td>
<td>36</td>
<td>1180-1750</td>
</tr>
<tr>
<td>3.4, no filler</td>
<td>1060</td>
<td>26</td>
<td>11.4</td>
<td>35</td>
<td>1530-1610</td>
</tr>
<tr>
<td>0.0</td>
<td>1270</td>
<td>26</td>
<td>7.6</td>
<td>21</td>
<td>780-1230</td>
</tr>
<tr>
<td>1.7</td>
<td>1320</td>
<td>25</td>
<td>8.1</td>
<td>17</td>
<td>70-1190</td>
</tr>
<tr>
<td>3.4</td>
<td>1450</td>
<td>28</td>
<td>7.2</td>
<td>19</td>
<td>960-1120</td>
</tr>
<tr>
<td>6.9</td>
<td>1620</td>
<td>29</td>
<td>6.9</td>
<td>28</td>
<td>0-10</td>
</tr>
</tbody>
</table>

$^{a}$Relative probable error 5%.
$^{b}$Relative probable error 2%.
$^{c}$Relative probable error 4%.
$^{d}$Relative probable error 10%.
$^{e}$The range of measured values is given.

The polymer blend with 3.4 wt% PE-PEG and HDPE, without clay, revealed properties similar to pure HDPE. This tells us, that the improvement of the nanocomposites is not caused by the PE-PEG, but by its delaminating effect on the clay. PE-PEG alone could not to improve the properties of HDPE, but its interaction with the modified montmorillonite leads to the tensile properties enhancement.

A literature search yielded one report only, where the addition of PE-PEG to PE nanocomposites improved the tensile modulus by 35% for 3 wt% filler [137] compared to the system without copolymer. Nevertheless, no value for the pure matrix was given and also the composition of the composites is unclear.

In Figure 4.21, the correlation between the tensile properties, the PE-PEG content and the interlayer distance. The deviations of the nanocomposite with a mineral fraction of 0.018 are well within the experimental error. The correlation is consistent with the results of section 4.1. For PE-PEG it is similar: the properties alter in correlation with the d-spacing. This result can be very useful for the design of nanocomposites. Instead of measuring all properties, the basal-plane spacing can be taken as an indicator. That both interlayer distance and PE-PEG content correlate in the same way with the tensile properties can be explained by the correlation among themselves as shown on the right side of Figure 4.22.
Figure 4.21: On the left side of the graph the dependence of the tensile properties on the copolymer content is plotted, on the right side the correlation with the basal-plane spacing.
Barrier Properties

Table 4.29: Oxygen permeability coefficient for 2C18-M880 nanocomposites at 2.8% inorganic volume fraction and different PE-PEG content.

<table>
<thead>
<tr>
<th>Copolymer fraction [wt%]</th>
<th>$p_{O_2}^a$ [cm³·μm/(m²·day·mmHg)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure HDPE</td>
<td>54</td>
</tr>
<tr>
<td>3.6 no filler</td>
<td>53</td>
</tr>
<tr>
<td>0</td>
<td>37</td>
</tr>
<tr>
<td>1.7</td>
<td>31</td>
</tr>
<tr>
<td>3.4</td>
<td>27</td>
</tr>
<tr>
<td>6.9</td>
<td>23</td>
</tr>
</tbody>
</table>

*aRelative probable error 8%.

In Table 4.29, the oxygen permeability coefficient is listed for the nanocomposites with different PE-PEG content. Similar to the tensile properties the barrier properties are improved by up to nearly 60% for the highest PE-PEG loading compared to pure HDPE and up to 40% compared to the composite without copolymer. The barrier properties correlate with the PE-PEG content and hence with the interlayer distance as shown in Figure 4.22. The improvement levels off at higher concentration. One possible explanation is, that with increasing amount of PE-PEG more and more clay is delaminated. After a certain point, the degree of delamination is so high, that it does not correlate linearly anymore with the amount of PE-PEG. However, we still observe a signal with WAXD, indicating that there are still some intercalated tactoids. Compared to the report presented by Kato et al. [84], where a reduction of nitrogen permeability by 30% with 5.4wt% filler and 30 wt% copolymer additive was observed, we could improve the gas barrier by 60% at 6.9 wt% copolymer additive. With only 3.4 wt% copolymer the barrier was enhanced by 50% and in addition the material was still ductile.

Summary

Different composites with PE-PEG additive were prepared. The gas barrier properties and elastic modulus could be improved by close to 60% for the nanocomposite with 6.9 wt% PE-PEG. With 3.4wt% the enhancement was only slightly smaller, but the material was still ductile. The material properties exceed those reported elsewhere. Furthermore, compared to reports in literature better results
Figure 4.22: The upper graph shows the correlation between barrier properties and PE-PEG content, below, the dependence of the interlayer distance on the copolymer content is plotted.
were achieved with low copolymer fractions. The blend containing 3.4 wt% PE-PEG and no mineral filler did not exhibit properties significantly different from pure HDPE. Hence, the properties of the nanocomposites did not change because of the presence of PE-PEG itself, but because of its interaction with the filler which led to delamination, as demonstrated by the TEM images.
5 Conclusions

New materials with enhanced gas-barrier and tensile properties were successfully synthesized. With a mineral volume fraction of only 0.028, the barrier properties and the elastic modulus were improved by 40%, the nanocomposites containing small additional amounts of block copolymer were further enhanced by up to 60% with respect to the matrix.

The crystallinity of all nanocomposites presented in this work is similar to that of pure HDPE - the OM does not significantly nucleate the polymer crystallization. Hence, the improvement of the material properties can not be assigned to an increased crystallinity. We demonstrated that dispersion, delamination and orientation of the montmorillonite platelets are the source of enhancement.

In section 4.1 we investigated the influence of the packing density of alkyl chains on the layered silicate and the surface coverage. We reported the synthesis of nanocomposites with tensile and barrier properties exceeding those reported in literature. It was found that the surface coverage and the interlayer distance play an important role for the properties of the nanocomposites. The material properties improved with increasing surface coverage as well as with increasing interlayer distance. A linear correlation between the tensile modulus and oxygen permeability was observed, suggesting that both depend on the delamination and alignment of the filler.

For chemically different structure of the organic cations, the basal-plane spacing and the mechanical properties do not correlate. We conclude that this behavior is only valid for organic cations with chemically identically tails.

Modifying the layered silicate using cations with alkyl tails led to materials with better barrier properties than cations with aromatic substituents. Aromatic groups have a negative influence on the dispersion and exfoliation of the clay in HDPE.

Theoretical predictions can only be used with caution, as the complex morphology, which we observed with TEM and WAXD, is not accurately described in the theoretical models. A scale dependence of the orientation of the filler was observed.
Increasing the amount of filler ameliorate most nanocomposite properties, following a linear dependence for small filler contents which levels off at higher contents. The stress and strain at break decrease with increasing filler content. The concentration dependence of the barrier properties qualitatively followed predictions of Gusev and Lusti as well as of Nielsen, however misalignment on the nanometer scale and incomplete delamination led to higher permeability coefficients.

The dispersion of the filler in the matrix is crucial. Fine-grained minerals are easier to disperse in the polymer. We were able to improve the nanocomposite properties remarkably, when the filler was freeze-dried before compounding.

Polymerizing ethylene, octene and styrene in the presence of surface modified montmorillonite under the conditions used in this study did not improve the properties of the nanocomposite, compared to nanocomposites containing commonly modified layered silicates.

Adding only small amounts of random copolymers improves the barrier properties but deteriorates the tensile properties compared to nanocomposites without additive.

The addition of PE\textit{-block\textendash}PEG has a positive influence on both, tensile and barrier properties, exceeding those reported in literature. We propose as a reason for the different influence of random and block copolymers, that the latter adsorbs differently on the clay surface as a result of differing chemical structures and molecular weights.
6 Experimental

6.1 Synthesis

6.1.1 Ammonium Salts

**Vinylbenzyldimethyldodecylammonium chloride (VDAC)**

[131] 4.22 ml 30 mmol vinylbenzyl chloride (Aldrich) was added dropwise to 12.2 ml, 45 mmol dimethyldodecylamine (Aldrich) dissolved in 100 ml diethyl ether (Aldrich) under stirring. The solution was stored at room temperature for 3 d. The precipitate was filtered, washed with dry diethyl ether and dried in vacuum at ambient temperature. The product, a white powder, was recrystallized from ethyl acetate (Aldrich).

$^1$H NMR (CDCl$_3$): $\delta=7.50$ (q, 4H, $\text{-C}_6\text{H}_4$); 6.70 (q, 1H, $\text{CH}_2=\text{CH}$); 5.75 (d, 1H, $\text{CH(cis)}=\text{CH}$); 5.30 (d, 1H, $\text{CH(trans)}=\text{CH}$); 5.02 (s, 2H, $\text{-C}_6\text{H}_4\text{-CH}_2$); 3.45 (m, 2H, $\text{-N(CH}_3\text{)}_2$); 3.24 (s, 6H, $\text{-N(CH}_3\text{)}_2$); 1.75, 1.20 (m, 20H, $\text{-CIV}$)

**Figure 6.1:** Reaction scheme for vinylbenzyldimethyldodecylammonium chloride

![](image)

**[4-(tert-butyldioxy)hexyl]trimethylammonium bromide (IniC6)**

[31]

A: 1,6-dibromohexane (Aldrich) (43.19 g, 200 mmol) was dissolved in 500 ml of dry diethyl ether (Aldrich). Cooled to 0°C, trimethylamine (Aldrich) (33% in ethanol, 4.2 M, 10 ml, 40 mmol) was added, and the mixture was stored for 3 days in the dark at room temperature. The product, [6-bromohexyl]trimethylammonium bromide, precipitated as colorless crystals. The mixture was filtered and the crystals were washed with dry diethyl ether and recrystallized from a mixture of ethanol an diethyl ether. The filtrate was left to stand for one more week and the procedure was repeated, so that a total yield
of at least 90% could be obtained.

$^1$H NMR ($D_2O$): δ=3.42(t, 2H, R-CH$_2$-Br); 3.29(m, 2H, R-CH$_2$-N$^+$(CH$_3$)$_3$); 3.07(s, 9H, R-CH$_2$-N$^+$(CH$_3$)$_3$); 1.80(m, 8H, -CH$_2$)

B: Potassium hydroxide (Aldrich) (1.06 g, 18.9 mmol) was dissolved in 98 ml of tert-butyl hydroperoxide (Acros)(70% in water). The solution was cooled to 0 °C and A (4.0 g, 13.2 mmol) was added. The solution was stirred for 20 hours while the temperature was allowed to rise to room temperature. The solvent was then evaporated under reduced pressure at a temperature below 35°C. The residue was dissolved in a large amount of diethyl ether/cyclohexane 1:1 to obtain a colorless solid. After decantation, the residue was treated with chloroform to separate the product from inorganic materials. After filtration, evaporation and drying at room temperature under reduced pressure the product was obtained with a yield of 50%. For cation exchange the product was used as obtained.

$^1$H NMR ($D_2O$): δ=3.99(t, 2H, R-CH$_2$-OOC(CH$_3$)$_3$); 3.28(m, 2H, R-CH$_2$-N$^+$(CH$_3$)$_3$); 3.07(s, 9H, R-CH$_2$-N$^+$(CH$_3$)$_3$); 1.74, 1.59, 1.39(3m, 8H, -CH$_2$); 1.22(s, 9H, -OOC-(CH$_3$)$_3$).

![Reaction scheme](image)

Figure 6.2: Reaction scheme for [4-(tert-butyldioxy)hexyl]trimethylammonium bromide.

Dimethyldiphytanylammonium bromide (2Phytyl)

B: [138] 50 g, 168.6 mmol Phytol(A, Aldrich, mixture of isomers) was dissolved in 250 ml Ethanol (Aldrich) and 20 g of Raney nickel slurry (Aldrich) were added. The mixture was purged with nitrogen and consequently flushed with hydrogen for 66 hours under stirring. The product was filtered over Celite (Aldrich) and the solvent was removed under reduced pressure. The crude product was distilled under reduced pressure to yield 42.3 g, 84% phytanol (B).

$n_{22}^2=1.452$

$^1$H NMR ($CDCl_3$): δ=0.8-0.9(m, 15H, CH$_3$-); 1.0-1.75(m, 24H, CH and CH$_2$ of the alkyl chain); 3.65-3.75(m, 2H, R-CH$_2$-OH)

C: [138, 139] 20 g, 67 mmol B were dissolved in 500 ml HBr 48%(Aldrich). To the solution, 50 ml of H$_2$SO$_4$ 98%(Aldrich) was added dropwise. The reaction mixture was then refluxed for 2 h. After cooling down to RT, the mixture
was extracted twice with diethyl ether (Aldrich). The unified organic phases were washed neutral with water, dried with MgSO₄ and concentrated. The raw product was distilled under reduced pressure to give the product, phytanyl bromide (C), the yield was 19.6 g, 81%.

$\text{n}^{18}_{\text{D}} = 1.456$

$^1\text{H NMR (CDCl}_3\text{)}$: $\delta = 0.8-0.9$ (m, 15H, CH₃-); 1.0-1.75 (m, 24H, CH and CH₂ of the main chain); 3.41 (m, 2H, R-CH₂-Br); impurity: 4.09 (m, 1H, R-CH₂-OH)

D: [140, 141] 20 g, 55.3 mmol C was heated together with 40 ml, 220 mmol dimethylamine (Aldrich, methanolic solution) for 24 h at 125°C in an autoclave. Consequently, the solvent was removed under reduced pressure, and the raw product was distilled under high vacuum. The yield of dimethylphytanylamine (D) was 10.6 g, 59%.

$\text{n}^{26}_{\text{D}} = 1.4495$

$^1\text{H NMR (CDCl}_3\text{)}$: $\delta = 0.8-0.9$ (m, 15H, CH₃-); 1.0-1.75 (m, 24H, CH and CH₂ of the alkyl chain); 2.21 (s, 6H, -CH₂-N(CH₃)₂); 2.25 (t, 2H, -CH₂-N(CH₃)₂); impurity: 3.70 (m, 1.3 H)

E: [142, 143] 10.00 g, 30.71 mmol (D) and 11.66 g, 32.25 mmol (C) in 25 ml Ethanol (Aldrich) were refluxed for 3 days in the presence of sodium carbonate (Aldrich). The solvent was evaporated under reduced pressure. In order to separate the product from the inorganic material, it was dissolved in chloroform (Aldrich) and filtered. The solvent was removed under vacuum. Evaluation of the NMR spectra indicated a yield of 76.2%. For ion exchange the raw product was used as it is. The impurities were the amine and the
bromide. For the cation exchange the amount taken was calculated according to the purity of the product. 

$^1$H NMR (CDCl$_3$): $\delta = 0.8$-0.9 (m, 30H, CH$_3$); 1.0-1.75 (m, 48H, CH and CH$_2$ of the main chain); 3.46 (s, 6H, -CH$_2$-N(CH$_3$)$_2$); 3.56 (t, 4H, -CH$_2$-N(CH$_3$)$_2$; impurity: 2.21 (s, 1.2H, R-CH$_2$-N(CH$_3$)$_2$); 2.25 (t, 0.7H, R-CH$_2$-N(CH$_3$)$_2$); 3.70 (m, 4H)

### 6.1.2 Surface Modification

The clay minerals used in this study are sodium montmorillonite, Nanofil 757 (in the following designated as M680), CloisiteNa (M880), Optigel CK (M900) and Optigel CMO (M1000). Their cation exchange capacities (CEC) are 680, 880, 900 and 1000 µequiv/g, respectively. In addition a commercial montmorillonite treated with dimethyldioctadecylammonium, Tixogel VP (abbreviated as VP), was used for experiments described in chapter 3.4. The supplier of Optigel CK/CMO, Nanofil 757 and Tixogel VP is Süd-Chemie AG (Moosburg, Germany), Cloisite NA$^+$ was supplied by Southern Clay Inc. The CEC was determined as described by Osman et al. [23].

Trimethyloctadecylammonium bromide (in the following designated as C18), dimethyldioctadecylammonium bromide (2C18), methyltriocadecylammonium bromide (3C18), tetraoctadecylammonium bromide (4C18), didecyldimethylammonium bromide (2C10), methyltrioctylammonium bromide (3C8), benzylhexadecyldimethylammonium bromide (BenzC16), tetraphenylphosphonium bromide (4Phenyl) and (ar-vinylbenzyl)trimethylammonium chloride (BenzVinyl) were used as purchased from Fluka (C18, 3C18, 4C18, 2C10, 3C8, 4Phenyl, BenzVinyl) and Acros (2C18, BenzC16). Vinylbenzylimethyldodecylammonium chloride (VDAC), [4-(tert-butyldioxy)hexyl]trimethylammonium bromide (IniC6) and Dimethyldiphytanylammonium bromide (2Phytyl) were synthesized as described in section 6.1.1.

**Cation exchange with C18, 2C18, 3C8, BenzC16 and 4Phenyl**

8 g of clay were stirred in 400 ml hot deionized water for one hour, 200 ml ethanol tech. was added and the mixture was sonicated for 10 min. at 50% Amplitude with a Branson sonifier 250 and sheared for 10 min with an IKA-Ultra-Turrax T 25 afterwards. 200 ml of an ethanolic solution of the ammonium salt was added dropwise under stirring. The amount of organic salt added was, with respect to the CEC of the clay, 100\%, 100\%, 200\%, 150\% and 200\% for C18, 2C18, 3C8, BenzC16 and 4Phenyl, respectively. The slurry was stirred overnight at 60°C, filtered, washed with ethanol (60°C), redispersed in a mixture of ethylacetate and ethanol, 9/1 vol/vol, filtered again and dried in the vacuum oven. The filtering funnel was connected to a thermostat, so that the solvent temperature
could be held above 50°C. The powder was analyzed with TGA. The OM was repeatedly washed, until no change in the TGA trace could be detected.

**Cation exchange with 2C10/2C18**

The modification designated 2C10/2C18 in Chapter 4.2, was done using a mixture of the two ammonium salts. The procedure was as described above, but the ethanolic solution, which was added to the dispersed clay, contained 50% 2C10 and 40% 2C18 with regard to the CEC of the clay. The addition of the ethanolic solution was carried out dropwise over a period of 30 hours.

**Cation exchange with 2Phytyl, 3C18 and 4C18**

These ammonium salts were more hydrophobic. For the cation exchange we used the same method as described for C18, 2C18 etc., but the salts were dissolved in n-propanol at 2/3 the concentration used in this description. The amount of ammonium salt was 95% of the CEC of the clay. For washing iso-propanol was used.

**Cation exchange with BenzVinyl, VDAC and IniC6**

For the clay modification prior to polymerization reaction it was important to exchange the vinyl- and peroxy cations at low temperatures. The montmorillonite for this modification was M880. For the surface modification different mixtures of dimethyldioctadecylammonium bromide, [4-(tert-butylidioxy)hexyl]trimethylammonium bromide, vinylbenzyldimethyldodecylammonium chloride, (ar-vinylbenzyl)trimethylammonium chloride and benzylhexadecyldimethylammonium bromide was used. Table 6.1 shows the composition

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>2C18</th>
<th>BenzC16</th>
<th>BenzVinyl</th>
<th>VDAC</th>
<th>IniC6</th>
</tr>
</thead>
<tbody>
<tr>
<td>VB10</td>
<td></td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VB20</td>
<td></td>
<td>80</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V10</td>
<td>90</td>
<td></td>
<td></td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>V30</td>
<td>70</td>
<td></td>
<td></td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>V50</td>
<td>50</td>
<td></td>
<td></td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>I30</td>
<td>70</td>
<td></td>
<td></td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>I50</td>
<td>50</td>
<td></td>
<td></td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>
of the surface modifications. After swelling, shear-mixing and sonification as described earlier, the dispersion of the clay was cooled to 10°C in an ice bath. An ethanolic solution containing the ammonium salts in the ratios listed in Table 6.1, was added dropwise at room-temperature over 2-3 hours. The mixture was put in a refrigerator overnight and was filtered cold the next day. The modified clay was washed twice with a mixture of ethanol and water, 1:1 vol/vol, twice with ethanol and twice with the solvent for polymerization. The washing solvents had a temperature of 5°C when added. The slurry was then diluted as required for polymerization.

6.1.3 Polymerization

For the polymerization two concepts were applied. One was to attach vinyl-groups to the surface of the montmorillonite, which can be copolymerized with the growing chains. Hence, the polymer chains can be chemically bonded to the mineral. This we call polymerization to the surface (PtoS). The other concept was to attach an initiator to the surface, so that the polymerization starts from the surface and the polymer can be attached to the surface. This we call polymerization from the surface (PfromS). For the polymerization of ethylene as well as octene, high molecular weight was neither expected nor wanted. A low molecular weight polymer chain was aspired, in order to facilitate the exfoliation of the clay during compounding.

6.1.4 Polymerization of Ethylene in Presence of OM

General procedure

A 1 l autoclave was filled with 600 ml of the reaction mixture. The mixture was shear-mixed beforehand for 10 min. at level 2 while being cooled in an ice bath. After purging the reaction vessel three times with 4 bars of nitrogen at room temperature it was flushed with 70 bars of ethylene. While the ethylene was dissolved in the dispersion, the pressure went down and the initial pressure had to be adjusted again with ethylene. The heating was started and the reaction was carried out for 20 h. During reaction time the pressure was kept above 50 bars with ethylene [130].

Polymerization to the Surface

The reaction dispersion consisted of montmorillonite, modified with VDAC and 2C18 as described above, and 1.99 g, 6.2 mmol (Aldrich, 25% water) of benzoylperoxide. The polymerization temperature was 72°C. The product, a white paste, was removed from the reaction vessel with the help of xylene (Aldrich). The paste was diluted further with xylene and filtered hot in order to remove the
polymer which was not attached to the filler surface. The residue was further extracted with hot xylene in a Kumagawa Soxhlet apparatus for 48 h. The product was filtered and washed several times with hot ethyl acetate (Aldrich) in order to remove the xylene and finally dried at 70 °C under reduced pressure.

Polymerization from the Surface

The reaction mixture contained M880 modified with IniC6 and 2C18 as described above, dispersed in the respective solvent. The reaction temperature was 95 °C. The slurry, which was obtained from PfromS, was filled without filtering into an extraction thimble and extracted with hot xylene in a Kumagawa Soxhlet apparatus for 48 h. The product was filtered and washed several times with hot ethyl acetate (Aldrich) in order to remove the xylene and finally dried at 70 °C under reduced pressure.

6.1.5 Polymerization of Octene in Presence of OM

The polymerization was carried out in a 1 l three neck flask. The reaction vessel was filled with 600 ml of the reaction mixture. The mixture consisted of 300 ml octene (Aldrich) and the dispersed clay, modified as described before, in the respective solvent. For PtoS 1.99 g, 6.2 mmol (Aldrich, 25% water) of benzoylperoxide was added as well. The dispersion was purged through a gas inlet under vigorous stirring with argon for 5 min. The mixture was then heated up to the polymerization temperature. The reaction temperature was 95 °C for PfromS and 72 °C for PtoS. The reaction was carried out while stirring for 16 hours under argon atmosphere. Consequently, the mixture was filled into an extraction thimble and extracted with hot xylene in a Kumagawa Soxhlet apparatus for 2 days. The product was filtered and washed several times with hot ethyl acetate (Aldrich) in order to remove the xylene and finally dried at 70 °C under reduced pressure.

6.1.6 Polymerization of Styrene in the Presence of OM

The montmorillonite for the polymerization with styrene as monomer was modified with BenzC16 and BenzVinyl. The OM containing 10% vinyl groups was stirred in 850 ml dry toluene and allowed to swell for 1 h at ambient temperature. Afterwards it was shearmixed for 10 min at level 2. 6.4 ml freshly distilled styrene and 13.9 mg AIBN (Aldrich, recrystallized twice) were added and the mixture was purged with argon. The polymerization was then carried out at 60 °C for 22 hours under an argon atmosphere. At the end of the reaction time 50 ml of ethanol were added in order to coagulate the clay. The mixture was filtered hot and washed four times with 250 ml of hot toluene. The sample was dried under vacuum. The OM containing 20% vinyl groups was stirred in 300 ml of freshly
distilled styrene and 300 ml of dry toluene and stirred for 1.5 hours at room temperature under argon atmosphere. The mixture was sheared for 15 min at level 2 under argon atmosphere. 1 g AIBN was added and the flask was heated to 60°C for 40 hours. The mixture was filtered hot, washed with hot toluene and extracted with hot toluene in a Kumagawa Soxhlet apparatus for 4 days. The product was filtered and washed several times with hot ethyl acetate (Aldrich) in order to remove the toluene and finally dried at 70°C under reduced pressure.

### 6.1.7 Preparation of Composites

Prior to compounding the OM was freeze-dried out of dioxane, the pristine clay out of water, and sieved with a 60 µm sieve in order to obtain a fine powder. The compounding was carried out in a Brabender Plasti-Corder with PL2000 mixer measuring head and evaluation software V1.4. After melting the polymer (HDPE, Basell GF9055) at 160°C the organoclay was added portion wise and the mixture was kneaded applying a torque of 20-23 Nm. 20 minutes were necessary for this process. When copolymers were added (Chapter 4.4), the copolymer was mixed with HDPE prior to melting. The characteristics of the copolymers are displayed in Table 6.2. For the compounding with poly[ethylene-co-(vinyl alcohol)] the working temperature was 175°C. The composite was pressed into sheets (98 mm x 59 mm x 1.4 mm) at 180°C for 5 min in a brass chamber under vacuum. The brass chamber was transferred into a second press with a preset temperature of 90°C and allowed to cool down to room temperature. The pressing was done twice. The dumbbell-shaped specimen for mechanical testing (type 5B-ISO 527) were cut out of these sheets. Foils for WAXD were prepared by cutting small pieces out of the sheets and pressing it at 180°C in normal atmosphere to foils of several hundred micrometers thick. To produce foils for the permeation measurements small pieces of the sheets were pressed between two PET foils with metal spacers outside the PET foils at 180°C under vacuum in a brass chamber. After five minutes the brass chamber was transferred into a second press with a preset temperature of 90°C and allowed to cool down to room temperature. The foils for the permeation measurement were approximately 30-60 µm thick.

The designation vol % refers to the mineral volume fraction (φ_m), as only the clay sheets and not the organic layer improve the properties of the composite. The required weight of i modified mineral (m_{om}) and ii polymer(m_{pol}) for compounding were calculated as follows:

\begin{align*}
\text{i modified mineral (} m_{om}) \\
\quad m_{om} &= m_m + m_{monolayer} \\
\text{with mass of mineral } m_m \text{ and } m_{monolayer} = \text{mass of monolayer} \\
\quad m_m &= (\phi_m \cdot V_{total}) \cdot \rho_m \\
\end{align*}
Table 6.2: Copolymers used in this study. \(M_n\) is the number average molecular weight, \(m.p.\) is the melting point, \(\Phi_w\) is the weight fraction of the comonomer and \(\rho\) is the density of the copolymer.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>(M_n) [g/mol]</th>
<th>(\Phi_w) [wt%]</th>
<th>(m.p.) [°C]</th>
<th>(\rho) [g/cm^3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene-block-polyethylene glycol (g)</td>
<td>575</td>
<td>20</td>
<td>91</td>
<td>(b)</td>
</tr>
<tr>
<td>Polyethylene-block-polyethylene glycol (g)</td>
<td>875</td>
<td>20</td>
<td>91</td>
<td>(b)</td>
</tr>
<tr>
<td>Poly[ethylene-co-{methacrylic acid}] (f)</td>
<td>68000</td>
<td>10</td>
<td>95</td>
<td>0.937</td>
</tr>
<tr>
<td>Poly[ethylene-co-{acrylic acid}] (g)</td>
<td>(_b)</td>
<td>10</td>
<td>100</td>
<td>0.95</td>
</tr>
<tr>
<td>Poly[ethylene-co-{acrylic acid}] (g)</td>
<td>3110</td>
<td>5</td>
<td>99</td>
<td>0.93</td>
</tr>
<tr>
<td>Polyethylene oxidized (g)</td>
<td>1700</td>
<td>17(^a)</td>
<td>106</td>
<td>0.96</td>
</tr>
<tr>
<td>Poly(ethylene-co-butylene) mono-ol (g)</td>
<td>4200</td>
<td>(_b)</td>
<td>(_c)</td>
<td>0.88</td>
</tr>
<tr>
<td>Poly(ethylene-co-octene)-graft-{(maleic anhydride)} (f)</td>
<td>(_b)</td>
<td>0.5(^d)</td>
<td>52</td>
<td>0.869</td>
</tr>
<tr>
<td>Poly[ethylene-co-{vinyl alcohol}] (g)</td>
<td>(_b)</td>
<td>68</td>
<td>165</td>
<td>1.140</td>
</tr>
<tr>
<td>Poly(ethylene-co-trialkoxyvinylsilane) (g)</td>
<td>(_b)</td>
<td>(_b)</td>
<td>116</td>
<td>0.927</td>
</tr>
<tr>
<td>Polyethylene-graft-{(maleic anhydride)} (g)</td>
<td>4000</td>
<td>&gt;1</td>
<td>94</td>
<td>0.905</td>
</tr>
</tbody>
</table>

\(a\) The value for the acid number is given, the unit is \(\text{mg KOH/g}\).

\(b\) Data was not available.

\(c\) Liquid at room temperature.

\(d\) Refers to maleic anhydride. The percentage octene is not known.

\(e\) Supplier was Eastman Chemical Company.

\(f\) Supplier was DuPont.

\(g\) The material was purchased from Aldrich.

\[m_{\text{monolayer}} = m_m \cdot CEC \cdot M_{\text{orgcat}} \quad (6.3)\]

where \(V_{\text{total}}\) = total volume of the sample and \(M_{\text{orgcat}}\) = molar mass of the organic cation. The total volume of the sample was given by the volume of the compounding chamber. This calculation could not be applied to the montmorillonites with the polymers on the surface, because there is no defined mass for the cation on the surface. In this case the mass of the monolayer per gram mineral was taken from the TGA.

\[m_{\text{pol}} = ((\phi_{\text{pol}} \cdot V_{\text{total}}) - V_{\text{monolayer}}) \cdot \rho_{\text{pol}} \quad (6.4)\]

with

\[V_{\text{monolayer}} = \frac{m_{\text{monolayer}}}{\rho_{\text{monolayer}}} \quad (6.5)\]

The density of the monolayer was assumed to be the same as that of octadecan (\(\rho = 0.81 \text{ g/ml}\)). Calculating the volume of the polymer the volume of the
monolayer was considered as a part of the polymer, since the volume fraction of the filler refers only to its inorganic part.

6.2 Methodology

6.2.1 Thermogravimetric Analysis (TGA)

Measurements were carried out on a TA Instruments Q500 in high resolution mode, i.e. the heating rate is sensitive to the weight loss, in the range from 50°C to 900°C. For evaluation Universal Analysis V3.8B TA was used. In order to obtain the amount of organic material on the surface of the mineral the measured weight loss had to be corrected. The percentage weight loss due to dehydration of the pristine clay between 200 and 900°C was subtracted. In addition, the weight loss between 50°C and 200°C due to solvent of moisture loss from the examined sample was subtracted to, obtain a corrected weight loss $I_{corr}$. The total of exchanged moles per gram clay $n_{ex}$ could be calculated using the molecular weight of the organic cation $M_{amm}$:

$$n_{ex} = \frac{I_{corr}}{(1 - I_{corr}) \cdot M_{amm}}$$  \hspace{1cm} (6.6)

6.2.2 Mechanical Testing

Mechanical testing was carried out on a Zwick Z020 tensile testing machine with testXpert 9.01 software and video extensometer V4.19.02 from MESSPHYSIK. At least five specimen of each sample were measured following EN-ISO 527.1. In order to minimize the effect of sample slipping during tensile testing on the measured tensile modulus and yield strain, the samples were marked with a permanent marker and up to 15% strain the elongation was monitored with a CCD-camera. The drawing speed was 0.1 mm/min up to 0.5% elongation, then increased to 6 mm/min. The tensile modulus was calculated between 0.05 to 0.25% elongation.

6.2.3 Oxygen Permeation

The measurements were carried out on an OX-TRAN 2/20 ML (Mocon, Minneapolis, USA) at 23°C, 1 atm and 0-2% RH. The permeation area for oxygen permeability measurements was 5 cm². The thickness of each foil was calculated using the weight, area and density of the sample. The density of the composite $\rho_c$ was determined by weighing a piece in air and in ethanol using an analytical balance (Mettler AE 260 Deltarange) and a home made device similar to the Mettler density-kit ME-33360. The following equation was used:
where $\rho_{\text{EtOH}}$ is the density of ethanol, $m_{\text{air}}$ is the sample mass in air and $m_{\text{EtOH}}$ is its mass in ethanol. The average value of three samples was taken. Layered-silicate polymer composites are anisotropic materials, this has to be taken into account on measuring the permeation properties. Since the flow through the material is perpendicular to the principal axis of diffusion, it is proportional to the concentration gradient in the material similar to isotropic matter [96].

6.2.4 Wide-Angle X-ray Diffraction (WAXD)

The samples were measured on a Scintag XDS 2000 (Scintag Inc., Cupertino, California) using Kα radiation ($\lambda = 0.15406 \text{nm}$) in reflection mode. $2\Theta$ was measured from 1.5° to 10°, step size 0.02°, 20 seconds per step, tube divergence slit width 0.5, scatter slit width 1 and detector scatter slit width 0.5 and receiving slit width 0.2. Using Bragg’s law the basal-plane spacing is obtained. Sample alignment of the focal plane was done with a home made micrometer instrument [16]. For evaluation the software Scintag DMSNT V1.37 was used. Thin foils of the polymer composites were pressed and measured using a mica platelet as internal standard ($2\Theta = 8.84^\circ$). The clay powder was measured in a similar way. In order to obtain the exact peak positions, the spectra were fitted with a split Pearson VII function (diffraction management system software 1.36b).

6.2.5 Dynamic Scanning Calorimetry (DSC)

DSC of the modified clay was carried out on a TA Instruments DSC Q1000. The sample was kept at -30°C for 10 min, heated at a rate of 10°C/min up to 160°C and cooled at a rate of 10°C/min down to -30°C. It was held for 10 min at this temperature and heated up again at a rate of 10°C/min up to 160°C. Evaluation was carried out using Universal Analysis V3.8B TA.

DSC of the nanocomposites was done on a Perkin-Elmer PE-DSC 7 TAC7/7, for analysis Pyris 4.0 was used. In order to determine the degree of crystallinity, $c_p$ was measured and the baseline was corrected by a method described elsewhere [144,145]. The sample was held for 10 min at 20°C, heated at a rate of 10°C/min up to 160°C and held again for 10 min at this temperature. The same was done for a sapphire reference and an empty pan. For the crystallinity calculation a melting enthalpy for the perfect crystal of $\Delta H_m = 293 \text{J/g}$ was used [146]. We corrected the value of the melting enthalpy with the weight fraction of filler in order to provide comparison with pure HDPE.
6 Experimental

6.2.6 Scanning Electron Microscopy (SEM)

A composite sheet, prepared for tensile testing, was cut perpendicular to the surface with a diamond knife of a microtome (Reichert Jung Ultracut E). Consequently the perpendicular sample surface was etched with cold oxygen plasma for 4 min. The etched surface was sputter coated with a 5 nm thick Pt layer. Images were taken with a Hitachi S-900 ‘in-lens’ field emission scanning electron microscope (FESEM) at 10 to 20 KV accelerating voltage.

6.2.7 Transmission Electron Microscopy (TEM)

For examination of the nanocomposites morphology, stripes of approx. 1 mm width were cut out of the foils used for permeation measurements, oxygen plasma-etched and subsequently embedded in an epoxy matrix (Epon 812 & Durcopan ACM 3:4, Fluka). 50-100 nm thick sections were cryocut at -150°C with a diamond knife from Diatome AG Biel. The transmission electron microscope employed was a Zeiss/LEO-912-Ω and an acceleration voltage of 120 KV was used. The pictures were taken in zero loss mode.

Pictures of Na-montmorillonite dispersed in water were taken on the same microscope for particle size measurements. For sample preparation 0.01-0.05 g montmorillonite in 10 ml water was shaken in a polypropylene vial overnight. The suspension was sonicated for 5 min. at 50% amplitude, while the vial was cooled with in ice bath in order to prevent overheating during sonification. The TEM grids were prepared using a home-built apparatus, following the method of Egelhaaf et al. [147]. The principle is to vitrify thin layers of the water dispersion in ethane as cryogen in such a way that the water does not crystallize. Thus the vitrified water appears transparent in the TEM, and single clay sheets can be observed. The pictures were taken at -190°C.

The image analysis program for determining the diameter of the single sheets of montmorillonite was analySIS (Soft Imaging System GmbH, Munster, Germany).

6.2.8 Nuclear Magnetic Resonance (NMR)

Measurements were carried out on a Bruker DPX 300 and bore Ultra shield magnets with observing frequencies of 300 MHz for the protons. The spectra were measured on a delta (δ) scale with reference to the peak of tetramethylsilane (TMS) set to zero.
Bibliography


Bibliography


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Bibliography


Bibliography


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<td>2000</td>
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<tr>
<td>May 2001 - Sept. 2004</td>
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