József Hári
PhD Thesis

Polymer/Silicate Nanocomposites: Competitive Interactions and Functional Application
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PhD Thesis

Prepared by
József Hári

Supervisor:
Béla Pukánszky

Laboratory of Plastics and Rubber Technology
Department of Physical Chemistry and Materials Science
Budapest University of Technology and Economics

Polymer Physics Research Group
Institute of Materials and Environmental Chemistry
Research Centre for Natural Sciences
Hungarian Academy of Sciences

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Chapter 1

INTRODUCTION

1.1. Factors determining the properties of particulate filled polymers

1.2. Surface characteristics and interactions

1.2.1. Surface characteristics

1.2.2. Interactions

1.2.3. Interphase structure and properties

1.3. Structure

1.3.1. Plates

1.3.2. Nanotubes and fibers

1.3.3. Spherical nanoparticles

1.4. Micromechanical deformation processes

1.5. Composite properties

1.5.1. Stiffness

1.5.2. Strength, reinforcement

1.5.3. Other properties

1.6. Possible applications, functionality

1.7. Conclusions

1.8. Scope

1.9. References

Chapter 2

COMPARISON OF THE REINFORCING EFFECT OF VARIOUS MICRO- AND NANOFILLERS IN PA6

2.1. Introduction

2.2. Experimental

2.2.1. Materials

2.2.2. Sample preparation

2.2.3. Characterization

2.3. Results and discussion

2.3.1. Structure

2.3.2. Interactions

2.3.3. Local deformation processes

2.3.4. Properties

2.3.5. Considerations, consequences

2.4. Conclusions

2.5. References
Contents

Chapter 1 ............................................................................................................................................ 9
INTRODUCTION

1.1. Factors determining the properties of particulate filled polymers ........................................ 10
1.2. Surface characteristics and interactions .............................................................................. 11
  1.2.1. Surface characteristics .................................................................................................. 11
  1.2.2. Interactions ................................................................................................................ 15
  1.2.3. Interphase structure and properties .......................................................................... 17
1.3. Structure .................................................................................................................................. 18
  1.3.1. Plates .......................................................................................................................... 18
  1.3.2. Nanotubes and fibers ................................................................................................. 23
  1.3.3. Spherical nanoparticles ............................................................................................. 24
1.4. Micromechanical deformation processes .............................................................................. 25
1.5. Composite properties ............................................................................................................ 26
  1.5.1. Stiffness ....................................................................................................................... 26
  1.5.2. Strength, reinforcement ............................................................................................. 27
  1.5.3. Other properties ......................................................................................................... 30
1.6. Possible applications, functionality ...................................................................................... 31
1.7. Conclusions ......................................................................................................................... 33
1.8. Scope ...................................................................................................................................... 35
1.9. References ............................................................................................................................ 37

Chapter 2 ........................................................................................................................................... 47
COMPARISON OF THE REINFORCING EFFECT OF VARIOUS MICRO- AND
NANOFILLERS IN PA6

2.1. Introduction .............................................................................................................................. 47
2.2. Experimental ........................................................................................................................... 48
  2.2.1. Materials ...................................................................................................................... 48
  2.2.2. Sample preparation ..................................................................................................... 48
  2.2.3. Characterization ........................................................................................................... 48
2.3. Results and discussion .......................................................................................................... 50
  2.3.1. Structure ....................................................................................................................... 50
  2.3.2. Interactions .................................................................................................................. 52
  2.3.3. Local deformation processes ...................................................................................... 55
  2.3.4. Properties .................................................................................................................... 58
  2.3.5. Considerations, consequences ..................................................................................... 62
2.4. Conclusions ............................................................................................................................ 64
2.5. References ............................................................................................................................. 64
Chapter 3................................................................................................................................. 67
COMPETITIVE INTERACTIONS, STRUCTURE AND PROPERTIES IN POLMER/LAYERED SILICATE NANOCOMPOSITES

3.1. Introduction .................................................................................................................. 67
3.2. Experimental ............................................................................................................... 67
    3.2.1. Materials ............................................................................................................... 67
    3.2.2. Sample preparation ............................................................................................. 68
    3.2.3. Characterization .................................................................................................. 68
3.3. Results and discussion ............................................................................................... 70
    3.3.1. Properties ........................................................................................................... 70
    3.3.2 Structure ............................................................................................................. 73
    3.3.3. Local processes .................................................................................................. 78
    3.3.4. Interactions ........................................................................................................ 81
    3.3.5. Discussion, correlations ................................................................................... 83
3.4. Conclusions ............................................................................................................... 86
3.5. References ............................................................................................................... 87

Chapter 4................................................................................................................................. 89
ADSORPTION OF AN ACTIVE MOLECULE ON THE SURFACE OF HALLOYSITE FOR CONTROLLED RELEASE APPLICATION: INTERACTION, ORIENTATION, CONSEQUENCES

4.1. Introduction ............................................................................................................... 89
4.2. Experimental ............................................................................................................. 90
4.3. Results and discussion ............................................................................................. 92
    4.3.1. Halloysite characteristic .................................................................................... 92
    4.3.2. Adsorption ....................................................................................................... 95
    4.3.3. Interactions ........................................................................................................ 96
    4.3.4. Location ........................................................................................................... 100
    4.3.5. Surface structure, consequences ...................................................................... 103
4.4. Conclusions ............................................................................................................. 104
4.5. References ............................................................................................................ 105

Chapter 5................................................................................................................................ 109
COMPETITIVE INTERACTIONS AND CONTROLLED RELEASE OF A NATURAL ANTIOXIDANT FROM HALLOYSITE NANOTUBES

5.1. Introduction ............................................................................................................. 109
5.2. Experimental ........................................................................................................... 109
5.3. Results and discussion ........................................................................................... 112
    5.3.1. Dissolution ........................................................................................................ 112
    5.3.2. Competitive interactions ................................................................................. 114
    5.3.3. Discussion, consequences .............................................................................. 117
5.4. Conclusions ............................................................................................................. 120
5.5. References ............................................................................................................. 120
Chapter 6 ................................................................................................................................. 123
LONG TERM STABILIZATION OF PE BY THE CONTROLLED RELEASE OF A
NATURAL ANTIOXIDANT FROM HALLOYSITE NANOTUBES

6.1. Introduction .................................................................................................................. 123
6.2. Experimental .............................................................................................................. 124
  6.2.1. Materials ................................................................................................................ 124
  6.2.2. Sample preparation .............................................................................................. 124
  6.2.3. Characterization ................................................................................................. 125
6.3. Results and discussion .............................................................................................. 126
  6.3.1. Characterization of active nanotubes ............................................................... 126
  6.3.2. Processing stability ............................................................................................ 128
  6.3.3. Long term stabilization, controlled release ...................................................... 132
6.4. Conclusions ............................................................................................................... 136
6.5. References ................................................................................................................ 137

Chapter 7 ............................................................................................................................. 139
SUMMARY

LIST OF SYMBOLS .............................................................................................................. 143
ACKNOWLEDGEMENT ........................................................................................................ 145
PUBLICATIONS .................................................................................................................. 146
Chapter 1

Introduction

About 25 -30 years ago the results of the Toyota group created much interest among researchers all over the world and initiated intensive research on layered silicate nanocomposites [1-3]. The group polymerized \( \varepsilon \)-caprolactam in the presence of a layered silicate filler and achieved remarkable properties. Many research groups launched projects related to layered silicates and even companies started to show interest in these new materials. The general idea of polymer nanocomposites is based on the concept of creating a very large interface between the nano-sized heterogeneities and the polymer matrix by the exfoliation of the clay and its homogeneous distribution in the polymer in the form of individual layers. This large interface and the corresponding interphase are supposed to result in exceptional properties not possible to reach with traditional particulate filled polymers. Advantages offered by nanocomposites were claimed to be large reinforcement at very small nanoparticle content, but functional properties like decreased flammability or increased conductivity were often mentioned as well. Unfortunately nanocomposites often did not and still do not fulfill the expectations and possess much worse properties than expected. The main reason for the inferior properties is that the basic idea usually does not work and the large interface necessary for efficient reinforcement cannot be created. The problems arise mostly from the fact that complete exfoliation can practically never be achieved, structure is not controlled or even known, and interfacial interactions are undefined. The limited degree of exfoliation is a major problem in composites containing plate-like reinforcements that leads to the formation of a complicated structure with several structural units. Aggregation is very difficult to avoid in composites containing fibers, tubes or spherical particles and in spite of their importance very little is known about competitive interactions prevailing in such composites.

Because of these difficulties the enthusiasm related to nanocomposites ebbed considerably, but in spite of all problems research continues in the area. Quite a few attempts are made to find new nanofillers and the number of papers published on carbon nanotubes and graphene is enormous. Nanocellulose, sepiolite and halloysite are other nanofillers which are also explored as possible reinforcements in polymers, but the number of possible materials, which is studied at least at experimental level, is quite large and grows continuously. The results of the research done up to now strongly indicated that the original idea does not work and nanocomposites probably will never be used in structural applications in large quantities because of their inferior properties or prohibitive price. On the other hand, it turned out that functional nanocomposites might find application in niche areas and these special materials are already applied in industry in increasing amounts. Food packaging is a possible application field, but the conductivity of carbon nanotubes as well as graphene can be utilized in antistatic and conductive composites.

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halloysite, but other active components can be also included to use the complex devices in paints, water treatment or corrosion protection. Medical applications usually can tolerate the larger expense related to nanomaterials, but it can be accepted in most specific applications. It is obvious that functional nanocomposites offer enormous possibilities, but further research must be carried out to exploit them.

The Laboratory of Plastics and Rubber Technology of the Department of Physical Chemistry and Materials Science at the Budapest University of Technology and Economics together with the Institute of Materials and Environmental Chemistry at the Hungarian Academy of Sciences have considerable experience in the modification of polymers. The group intensively studied particulate filled polymers and polymer blends for years and gained extensive knowledge about structure-property correlations and especially about interfacial interactions in such materials. Considering the experience obtained on particulate filled polymers, it seemed to be obvious to use it in the study of nanocomposites. The group started a project on layered silicate nanocomposites which resulted in the preparation of three PhD theses [4-6]. First we got acquainted with these materials and after exploring the factors determining their properties, we focused on specific questions which might have led to better materials. As a result of these studies, most problems related to layered silicate nanocomposites surfaced and the crucial questions which need further attentions have been identified. Thorough literature search showed that the nano hype was based mainly on assumptions and pure belief and, even the claimed benefits of nanocomposites over traditional microcomposites have basically never been checked. As a result of all these questions and contradictions, we decided to explore problems largely unattended up to now. First we compared layered silicate nanocomposites to traditional particulate filled and fiber reinforced materials. Since previous research proved that interfacial interactions play a crucial role in the determination of composite structure and properties, we studied the effect of matrix/filler interactions in these materials. Finally, we looked for alternative fillers and functional applications and investigated the use of halloysite nanotubes as controlled release carrier material. This thesis summarizes the most important scientific results of the research done lately, its main conclusions and further potentials.

1.1. Factors determining the properties of particulate filled polymers

Although nanocomposites might have particular differences compared to traditional microcomposites, the general rules of heterogeneous materials apply also for them and their properties are determined by the same four factors, i.e. component properties, composition, structure and interactions. The characteristics of both the matrix and the filler or reinforcement influence composite properties strongly. The direction of the change in yield stress or strength is determined by the relative load bearing capacity of the components [7,8]; larger reinforcement is achieved in a soft matrix than in a stiff polymer. Numerous filler characteristics influence the properties of composites [9,10]; the most important particle characteristics to consider are particle size, size distribution, aspect ratio, specific surface area and surface energy.
Chapter 1

1.1. Factors determining the properties of particulate filled polymers

All properties depend on composition, on the amount of filler added to the polymer. The goal of the use of fillers is either to decrease cost or to improve properties, e.g. stiffness, dimensional stability, etc. [11]. These goals require the introduction of the largest possible amount of filler into the polymer, but the improvement of the targeted property may be accompanied by the deterioration of others. Since various properties depend in a different way on filler content, composite properties must be always determined as a function of composition [11].

The structure of particulate filled polymers seems to be simple, the homogeneous distribution of particles in the polymer matrix is assumed in most cases. This, however, rarely occurs and often special, particle related structures develop in the composites [11]. Aggregation and orientation of anisotropic particles may appear in all systems, but structure is even more complex in the case of nanoreinforcements and several structure related phenomena must be considered in their composites.

Interactions can be divided into matrix/particle and particle/particle interactions. Matrix/particle interaction leads to the development of an interphase with properties different from those of both components, while particle/particle interactions induce aggregation. Secondary, van der Waals forces play a crucial role in the development of both kinds of interactions [11]. Unfortunately interactions are even more complex in nanocomposites, especially in the case of layered reinforcements like silicates or double hydroxides, because of the presence of surfactants, coupling agents and other additives.

1.2. Surface characteristics and interactions

Because of their increased importance in nanocomposites the attention must be focused mainly on structure and interfacial interactions. Structure is not characterized properly in a large number of publications, usually the formation of an intercalated/exfoliated structure is claimed in layered silicate nanocomposites without defining the extent of exfoliation or looking for other structural units. Similarly, interactions are treated in very general terms using expressions like compatibility, miscibility, hydrophobicity, polarity, etc. [12-17] without their definition or quantitative characterization. The use of such terms and much of the information published in the literature are misleading, several contradictions can be pointed out which are neglected or not studied in sufficient detail when discussing nanocomposite preparation, structure and properties.

1.2.1. Surface characteristics

The specific surface area of totally exfoliated montmorillonite, for example, is around 750 m²/g [15,18,19] and that of graphene was reported to be even larger [20]. Limited information is published on the surface characteristics of nanofillers, although they are very important since they determine all interactions in the composite, but also structure and properties. Presently organically-modified silicates are used in the largest amount for the preparation of nanocomposites. Organophilization modifies the surface energy of the silicate drastically. The majority of papers published on polymer/layered silicate nanocomposites containing an organically-modified silicate claim that surface
modification renders the hydrophilic silicate hydrophobic, decreases its polarity, facilitates intercalation and exfoliation, improves wetting and the compatibility of the phases, and results in advantageous properties [12,15,21,22]. Unfortunately, this explanation does not agree with the fact that nanocomposite cannot be prepared from organically-modified silicates (OMMT) and polypropylene (PP) without an additional compatibilizer, although both are apolar and hydrophobic [21,23,24]. Moreover, apart from nanocomposites prepared from polyamide, the properties of most polymer/layered silicate nanocomposites are relatively poor, but they definitely do not reach the expected values or those predicted on the basis of the principles mentioned above (extensive exfoliation, large interface) [15,25].

It is completely true that the treatment of silicates renders them hydrophobic and decreases their polarity. However, the claim that decreased polarity leads to better compatibility and wetting is false. Organophosphilization decreases the surface energy of the fillers leading to the decrease of the strength of interaction between the filler and the polymer [26]. The interaction of the reinforcement and the polymer is an adsorption process. The strength of adsorption can be characterized by the reversible work of adhesion [27,28], which considerably decreases upon treatment with an organic substance. Strong polarity of the neat silicate helps adsorption and increases the strength of interaction, while organophosphilization has the opposite effect. Similarly, the wetting of silicates by polymers is also claimed to improve upon organophosphilization. Wettability is usually characterized by the thermodynamic quantity

\[ S_{mf} = \gamma_f - \gamma_m - \gamma_{mf} \]  

(1.1)

where \( \gamma_f \) and \( \gamma_m \) are the surface tension of the filler and the matrix polymer, respectively, \( \gamma_{mf} \) interfacial tension and \( \gamma_f > \gamma_m \). Accordingly, wettability decreases on organophosphilization due to the drastic decrease of the surface tension of the filler. In PP/MMT composites the value of \( S_{mf} \) is around 160 mJ/m² for neat montmorillonite (NaMMT), which decreases to 15 mJ/m² at 100 % surface coverage with a long chain aliphatic surfactant [29].

The orientation of surfactant molecules influences the distance between the individual silicate layers (gallery distance), but the amount used for organophosphilization and being present in different forms (ionically bonded or attached by dipole interactions) within the galleries of the silicate is also important in the determination of surface characteristics and behavior. The amount used for the surface modification of commercial silicates covers a relatively wide range from 20 to 45 wt% corresponding to surface coverages of 90-120 % (see Table 1.1).
Introduction

Table 1.1 Surface modification, gallery structure and the dispersion component of surface tension for selected commercial organically-modified layered minerals, and two laboratory products modified with N-cetylpyridinium chloride (CPCM/MMT) or trichlyl-tetradecyl-phosphonium chloride (PhoMMT), respectively [5].

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Amount (wt%)</th>
<th>No. of peaks</th>
<th>Gallery structure</th>
<th>Distance (nm)</th>
<th>Surface tension, $\gamma_d$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaMMT</td>
<td>C$<em>{10}$H$</em>{22}$N$^+$(CH$<em>2$)$</em>{17}$Cl</td>
<td>0</td>
<td>1</td>
<td>-</td>
<td>257</td>
<td>2.0</td>
</tr>
<tr>
<td>CPCM/MMT</td>
<td>C$<em>{12}$H$</em>{23}$N$^+$(CH$<em>2$)$</em>{17}$Cl$_2$Cl</td>
<td>22</td>
<td>2</td>
<td>9.0</td>
<td>1.0</td>
<td>2.3</td>
</tr>
<tr>
<td>PhoMMT</td>
<td>[CH$_3$(CH$_2$)$_3$]COOH</td>
<td>20</td>
<td>1</td>
<td>5.0</td>
<td>1.8</td>
<td>2.3</td>
</tr>
<tr>
<td>Nanofil 784</td>
<td>NH$_2$(CH$_2$)$_3$NH(CH$_2$OH)$_2$COOH</td>
<td>27</td>
<td>2</td>
<td>3.8</td>
<td>3.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Nanofil 804</td>
<td>CH$_3$(CH$_2$)$_3$NH$_2$</td>
<td>30</td>
<td>1</td>
<td>5.2</td>
<td>4.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Nanofil 848</td>
<td>CH$_3$(CH$_2$)$_3$NH$_2$</td>
<td>35</td>
<td>1</td>
<td>4.9</td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Nanofil 919</td>
<td>[CH$_3$(CH$_2$)$_3$]$^+$N(CH$_2$Cl)$_2$Cl</td>
<td>25</td>
<td>1</td>
<td>4.9</td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Claye 20A</td>
<td>[CH$_3$(CH$_2$)$_3$]COOH</td>
<td>30</td>
<td>1</td>
<td>4.9</td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Cloisite 20A</td>
<td>[CH$_3$(CH$_2$)$_3$]COOH</td>
<td>45</td>
<td>1</td>
<td>4.9</td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Nanofil 911NT</td>
<td>[CH$_3$(CH$_2$)$_3$]N$^+$(CH$_2$OH)$_2$Cl</td>
<td>38</td>
<td>2</td>
<td>3.3</td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Soboce 911NT</td>
<td>CH$_3$(CH$_2$)$_3$COOH</td>
<td>0</td>
<td>1</td>
<td>11.6</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Amount and number of silicate peaks were determined by XRD measurements; gallery distance was calculated based on peak position according to Bragg's law.

*Surface characteristics and behavior. The amount used for the surface modification of commercial nanofillers, although limited information is published on the surface characteristics of nanofillers, although contradictions can be pointed out which are neglected or not studied in sufficient detail.

Chapter 1

Table 1.1

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*Surface characteristics and behavior. The amount used for the surface modification of commercial nanofillers, although limited information is published on the surface characteristics of nanofillers, although contradictions can be pointed out which are neglected or not studied in sufficient detail.
The analysis of several commercial silicates indicates that they are usually coated near to 100% of their ion exchange capacity leading to monolayer coverage. Inverse gas chromatography (IGC) is frequently used for the surface characterization of particulate fillers [30-35] and also of silicates [36]. The surface energy of neat, NaMMT was found to be quite large, around 260 mJ/m² was measured for its dispersion component at 100 °C. Helmy et al. [37] determined a somewhat smaller value (205 mJ/m²) for total surface energy, which is somewhat surprising. The coating of the high energy surface of the silicate with organic compounds, i.e. surfactants, leads to the decrease of surface tension [38-41]. The correlation of surface tension and coverage is plotted in Figure 1.1 for a series of silicates. Similar values obtained on calcium carbonate (CaCO₃) are presented for comparison. The character of the correlation is the same in the two cases, but the surface tension of neat NaMMT is much larger than that of CaCO₃. The surface energy of the coated fillers is very similar to each other, irrespectively of filler type (clay, CaCO₃) or the chemical composition of the surfactant used for treatment. These results prove that organofilization decreases surface energy, which leads to decreased matrix-filler interaction and inferior strength. These observations agree well with current experience and published results as well [15,25,42].

![Figure 1.1](image_url)  
*Figure 1.1  Effect of surface coverage on the surface tension of layered silicates (●); comparison to CaCO₃ coated with stearic (△) and lauric (□) acid.*
1.2.2. Interactions

The role of interactions and their modification are relatively simple in nanotube and spherical nanoparticle modified polymers and very similar to other heterogeneous polymer systems (for instance microcomposites) in spite of the nanometric dimensions of these reinforcements. However, particle-particle interactions play a much more important role in the case of nanofillers than for traditional reinforcements. Interactions are much more complicated in nanocomposites containing plate-like reinforcements, since they influence exfoliation and structure, and the number of possible competitive interactions can be also much larger in them than in composites containing other, non-layered reinforcements.

The thermodynamics of exfoliation and component interactions was considered by several groups. Jang et al. [43] used the solubility parameter (\(\delta\)) approach and showed that structure can be related to the solubility parameter of the polymer. The \(\delta\) value of the surfactant had smaller effect on structure. Vaia et al. [44] developed a mean-field lattice model for the description of the thermodynamics of polymer melt intercalation into organically modified layered silicates. The model predicts entropy and internal energy, which change with increasing gallery distance during intercalation. Although the results of static melt intercalation experiments seemed to agree well with the prediction, the terminology and approach is rather confusing. The use of the terms "unfavorable" and "favorable" for disperse and specific interactions as well as the treatment of nanocomposites as blends contradicts the fact that the 500-1000 nm large silicate platelets are 3 to 5 orders of magnitudes larger than lattice sizes in blends and that interaction is an adsorption process in which all interactions are favorable. Balazs et al. [45-47] also proposed various thermodynamic models for the prediction of the intercalation of polymers into organically-modified silicates, but their conclusions do not agree with those of Vaia and agree even less with experience.

The interactions developing in layered silicate polyamide (PA) nanocomposites were analyzed by molecular dynamics modeling by Sikdar et al. [48]. They proved that the strongest interaction forms between the silicate layer and the ammonium ion, but the backbone of the surfactant also interacts with the silicate rather strongly (Table 1.2). The various functional groups of the polymer and the surfactant, and the presence of additional components like solvents, additives and compatibilizers increase the number of possible interactions even more. Obviously, various groups of the components compete for active sites on the silicate surface, but also interact with each other and these competitive interactions determine the extent of exfoliation, the developed structure, polymer/silicate adhesion and finally the properties of the composites.

Two main factors must be considered in composites reinforced with nanofibers or nanotubes: stress transfer and dispersion. Large surface energy resulting in strong interaction is needed for the first, but it results in the aggregation of the fibers. Although experiments directed towards the determination of interfacial fracture energy in multiwalled carbon nanotubes (CNT) reinforced composites indicated the existence of a “relatively” strong interface [49], whatever that means, interfacial adhesion is usually quite weak in CNT or carbon nanofiber reinforced composites. Carbon nanotubes have a very regular structure almost exclusively consisting of carbon atoms. The surface energy of the tubes
is small and the tubes do not contain reactive groups necessary for coupling. This statement is strongly supported by the surface tension of carbon nanotubes, nanofibers and carbon fibers. Although polar and dispersion components may differ considerably depending on the source, total surface tension is between 30 and 45 mJ/m² in each case [35, 50-52]. This is rather small compared to that of NaMMT, for example, the dispersion component of which is around 250 mJ/m² at 100 °C (see Figure 1.1).

Table 1.2  Interactions acting in PA nanocomposites as determined by molecular dynamics calculations by Sikdar et al. [48]

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>Interacting site</th>
<th>Interaction energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>surfactant</td>
<td>functional group</td>
<td>-330</td>
</tr>
<tr>
<td>Clay</td>
<td>surfactant</td>
<td>backbone</td>
<td>-217</td>
</tr>
<tr>
<td>Clay</td>
<td>polymer</td>
<td>backbone</td>
<td>-108</td>
</tr>
<tr>
<td>Polymer functional group</td>
<td>surfactant</td>
<td>functional group</td>
<td>-143</td>
</tr>
<tr>
<td>Polymer functional group</td>
<td>surfactant</td>
<td>backbone</td>
<td>-23</td>
</tr>
</tbody>
</table>

The surface of nanotubes is also modified but the methods are similar to the surface treatment of traditional fillers. Usually two approaches are applied to control dispersion and improve interactions. Several groups use surfactants to facilitate the dispersion of the tubes [52-62] and the surface of the nanotubes is covered with a polymer or a surfactant through physical adsorption. The surface can be also modified chemically (“grafting to” or “grafting from” techniques) in order to improve interfacial adhesion [63-91].

The methods used for the surface modification of nanotubes can be and are applied also to spherical nanofillers. The surface of the particles is modified either by surfactants or by the proper reactants to introduce functional groups onto the surface of the filler [92-96]. These groups can react with the polymer during polymerization or cross-linking. This technology may lead to nanocomposites with controlled structure and interfacial adhesion, thus materials with tailor made properties can be produced for the most diverse applications. Polyhedral oligomeric silsesquioxane (POSS) is a modifier having great potentials. Sometimes it is regarded as a molecule, while others treat it as nanofiller [97,98]. Besides POSS, other hybrid organic-inorganic supermolecular assemblies can be also prepared e.g. from butyltin oxo-hydroxoxo nanobuilding blocks and dicarboxylates by the related chemistry [99]. Although the chemistry is not simple, the potentials of the approach are large and homogeneity, as well as interactions can be kept under control relatively easily, at least compared to traditional homogenization technologies.
1.2.3. Interphase structure and properties

The formation of an interphase in heterogeneous polymers is a well-accepted fact [100,101] and interphase volume, thickness and characteristics considerably influence composite properties. Interfaces form both in micro- and nanocomposites, but much larger interfaces and a significant interphase volume should develop in composites containing fillers or reinforcements with dimensions in the nanometer range. The importance of the interphase was emphasized in composites containing spherical nanoparticles [102], but interphase formation has not been mentioned practically at all yet in layered silicate nanocomposites. The detection and analysis of the interphase is difficult both by direct and indirect methods. First of all the interphase cannot be present in sufficient amounts to detect it, if the extent of exfoliation is small that happens quite frequently. Nuclear magnetic resonance (NMR) and dielectric spectroscopy indicated an increase in the mobility of polymers confined in the galleries of layered silicates, and the appearance of a second glass transition temperature lower than that of the bulk material was assigned to the interphase [98] that might explain the less than expected reinforcement in several nanocomposites. These results also indicate that the polymer interacts mainly with the surfactant and not with the silicate surface and only weak interactions form, which do not decrease mobility. The results and conclusions described above are contradicted by the measurements and calculations of Utracki et al. [103-105]. The authors prepared various polymer/layered silicate nanocomposites, determined their pressure-volume-temperature (PVT) behavior and applied the Simha-Somcynsky [106] equation of state for the determination of the free (hole) fraction of the materials. Adsorption and the decrease of free volume indicated the formation of a hard interphase. Unfortunately, none of the parameters derived from the model correlated with the actual mechanical properties of the composites.

Recently an attempt was made to determine interphase formation and to characterize interphase properties in PP/MMT composites [107]. Interphase thickness and properties were deduced from the composition dependence of mechanical properties with the help of a model [7,8] using silicates with different particle sizes. The model yields a parameter \( B \) which expresses the reinforcing effect of the nanofiller and depends on the specific surface area of the latter as well as on interphase properties (thickness, yield stress). The obtained results proved the formation of an interphase in the PP composites studied, but the determination of its properties was hampered by the fact that particle size changed quite considerably during homogenization. As a consequence, the estimation of the contact surface between the silicate and the polymer became extremely difficult. In spite of the problems, overall values of interphase properties were obtained using the results of all composites prepared (interphase thickness of 0.23 \( \mu m \) and interphase yield stress of 51.2 MPa). Unfortunately, these estimates neglected the different interactions developing in composites containing uncoated (NaMMT) and modified (OMMT) silicate, respectively. The results indicate that composition [type of the montmorillonite and maleated polypropylene (MAPP) content] had larger effect on reinforcement than the surface area of the fillers, at least in the range studied, which further emphasizes the importance of exfoliation and structure in the determination of nanocomposite properties.
1.3. Structure

Nanocomposites can be classified in many ways; in this work we discuss them according to the dimensionality of the nano-sized heterogeneity. The size is in the nanometer range in all three dimensions for particles like silica (SiO₂), titanium-dioxide (TiO₂), calcium carbonate (CaCO₃) or polyhedral oligomeric silsesquioxane (POSS). Nanotubes and fibers [carbon nanotubes (CNT); halloysite nanotubes (HNT)] are small in two dimensions, but can be micrometer long, while the individual platelets of layered minerals [montmorillonite (MMT); layered double hydroxide (LDH)] are approximately 1 nm thick, but their other two dimensions are usually much larger.

1.3.1. Plates

The structure of nanocomposites containing plate-like reinforcements (MMT, LDH) differs in two aspects from that prepared with the other two reinforcements discussed here, i.e. nanotubes or fibers, and spherical nanocomposites. In order to prepare composites reinforced with plates, the original particles must be exfoliated, separated to individual layers. These composites also may contain several structural entities with different dimensions thus structure must be considered and studied in a very wide length scale from the nanometer range to microns.

Particle structure. The existence of original particles, i.e. large clay entities in the dimension of the original filler added to the polymer, is hardly ever mentioned in studies on nanocomposites [108-119]. One may deduce from this fact that particles are not present in the composites; i.e. they break down to smaller units, into intercalated stacks or to individual platelets during mixing. This is not very surprising since mostly X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM) are used for the characterization of the composites and those do not necessarily detect the presence of large particles. The lower 2θ range of the XRD trace of two polypropylene composites is presented in Figure 1.2.

Exfoliation does not take place in the composite containing only organically-modified silicate (OMMT). It is dispersed in the matrix as large particles shown also by the presence of the silicate reflection in the XRD trace (trace a). Exfoliation is facilitated by a coupling agent, maleic anhydride grafted PP (MAPP) in the other composite. The incorporation of 25 vol% MAPP leads to the complete disappearance of the silicate peak (trace b). Based on these results one could claim that the original particles disappeared and the silicate is completely exfoliated [21,24,120,121]. However, XRD detects only ordered clay structures [122], and scanning electron microscopy (SEM) done on the etched surfaces of PP/OMMT (Figure 1.3a) and PP/OMMT/MAPP (Figure 1.3b) composites show distinct particulate structure in both cases. As a consequence, we can conclude that in spite of the absence of the silicate reflection in the corresponding XRD pattern (Figure 1.2 trace b), complete exfoliation has not been achieved, and clay particles in the length scale of microns are also present in the composite. Their amount and size must influence strongly all properties. Similar observation was made by Luduena et al. [112] in polycaprolactone/OMMT composites and Costa et al [123] in low density polyethylene (LDPE)/LDH composites.
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**Figure 1.2** XRD traces of PP nanocomposites containing 2 vol% silicate (Nanofil 848); a) PP/OMMT, b) PP/OMMT/MAPP (25 vol%).

**Figure 1.3** SEM micrographs taken from the etched surface of PP nanocomposites containing 2 vol% organically-modified clay. a) PP/OMMT, b) PP/OMMT/MAPP (25 vol%).

**Gallery structure.** The gallery structure of layered minerals is routinely determined by XRD both before compounding and in the composites. The number of reflections and layer distance are determined by the type and amount of surfactant used for
modification. Gallery distance is inversely proportional to the position of the silicate reflection recorded at low 2θ angles. Surface modification and the characteristics of gallery structure are compiled in Table 1.1 for selected layered minerals. XRD traces are presented in Figure 1.4 for five silicates. Large differences can be observed in the number, shape, intensity and location of the silicate reflection.

![XRD traces of five silicates.](image)

**Figure 1.4** XRD traces of five silicates. a) NaMMT, b) Nanofil 848 (stearyl-amine), c) Cloisite 20A (distearyl-dimethyl-ammonium chloride), d) Nanofil 948 (distearyl-dimethyl-ammonium chloride), e) PhoMMT (trihexyl-tetradecyl-phosphonium chloride)

Several studies were carried out to investigate the effect of the type and amount of the surfactant on the gallery structure of layered minerals [21,44,124,125]. Possible arrangements were shown already by Lagaly [126,127] and they were confirmed by other studies [29]. The orientation of the surfactant depends mainly on the ion density of the clay, which is relatively small for MMT [127-129], and on the type and amount of surfactant used.
Other groups studied the effect of the chemical structure of the surfactant on exfoliation, composite structure and properties. Reichert et al. [21] found in PP/OMMT composites containing also a MAPP coupling agent that large extent of exfoliation cannot be achieved if the length of the aliphatic chain is equal or less than 8; better dispersion was obtained at chain lengths of 12-18 carbon atoms. In PA nanocomposites Fornes et al. [124] showed that surfactants with two long tails are less advantageous than those having a single aliphatic chain attached to the nitrogen atom, smaller head groups lead to increased exfoliation compared to large ammonium cations, and excess surfactant is disadvantageous for exfoliation, structure development and properties. They obtained similar results also in thermoplastic polyurethane matrices [125]. Contrary to Fornes et al. [124], Vaia [44] found in polystyrene (PS) nanocomposites that head groups do not influence intercalation and two long aliphatic chains are more advantageous than one. These apparent contradictions obviously originate from the complex structure of the nanocomposites usually not characterized sufficiently, the insufficient information available and/or supplied (ion exchange capacity of the clay, the amount of surfactant used, its composition, orientation, etc.) and from the dissimilar polymers, processing/preparation conditions and characterization methods. These contradictions clearly prove that unambiguous, general correlations have not been established yet among the gallery structure of the silicate, interactions and composite properties.

Exfoliation, platelets. Exfoliation is usually studied by TEM, which is able to detect also individual mineral layers [130]. Very few publications present micrographs in which only individual layers are dispersed in the polymer for any matrix and especially for polyolefins. Usually, intercalated stacks or tactoids with a range of gallery distances form in the composites and such tactoids appear in the micrographs. “Very good” composites with a high degree of dispersion may contain stacks of silicates with 3 to 10 layers [124,131,132], but even this can be achieved only with the proper selection of components and processing conditions. A variety of structural units were detected in PP/OMMT composites. SEM micrographs proved the presence of larger particles (see Figure 1.3), a large tactoid with varying degree of intercalation and individual layers are shown in the TEM micrograph of Figure 1.5a and the process of intercalation and complete exfoliation can be seen in Figure 1.5b.

Network structure. Silicate platelets may interact with each other; face-to-face interaction leads to aggregation, while edge-to-face orientation results in the formation of a network structure. Both phenomena have been observed also in polymer composites [21,133,134]. The silicate network is usually detected by TEM [21,135,136] or by the analysis of the linear viscoelastic properties of nanocomposite melts [108,120,137]. The increase of complex viscosity or storage modulus \( G' \) and/or the appearance of a yield stress in the low frequency range of the spectrum are usually interpreted as network formation [138], [139].
In polypropylene nanocomposites large extent of exfoliation occurs at very small silicate and large MAPP content, and an occasional overlapping of the silicate layers may be observed as a result as shown in Figure 1.6. Rheology supplies further proof for network formation. The plotting of the two components of dynamic viscoelastic characteristics against each other, i.e. $G''$ (loss modulus) vs. $G'$ (storage modulus) or $\eta''$ (imaginary part of the complex viscosity) vs. $\eta'$ (real part), yields an arc-shaped curve, if the process can be described with a single relaxation time (Cole-Cole plot) [140], [141]. Since a network obviously deforms with different relaxation times than the homogeneous melt, we expect a correlation deviating from a semicircle thus Cole-Cole plots are very convenient for the detection of network formation. The probability of network formation increases with increasing extent of exfoliation. Although TEM, XRD and rheology supplies the same qualitative information about structural changes in polymer/layered silicate composites, the quantitative determination of the relative amount of the various structural elements is very difficult with all three of them [107,142]. The observed structure the number of individual platelets and the threshold concentrations for silicate network formation all depend also on the amount of MAPP present [142]. These results prove that a wide range
of structural units may be present in PP/silicate, but also in other composites. Similar structures were detected, for example in polyamide/montmorillonite (PA/MMT) composites as well [143].

Figure 1.6 Interaction of silicate layers in a PP nanocomposite at small clay (0.5 vol%) and large (60 vol%) MAPP content; possible network formation of the silicate sheets.

1.3.2. Nanotubes and fibers

Nanotubes and nanofibers have two dimensions in the nanometer range; they are usually micrometer or even millimeter long. They attracted the interest mainly because of their exceptional mechanical [144] and electrical properties [145]. Theoretical and experimental investigations proved that carbon nanotubes have Young’s modulus in the range of 1.2 TPa, but they are also flexible [146]. The extremely high stiffness would make these materials ideal reinforcements for composites. Unfortunately, although the fibers have large aspect ratio, the other two conditions of efficient reinforcement, i.e. alignment parallel to the direction of the load and good stress transfer, are difficult to satisfy.
Dispersion. The properties of polymer/CNT composites depend on many factors including the technology of preparation and purification, the type and amount of residual contaminations, the structure of the nanotube (single or multi wall), diameter, the length and aspect ratio of the tubes, as well as their association or aggregation (individual tubes, bundles). Numerous methods are used for the preparation of polymer/CNT composites [52,147-156] and their main goal is practically always the achievement of homogeneous dispersion. Dispersion is aided by stirring, the use of surfactants, other surface modification techniques including functionalization, and ultrasound assisted homogenization.

Orientation. The orientation of the tubes was attempted in various ways, for instance pre-orientation [157,158] or magnetic field orientation assisted in-situ polymerization. The discontinuous technology and the non-conventional method make these techniques rather cumbersome and disadvantageous. More attempts are made to orientate the fibers during processing or by stretching the extruded product [159], by fiber spinning from the melt [160] or by electrospinning [161]. The largest extent of orientation is achieved by the last two methods. Nevertheless, the orientation and dispersion of carbon nanotubes remain the main obstacles before using them routinely as reinforcements in polymer composites.

1.3.3. Spherical nanoparticles

Numerous attempts have been made to distribute spherical nanoparticles in a polymer matrix with the most different methods, since aggregation is the major issue in these composites. The most frequent approach is the use of traditional thermoplastic or thermoset technologies to homogenize the previously prepared particles into the matrix polymer. Carbon black, precipitated calcium carbonate and silica are the most often used representatives of this class of materials. Interaction and its control is the key for success in the application of these materials, but particle-particle interactions are usually more important than polymer-filler adhesion. It has been shown earlier that the occurrence and extent of aggregation depends on the relative magnitude of adhesion and separating forces [162]. The ratio of the two forces depends on interfacial adhesion, shear forces and the size of the particles. The aggregation tendency of fillers increases strongly with decreasing particle size. Shear forces can be changed in a limited range thus the main factor to control aggregation is the surface characteristics of the filler. Various treatments and modification techniques are used to control them, like the surface grafting of the silica [163,164], but aggregation can be rarely avoided.

The simultaneous formation of the particles and the polymer matrix, usually in sol-gel technology, seems to have much larger potentials. The interest in organic-inorganic hybrids dates back to the 80’s and several reviews are available in this field summarizing the technical possibilities, structure, properties and potential applications of these materials [97,165,166]. Usually silicate chemistry is used to produce particles of different sizes [167] or organic-inorganic networks [168]. The size of the particles can be changed from 10 to 500 nm by modifying the conditions of the polymerization, hydrolysis and condensation of the silica precursors [167]. The homogeneity of the composite is much better in these materials, although depending on chemistry aggregates can form even in this case [167].
1.4. Micromechanical deformation processes

Polymer nanocomposites are heterogeneous materials. Under the effect of external load, stress concentration develops around the heterogeneities and local stress maximums initiate local deformation processes. The final properties of such materials depend on the mechanism of the dominating local deformation process. Most nanocomposites are applied as load bearing, structural materials thus the knowledge of local deformation processes is crucial for their successful application. However, few attempts have been made to study these processes in nanocomposites in detail [169], certain aspects of structure are ignored completely and competitive interactions among the components are treated in general terms practically always.

The deformation of layered silicate nanocomposites may be dominated by processes related to the matrix or to the reinforcement. The possible deformation mechanisms of the polymer are relatively few and simple. The matrix may deform by shear yielding, but micro-cracking or fracture can also take place. Voiding or cavitation was also observed during the deformation of neat polyamide [170]. Much larger is the number of the possible deformation processes related to the reinforcement especially in the case of layered fillers such as silicates or LDHs. According to the model of Kim et al. [169] the fracture or peeling of the silicate layers and the slipping of individual layers or stacks may occur during the deformation of PA/MMT composites. The model of the authors includes the deformation and fracture of clay particles and tactoids, which indicates that exfoliation was not complete in their case. If larger entities are present in the composite – for instance in the case when NaMMT is used as filler – debonding of the silicate from the matrix must be also considered as a possible deformation mechanism, as found by Lefebvre et al. [171]. The volume strain of PA nanocomposites was analyzed in detail and the researchers concluded that besides elastic deformation, considerable debonding and plastic flow also takes place during the elongation of the samples [171].

Micromechanical deformation processes were also analyzed by volume strain and acoustic emission measurements in polycaprolactam (PA6)/layered silicate composites [143]. The results showed that the matrix polymer and the composites deform according to different mechanism. Sound is emitted by cavitation in the neat matrix, while acoustic activity is related to larger structural entities, i.e. to tactoids and non-exfoliated particles in the composites. Acoustic events are generated mainly by the fracture of particles and volume increase is initiated primarily by this mechanism because matrix/silicate adhesion seems to be strong, debonding rarely takes place [143]. The type and amount of the surfactant used for organophilization of the silicate played on important role in the determination of deformation processes and properties through influencing both matrix/filler interaction and the internal adhesion of silicate particles [143,172]. Basically all silicate related processes depend on interactions, both on the forces acting among the layers and matrix/filler adhesion. As a consequence, besides the quality of the surfactant used for organophilization, also the type of the matrix polymer is expected to influence the mechanism of deformation and the properties of the composites considerably.
1.5. Composite properties

Composite materials are mostly used as load bearing elements. Accordingly, the most important and frequently measured properties are stiffness and strength, both in the case of micro- and nanoreinforced composites. Review papers and books [12,22,98,106,173-177] offer a detailed account on various properties of polymer nanocomposites prepared from the most diverse matrices and reinforcements.

1.5.1. Stiffness

Stiffness is the most often measured, modeled and discussed property of nanocomposites [178-184]. Percentage increase in modulus is often used to prove the exceptional properties of this class of materials [185-188] and also the large degree of exfoliation in nanocomposites prepared with layered reinforcements. Large increase in stiffness is observed in elastomers, indeed, but much more moderate in glassy or crystalline polymers [175,189-191]. Because of its assumed importance, the stiffness of nanocomposites is modeled quite frequently. In their paper, Valavala and Odegard [192] compares the theoretical background, advantages and drawbacks of the various approaches used. Usually the composition dependence of stiffness is modeled by continuum mechanical models developed for traditional composites. The Halpin-Tsai [193] and the Mori-Tanaka [194] models are used the most frequently [124,178,179,181,185,195-197], but other micromechanical models are also applied or developed occasionally [179,181,198]. Although the papers usually claim good agreement between measured and predicted properties, the general validity of the conclusions is limited for several reasons. Various assumptions are used during the development of these models, like the linear elasticity of the components, homogeneous distribution of the reinforcement in the matrix, its unidirectional alignment, as well as the perfect adhesion of the phases. Obviously, most of the assumptions applied are not realistic and these conditions are difficult to satisfy in nanocomposites.

One encounters enhanced difficulties during modeling in layered silicate nanocomposites because of their complicated structure. Many of the models use various assumptions for structure and try to account for the structural diversity of these materials [179,181,195,198]. Structure is usually simplified in the calculations, i.e. particles and silicate network are neglected and only individual layers and tactoids are considered. In spite of such simplifications the proper accommodation of the varying degree of exfoliation and changing orientation within the composite into the model presents serious difficulties. Forges and Paul [124] proved that very tedious and meticulous procedure is needed to obtain acceptable data for model calculations. Accordingly, most of the modeling efforts are focused around assumptions concerning the structure of the composite and most output information is related to structure as well. The resulting characteristics are, for example, the number of platelets per stack or the aspect ratio of the dispersed clay units. However, Osman et al. [178] expressed their doubts about the validity of such estimates based on the argument that composite modulus depends also on particle orientation and on the Poisson’s ratio of the matrix, and they came to the conclusion that the aspect ratio of the inclusions cannot be estimated from the Halpin-Tsai equation for layered silicate nanocomposites [178].
1.5.2. Strength, reinforcement

The basic condition of efficient reinforcement is strong adhesion between the matrix and the reinforcing component. The composition dependence of strength or yield stress gives more accurate information about interfacial interactions and reinforcement in all heterogeneous polymer systems, including nanocomposites, than modulus [7,8,133]. The effect of interfacial interactions depends on its strength and on the contact surface between the phases. Although strong interaction is assumed in layered silicate nanocomposites, interaction is usually weak between OMMT and any matrix due to the surface modification of the clay. Weak interaction, however, might be compensated by large surface, if the degree of exfoliation is sufficiently large. The composition dependence of the tensile yield stress of heterogeneous polymer systems can be described by the simple equation [7,8,26]

$$\sigma_y = \sigma_{y0} \frac{1 - \varphi}{1 + 2.5 \varphi} \exp(B \varphi)$$

(1.2)

where $\sigma_y$ and $\sigma_{y0}$ are the yield stress of the composite and the matrix, respectively, $\varphi$ the volume fraction of the filler in the composite and $B$ is related to the load carried by the dispersed component, i.e. it depends on interaction [7,8,40,133,199]. The second term $(1 - \varphi)/(1 + 2.5 \varphi)$ expresses the effective load-bearing cross-section of the matrix. At zero interaction all the load is carried by the polymer and the load-bearing cross-section decreases with increasing filler content. The same correlation can be used to describe the composition dependence of tensile strength, if the elongation of the composite is small, usually less than 100 % [8]. The value of parameter $B$ depends on all factors influencing the load-bearing capacity of the filler, i.e. on the strength of interaction and on the size of the contact surface. The effect of these factors on $B$ is expressed as

$$B = (1 + A_f \rho_f l) \ln \frac{\sigma_{yi}}{\sigma_{yi0}}$$

(1.3)

where $A_f$ is the specific surface area of the filler (contact surface), $\rho_f$ is its density, while $l$ and $\sigma_{yi}$ are the thickness and the yield stress of the interphase forming spontaneously in all heterogeneous polymer systems. These two parameters were shown to depend on the strength of matrix-filler interaction [200,201]. The load carried by the second component depends also on the properties of the matrix (see $\sigma_{yi0}$ in Eq. 1.3); the extent of reinforcement is larger in a softer than in a stiffer polymer.

If the model is valid, we should obtain a straight line when the natural logarithm of reduced or relative yield stress is plotted against filler content,

$$\ln \sigma_{yrel} = \ln \frac{\sigma_y}{\sigma_{y0}} \frac{1 + 2.5 \varphi}{1 - \varphi} = B \varphi$$

(1.4)

i.e. points should fall on a straight line with zero interception and with a slope proportional to the extent of reinforcement ($B$). PA nanocomposites are undisputedly the reference materials in which layered silicates exert the largest reinforcing effect [42,202]. Extensive exfoliation and strong reinforcement are almost invariably assumed and expected in PA/layered silicate composites [180,203-206]. However, if we thoroughly examine and
compare published data, we find that the properties of these materials vary in a very wide range and the silicate often has only a moderate reinforcing effect. The tensile yield stress of six materials, including a PA/LDH composite, is plotted against filler content in Figure 1.7 in order to support our statement; the yield stress of the composites covers a very wide range, indeed.

![Graph](image)

**Figure 1.7** Wide range of absolute values and different composition dependence of tensile yield stress in PA/nanocomposites. Symbols: (□) Liu [204], (△) Rácz [206], (○) Fornes [180], (◇) Peng [207], (▽) Hedicke-Höchstötter [208], (●) Shelley [205].

The composition dependence of the yield stress of the composites of Figure 1.7 was analyzed by the model presented above. The logarithm of relative yield stress is plotted as a function of silicate content in Figure 1.8. Straight lines are obtained in all cases; the deviation from the lines is negligible proving the validity of the approach. The slopes of the lines differ considerably from each other indicating widely differing reinforcing effects. Rather surprisingly very small $B$ values of about 4 or 5 are obtained in some cases even when organically-modified MMTs were used, in spite of the general belief that silicates exfoliate in a large extent in PA and properties improve considerably [25,121]. Although the use of $\omega$-amino acid as surfactant creates strong interaction between the silicate and the matrix [1-3], most of the clays were treated with aliphatic amines resulting in weak interaction [180,203,204]. The results clearly prove again the pitfalls of false generalization assuming that all PA nanocomposites are strong simply because the first composites of the Toyota group [1-3] showing excellent properties were prepared with an amino acid surfactant.
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![Figure 1.7](image1.png)

**Figure 1.7** Relative tensile yield stress of the PA composites of Figure 1.7 plotted as a function of silicate content. Symbols are the same as in Figure 1.7.

The determination of $B$ values offers the possibility to estimate also the extent of exfoliation in these composites. We assume that NaMMT does not exfoliate at all, while the specific surface area of completely exfoliated silicate is known to be about 750 m$^2$/g [15,18,19]. These two cases represent the boundaries for zero and maximum reinforcement. $B$ depends linearly on specific surface area if all other factors including interaction are the same (see Eq. 1.3). Using PP/CaCO$_3$ composites as reference we obtain the results listed in Table 1.5. This shows that $B$ values of about 200 should be obtained if exfoliation were complete down to individual silicate layers. The largest $B$ value calculated for the PA/silicate composite of Shelley [205] corresponds to a specific surface area of about 90 m$^2$/g. This indicates the formation of stacks containing approximately 10 silicate layers in the average. This result agrees well with the experience that complete exfoliation is very difficult to achieve and nanocomposites always contain different structural formations including individual silicate platelets, intercalated stacks, but often even large particles.
Cost is an important attribute of every engineering material and it decreases with increasing filler content in traditional composites, but usually increases in nanocomposites 

Table 1.5  

*Estimation of the extent of exfoliation from parameter B determined in PP composites*

<table>
<thead>
<tr>
<th>Filler</th>
<th>Parameter B</th>
<th>Specific surface area (m²/g)</th>
<th>Extent of exfoliation (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>1.5</td>
<td>3.3</td>
<td>0</td>
<td>[40]</td>
</tr>
<tr>
<td>NaMMT</td>
<td>1.8</td>
<td>26.0</td>
<td>0</td>
<td>[209]</td>
</tr>
<tr>
<td>OMMT</td>
<td>195ᵃ</td>
<td>750</td>
<td>100</td>
<td>[15,18,19]</td>
</tr>
<tr>
<td>OMMT</td>
<td>22.9</td>
<td>91.0ᵇ</td>
<td>11.7</td>
<td>[205]</td>
</tr>
</tbody>
</table>

ᵃCalculated from published specific surface area assuming complete exfoliation  
ᵇCalculated from the largest B value published

1.5.3. Other properties

Compared to stiffness and sometimes to strength, other characteristics of nanocomposites are investigated much less. One of the characteristics mentioned quite frequently in relation to layered silicate nanocomposites is heat deflection temperature (HDT). This property is closely related to stiffness and changes with composition in a similar way. The introduction of any reinforcement may modify also other characteristics like the appearance of the product (color, surface) or influence the stability of the compound [204]. These are not discussed here, but two properties must be mentioned specifically.

The inherent flammability of plastics is one of their major drawbacks and the use of flame retardants is required today in most applications, especially in construction and transportation. Layered silicates, carbon nanotubes and halloysite were shown to decrease the flammability of plastics. Although they cannot provide the V0 specification of the UL 94 standard for the polymer as a single additive, but they increase flame retardancy considerably in combination with traditional flame retardants [210,211].

Polymers are basically insulators with surface resistivity of around $10^{14}$-$10^{18}$ Ωcm. Applications exist which require a certain conductivity, like air ducts in mines, pipes for solvent transport, electromagnetic (EMI) shielding and some other areas. Conductivity is usually achieved by the introduction of conductive fillers. Traditionally special conductive carbon blacks or metal fillers, particles or flakes, are used in such applications, but recently intensive research is going on to use carbon nanofibers, nanotubes or graphene for this purpose [174,212-214].
1.6. Possible applications, functionality

Cost is an important attribute of every engineering material and it decreases with increasing filler content in traditional composites, but usually increases in nanocomposites. Moreover, decreasing polymer prices and increasing compounding costs make any composites competitive only if technical benefits are utilized in their full extent.

One of the first target areas of most composites prepared with anisotropic particles (fibers, tubes, plates) is their use as load-bearing parts utilizing the large surface area, stiffness and aspect ratio of these reinforcements. In the case of nanocomposites serious obstacles were met during the production of parts with the desired properties for reasons described in previous sections, i.e. difficulties with the control of structure, dispersion, orientation, adhesion and last, but not least price. Nanocomposites can be used as structural elements in certain areas, but the real potentials of these materials are in special, niche application utilizing their functional properties. In previous sections we mentioned several application areas but the real potentials of nanocomposites are in special applications like membrane technology, electronics, as well as biomedical and environmental devices.

The gas barrier properties of polymers are claimed to be modified significantly by layered fillers. The general idea is that individual silicate layers with large aspect ratio increase the diffusion path of gases considerably especially if they are oriented parallel to each other. Several groups observed significant decrease in the gas permeability of layered silicate nanocomposites [215-217]. The main field of application for these materials is packaging where the targeted combination of properties is achieved by the preparation of coextruded films. One solution already introduced into practice is the PA6 based Imperm nanocomposite offered by Nanocor for the production of multilayer films, and bottles for the packaging of soft drinks. The same principles are used in graphene composites as Figure 1.9 shows, the permeability of the polymer for various gases decreases considerably in the presence of graphene [219].

In the last decades significant progress was made in the production of polymer based membranes. One limiting factor in improving the performance of these membranes is that selectivity decreases with increasing permeation, while productivity decreases with increasing temperature [220]. One way to circumvent these problems is the preparation of nanocomposite membranes, which show improved permeation and selectivity at the same time [221-223]. Nanocomposite membranes are used already in fuel cells as well. The performance of the electrodes could be improved, when carbon nanotubes were used instead of carbon black [224]. The diffusion of methanol is one of the main problems in methanol fuel cells decreasing efficiency considerably. Nanocomposite membranes decrease methanol permeation thus improving the performance of these cells [225].

Another area discussed here is electronics where size reduction requires the use of nanotechnology. The size of active electronic parts is already in the nanometer range in most devices. Both the type and the specific application of nanocomposites are very diverse in this field. Sensors, photo diodes, super condensers, LEDs and transistors [226], various shielding applications, conductive coatings [145] or electronic displays are prepared from nanocomposites containing carbon nanotubes, metal oxide nanofibers, gold, silver, platinum and palladium nanoparticles [226,227].
Chapter 1

Figure 1.9  Reduced relative gas permeability of polycarbonate nanocomposites produced by melt compounding [219]. Symbols: (○) nitrogen, (□) helium; full symbols: graphite, empty symbols: graphene.

Large efforts are done to explore the possible use of nanocomposites in environmental applications, in fact environmental nanotechnology is expected to play an important role in environmental engineering and science in the near future [228]. A detailed review of the field is offered by the paper of Zhao et al. [228]. Possible applications include catalytic and redox degradation of contaminants like phenol [229,230], trichlorobenzene [231,232], nitrobenzene [232] and other compounds, biocatalysis, adsorption of pollutants like arsenic [233-235] and other metallic contaminants (\(\text{Pb}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}\)) [236,237], but other applications like pollutant sensing and detection are also envisaged in this field.

Nanotechnology and nanocomposites play an increasing role in many biomedical applications. One important application is the production of scaffolds from nanofibers for cell and tissue growth [238] and the preparation of prosthesis [239] sometimes using the antibacterial effects of nanofillers [240]. But controlled drug release and targeted drug delivery are promising fields also in which nanocomposites may play a role in the future. Nanoparticles are used in increasing quantities also in various drug formulations. For instance halloysite nanotubes (HNT) are thought to slow down and regulate drug release [226,227,241-245]. HNT is a naturally occurring aluminosilicate clay with tubular structure. Due to their high mechanical strength, thermal stability, biocompatibility, HNTs have a number of exciting potential applications in controlled release devices. Intensive
research activity is going on recently related to the application of HNT as a carrier of active agents [246].

Although the potentials of nanocomposites are great, several outstanding issues (competitive interactions, optimum properties) need resolution in the future. Moreover, the majority of recent ideas are based on laboratory tests which must be verified by field application experiments. Industrial production needs further efforts. The potentials of nanocomposites are extremely large in many fields, but progress towards practical applications is slower than expected. Nevertheless, nanocomposites have found functional application in several areas; Table 1.6 gives an overview of selected products used in industrial practice already.

1.7. Conclusions

The properties of all heterogeneous materials including nanocomposites are determined by the same four factors, i.e. component properties, composition, structure and interfacial interactions. On the other hand, usually more complicated structure develops in nanocomposites than in traditional particulate filled polymers, and that is especially valid for composites prepared from plate-like nanofillers. Interfacial interactions should play an increased role in nanocomposites compared to traditional composites because of the assumedly very large interfacial area developing in them. Unfortunately competitive interactions among the components and structure-property correlations are rarely determined quantitatively. The largest amount of nanocomposites are prepared with layered reinforcements and these materials are used mostly as load-bearing parts. However, in such applications the failure of the part and deformation mechanism are crucial questions which are strongly influenced by interfacial interactions. Besides the quality of the nanofiller the type of the matrix polymer is also expected to influence the interfacial interactions, the mechanism of the dominating micromechanical deformation process and the properties of the composites considerably. The stiffness and strength of nanocomposites are usually far from the expectations, their performance is still comparable with the properties of the traditional filled composites, the main reason being insufficient homogeneity, undefined structure and improper adhesion. In spite of considerable difficulties nanocomposites have great potentials especially in functional applications. Several nanocomposite products are already used in industrial practice but emerging functional properties are needed for economic application and further progress.
## Table 1.6. Application of nanocomposites in industrial practice; areas and products

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Nanofiller</th>
<th>Targeted property</th>
<th>Application area, product</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>layered silicate</td>
<td>stiffness</td>
<td>automotive, engine room</td>
<td>Toyota, Ube</td>
</tr>
<tr>
<td>thermoplastic olefin</td>
<td>layered silicate</td>
<td>stiffness, strength</td>
<td>automotive, body elements</td>
<td>General Motors</td>
</tr>
<tr>
<td>epoxy</td>
<td>carbon nanotube</td>
<td>stiffness, strength</td>
<td>tennis racket</td>
<td>Babolat</td>
</tr>
<tr>
<td>epoxy</td>
<td>carbon nanotube</td>
<td>stiffness, strength</td>
<td>ice hockey stick</td>
<td>Montreal</td>
</tr>
<tr>
<td>various matrices</td>
<td>multiwalled nanotubes</td>
<td>electrical conductivity</td>
<td>antistatic painting</td>
<td>Hyperion Catalysis</td>
</tr>
<tr>
<td>Nylon MXD 6</td>
<td>layered silicate</td>
<td>barrier property</td>
<td>food packaging</td>
<td>Nanocor</td>
</tr>
<tr>
<td>not published</td>
<td>silver particles</td>
<td>antimicrobial effect</td>
<td>wound dressing</td>
<td>Beiersdorf, Elastoplast</td>
</tr>
<tr>
<td>not published</td>
<td>silver particles</td>
<td>antimicrobial effect</td>
<td>antibacterial wall paint</td>
<td>Nanovations</td>
</tr>
<tr>
<td>not published</td>
<td>not published</td>
<td>decreased gas permeability</td>
<td>food packaging</td>
<td>InMat, Nanolok</td>
</tr>
<tr>
<td>halogenated polymers</td>
<td>hydrotalcite</td>
<td>HCl scavenger</td>
<td>PVC products</td>
<td>Akrochem, Süd-Chemie</td>
</tr>
<tr>
<td>polyolefin</td>
<td>hydrotalcite</td>
<td>flame retardancy</td>
<td>-</td>
<td>Akrochem, Süd-Chemie</td>
</tr>
<tr>
<td>ethylene-vinyl acetate</td>
<td>layered silicate</td>
<td>flame retardancy</td>
<td>coaxial cable jacketing</td>
<td>Kabelwerk Eupen AG</td>
</tr>
<tr>
<td>polyolefin, nylon</td>
<td>halloysite</td>
<td>stiffness, strength</td>
<td>-</td>
<td>Naturalnano</td>
</tr>
<tr>
<td>not published</td>
<td>layered material</td>
<td>stiffness, strength</td>
<td>body of wave runners</td>
<td>Nanoxcel, Yamaha</td>
</tr>
<tr>
<td>not published</td>
<td>carbon nanotube</td>
<td>conductivity, transparency</td>
<td>films for display systems</td>
<td>Invisicon, Eikos</td>
</tr>
</tbody>
</table>
1.8. Scope

As described in the introductory part of this thesis, although the interest in nanocomposites, or at least in layered silicate nanocomposites, decreases somewhat, research continues. The basic idea is still attractive, only the solution is missing and researchers hope that new combinations of materials, a novel surface modification or the appropriate processing technology will lead to the desired material possessing exceptional properties. Our previous research has shown that one of the key questions in the preparation of layered silicate nanocomposites is the exfoliation of the clay. We could show several times that exfoliation is practically never complete and the composites contain various structural entities, individual silicate layers, intercalated stacks or tactoids, large silicate particles and sometimes a silicate network. The characterization of structure is of utmost importance, but the determination of the relative amount of the various structural entities has never been done before and we could not determine it either. Additionally, the claimed benefits of nanocomposites or their benefits over traditional microcomposites have never been proved either. Because of the limited success achieved in the preparation of layered silicate nanocomposites with good properties, we raised several basic questions at the beginning of this phase of the research about properties which can be achieved, interactions and alternative nanofillers.

Research groups working in the field of nanocomposites always assume and claim that nanocomposites are superior to traditional composites. The claim is rarely supported by experimental evidence, but presentations and sometimes even publications compare the properties of the two types of materials. One of the papers often cited was authored by the Toyota group [3] and shows that the heat deflection temperature of nanocomposites increases steeply with increasing silicate content. A thorough study of the paper, however, reveals that the layered silicate nanocomposites prepared are not compared to traditional composites there, any comparison shown in presentations takes data from different sources. The comparison is very questionable as the result, since in all probability the polymer, the processing technology and every other factor determining structure and interactions differ considerably in the two cases. Another good example is the paper of Fornes and Paul [124] cited more than 600 times. In their first figure the authors compare the relative stiffness of layered silicate PA composites to that of a PA/glass fiber composite at 7 wt% filler content showing a 2.1 fold increase of modulus for the nanocomposite against 1.1 for the glass fiber reinforced material. However, the examination of the sources of the data reveals again that those for the nanocomposite were taken from a paper and an MSc thesis, while those for the traditional fiber reinforced composite from a completely different paper. A thorough search with different search machines resulted in zero hit, we did not find a single paper comparing the effect of layered silicate nanofillers to that of traditional fillers or reinforcements. As a consequence, we decided to carry out such a study and compare nano and microfillers in a polyamide matrix polymer. The results are collected and described in Chapter 2 of the thesis. Nanocomposites were prepared in a narrower, while traditional composites in a wider composition range in accordance with the concentration ranges usually used for these materials, which also corresponded to the expectations mentioned several times already. The structure of the composites was studied with a variety of methods, interactions were estimated by two independent approaches and also the local deformation processes taking place in the materials
sequences of the latter are also considered in the chapter. During deformation were followed by two techniques. The composition dependence of properties was compared to the results of these measurements and the practical consequences of the latter are also considered in the chapter.

Another crucial issue of layered silicate nanocomposites is the competitive interactions developing during their preparation and acting during their use. Quite a few studies published in the literature proved that the type and amount of the surfactant used for the modification of the silicate surface plays an important role in the determination of the extent of exfoliation, structure and properties. In one of our earlier projects, we modified the surface of montmorillonite with a phosphonium salt instead of the more common ammonium salt and compared the structure and properties of composites prepared with the two silicates. The results clearly proved that the type of the surfactant and the extent of modification are important factors and better exfoliation as well as properties were achieved with the phosphonium salt in spite of the smaller surface coverage in the latter case. Although the results of these experiments were clear, they showed only one aspect of interactions, the surface modification of the clay. However, in layered silicate nanocomposites a multitude of interactions develop among the silicate layers themselves as well as among the silicate surface, the polymer, the surfactant and the coupling agent used occasionally. To our greatest surprise, it turned out that competitive interactions have also been largely neglected and interactions developing between the same silicate and different polymers have never been studied. As a consequence, we decided to compare the structure and behavior of composites prepared with four different polymer matrices and a montmorillonite modified with the ammonium salt of a fatty acid surfactant. The results of the experiments are collected in Chapter 3. Structure was analyzed in detail again, interfacial adhesion was estimated with three independent methods, micromechanical deformation processes were analyzed and properties determined as a function of composition. Although complete exfoliation could not be achieved in this case either, the results unambiguously proved the crucial role of competitive interactions in the determination of the extent of exfoliation, structure and properties.

As mentioned earlier, because of the problems related to the exfoliation of layered silicates and to the proper characterization of the structure formed, many research groups looked for alternative nanofillers for various purposes. Polyethylene is stabilized routinely with additive packages usually containing a hindered phenol primary antioxidant and a phosphor or sulfur containing secondary stabilizer. However, about a decade ago some concerns were raised about the environmental and health effect of the hindered phenolic antioxidants routinely used in industry. Since nature produces and uses a number of antioxidants, it seemed to be obvious to use such natural compounds for the stabilization of polymers. We investigated the stabilization efficiency of a number of natural antioxidants and quercetin proved to be very efficient. It protected PE against degradation during processing already at 50 ppm stabilizer content compared to the usually used 500-1000 ppm and rendered the polymer sufficiently stable at 250 ppm in long term application. Unfortunately, natural antioxidants have some drawbacks, quercetin, for example, has a melting point of 316 °C, well above the processing temperature of PE, and its solubility in the polymer is extremely small, around 20 ppm. An obvious way to overcome these drawbacks is to add the stabilizer to the polymer with the help of a carrier material and halloysite nanotubes offer the possibility to insert the stabilizer into the tubes and thus deliver it to the polymer. Based on literature information it was a clear possibility that the
nanotubes could control the release of the stabilizer and improve the long term stability of the polymer. However, before the preparation of the controlled release device, the nanotubes had to be characterized and the release action checked. The results of extensive experiments directed towards the characterization of the nanofiller are presented in Chapter 4. The dimensions of the tubes including the internal and external diameter, but also pore size and volume were determined by various methods. The layered structure of the silicate, the adsorption of the quercetin on its surface, the location of the stabilizer (inside or outside surface, interlayer) were all studied together with the interactions acting among the components. After the characterization of halloysite and the adsorption of the stabilizer onto its surface a release study was carried out to model the dissolution of quercetin into the polymer. The results of these experiments are described in Chapter 5. The polarity of all components as well as interactions have been estimated and the release of the stabilizer into various solvents was determined. Preliminary stabilization experiments were also carried out to check the effect of the device on long term stability and its possible controlled release action. Since the results of the stabilization experiments proved to be promising, a new project was set up to study stabilization with the new stabilizer agent prepared from the combination of halloysite nanotubes and quercetin. The experiments were carried out according to the routine used for the determination of the efficiency of normal stabilizer packages, but long term ageing was also included into the experimental design. The results are collected in Chapter 6 of the Thesis. The chapter describes the effect of stabilizer content, the technique of addition (separate addition, pre-adsorption into the tubes), the role and influence of the individual components on stability and extensively discusses the role of interactions in stabilization. These latter decide release rate and efficiency and in spite of some positive aspects prove that stabilization of polyethylene might not be the optimal application for the controlled release device prepared from halloysite nanotubes.

In the final chapter of the thesis, in Chapter 7, we briefly summarize the main results obtained during the work, but refrain from their detailed discussion, because the most important conclusions were drawn and reported at the end of each chapter. This chapter is basically restricted to the listing of major thesis points. The large number of experimental results obtained in the research supplied useful information and led to several conclusions, which can be used during further research and development related to the preparation and use of nanocomposites, but also in other areas of heterogeneous polymers. As usual, quite a few questions remained open in the various parts of the study, their explanation needs further experiments. Research continues in this area at the Laboratory and we hope to proceed successfully further along the way indicated by this and by previous Theses.

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Introduction

Introduction

41


42


43

22243, (2005)

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8197-8203, (2005)

45


46

127

343

109

Chem. Mater.

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123

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310


48

125

102

296

35

49

108

143. Renner, K., Henning, S., Móczó, J., Yang, M. S., Choi, H. J., Pukánszky, B.,
Introduction


Introduction


Chapter 2

Comparison of the reinforcing effect of various micro- and nanofillers in PA6

2.1. Introduction

Considerable amounts of polymers are used in structural applications and for that purpose their mechanical properties are often modified by a second component, which is usually glass or carbon fiber, or recently wood flour or natural fiber. Fiber reinforcement results in large stiffness and strength allowing the design of parts with smaller wall thickness. Fiber reinforced polymers are used routinely in the automotive, machine and construction industry, but in order to save weight, improve properties or decrease price the search for new materials and solutions goes on continuously. As mentioned in the scope of this thesis the results of the Toyota group created considerable interest and initiated intensive research in the field of layered silicate nanocomposites. Many attempts were made since them to create nanocomposites with the promising excellent properties, usually without success. Nevertheless often better properties were claimed for nanocomposites than for traditional fiber reinforced polymers. However, the superiority has never been proved and the comparison, if were made, was based on data taken from different sources [1].

In spite of the limited success achieved up to now, research is going on continuously and a large number of papers are published on layered silicate nanocomposites. However, according to our search basically none of the papers compare layered silicates with traditional fillers or reinforcements, but lately focus on the preparation of hybrid composites. Layered silicates are combined with natural fibers and flours [2-9] as well as with polymer [10], glass [7,9,11,12] or carbon fibers [7,9,12-14]. Sometimes even the goal of the experiments or the expected advantage are unclear [11,14], but the benefit of such combinations is rarely confirmed convincingly. Obviously, most of the statements on the superiority of layered silicate nanocomposites over traditional particulate filled or reinforced materials is based on hearsay and wishful thinking and very few solid information or results are available in the open literature.

Considering the above conclusions, the goal of our paper was to compare the effect of layered silicate nanofillers to that of traditional fillers and reinforcements. Neat, non-modified sodium montmorillonite and an organophilic silicate was compared to glass beads, wood flour and glass fibers in PA6 composites. Special attention was paid to structure, interactions and local deformation processes determining the overall properties of the composites. Keeping structural applications in mind, the attention is focused on mechanical properties, and some comments on the impact of the results on practice are also included in the last section of the paper.

Hári, J., Horváth, F., Renner, K., Móczó, J., Pukánszky, B. in preparation
2.2. Experimental

2.2.1. Materials

Domamide 27 polyamide 6 (density: 1.14 g/cm³, MFI: 4 g/10 min at 230 °C and 2.16 kg) was used as matrix polymer and it was obtained from Domo Chemicals. Cloisite 20A modified with bis(hydrogenated tallowalkyl) dimethyl ammonium chloride (OMMT) and sodium montmorillonite (NaMMT) were obtained from Rockwood Additives Ltd. The silicates were characterized extensively by X-ray diffraction (XRD), thermogravimetric analysis (TGA), nitrogen adsorption and inverse gas chromatography (IGC). The characteristics of the clays were described in detail in our previous paper [15]. PA/layered silicate composites contained the clays in 0.5, 1.5, 1, 2, 3, 5 and 7 vol%.

Three traditional microfillers or reinforcements were used in the experiments for comparison: glass beads, wood flour and glass fibers. The Sphericlass 5000 glass beads (GB) were obtained from Potters Industries, the Filtracel EFC 1000 wood flour (WF) was acquired from Rettenmaier GmbH, while the OCV Reinforcement 995 13C glass fibers (GF) covered with a sizing optimized for PA were supplied by Owens Corning. The most important characteristics of the fillers and reinforcements used in the experiments are listed in Table 2.1. Polyamide contained the traditional fillers and reinforcements at 3, 5, 7, 10 and 20 vol%.

2.2.2. Sample preparation

PA was thoroughly dried before each processing step (homogenization, injection molding) at 80 °C for 4 hours in an air-circulation oven. The components were homogenized by twin-screw extrusion (Berstorff ZE 34 Basic extruder, at 60-210-225-230-230 °C and 50 rpm). The granules produced in the compounding step were injection molded into standard ISO 527 1A tensile bars using a Demag IntElect 550-30 machine. The temperature profile used was 40-235-240-250-260 °C and the injection rate 50 mm/s. The temperature of the mold was 60 °C, while holding pressure and time were 350 bar and 20 s, respectively.

2.2.3. Characterization

The morphology of the composites was characterized by various techniques. The presence of individual platelets in nanocomposites was checked by transmission electron microscopy. Micrographs were taken from ultrathin sections prepared with a Leica EM FC6 apparatus by a Tecnai G2 Twin microscope (LB6, 200 kV). SEM micrographs were recorded using a Jeol JSM 6380 LA apparatus on fracture surfaces created by the cryogenic fracture of neat and deformed samples. XRD traces were recorded on nanocomposites using a Phillips PW 1830/PW 1050 equipment with CuKα radiation at 40 kV and 35 mA anode excitation. The possible formation of a silicate network was checked by rotational viscometry using a Paar Physica USD 200 apparatus at 280 °C.
Comparison of micro- and nanofillers

Table 2.1  The most important characteristics of the fillers and reinforcements used in the experiments

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Density (g/cm³)</th>
<th>Water content (wt%)</th>
<th>Surface areaa (m²/g)</th>
<th>Particle sizeb (µm)</th>
<th>Average particle size (µm) Length Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaMMMT</td>
<td>2.8</td>
<td>6.3</td>
<td>15</td>
<td>19.1</td>
<td>12.9</td>
</tr>
<tr>
<td>OMMMT</td>
<td>1.8</td>
<td>0.9</td>
<td>11</td>
<td>20.5</td>
<td>13.9</td>
</tr>
<tr>
<td>GB</td>
<td>2.5</td>
<td>–</td>
<td>0.2</td>
<td>8.6</td>
<td>5.2</td>
</tr>
<tr>
<td>WF</td>
<td>1.5</td>
<td>4.5</td>
<td>2.0</td>
<td>162.9</td>
<td>137.4</td>
</tr>
<tr>
<td>GF</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4000c</td>
</tr>
</tbody>
</table>

a) Determined by nitrogen adsorption using the BET method.
c) Data supplied by the producer.

Mechanical properties were characterized by tensile testing using an Instron 5566 apparatus. Tensile modulus was determined at 0.5 mm/min cross-head speed and 115 mm gauge length, while other tensile characteristics were measured at 5 mm/min speed. All tensile bars were conditioned in an atmosphere of 50 % relative humidity (RH) and 23 °C for 2 days before testing. Acoustic emission (AE) signals were recorded with a Sensophone AED 40/4 apparatus. A single A11 resonance detector with the resonance frequency of 150 kHz was attached to the center of the specimen. Pre-amplification was 20 dB and the peak amplitude detected by the equipment was 108 dBµV. Reference voltage was 1 mV. The threshold level of detection was set to 20 dB. Volume strain (VOLS) was determined by measuring also the change in one lateral dimension of the specimen by a strain transducer. The same dimensional changes were assumed to occur in both lateral directions. The measurements were carried out at 5 mm/min cross-head speed. Five parallel measurements were done in all mechanical and micromechanical experiments. Impact resistance was determined by notched Charpy impact testing using a Ceast Resil 5,5 apparatus with a 1 J hammer. The specimens of 80 x 10 x 4 mm dimensions used were cut from the middle section of the injection molded bar. The notch of 2 mm depth was machined into the 10 mm side of the specimen. The strength of interfacial adhesion was estimated by the determination of the effective load bearing capacity of the silicate from the composition dependence of tensile strength by an appropriate model [16,17]. Debonding stress [18] and a quantity further characterizing interfacial adhesion was also derived from the results of acoustic emission experiments [19].
2.3. Results and discussion

The results are presented in several sections. The structure of the composites is discussed in the first followed by considerations about interfacial interactions. Local deformations strongly related to the final properties of the composites are analyzed next and then the composition dependence of properties are shown in the following section. Correlations and consequences for practice are presented in the last section of the paper.

2.3.1. Structure

As mentioned earlier the properties of all composites, micro and nano alike, are determined by four factors, by component properties, composition, structure and interfacial interactions. In polymer composites we understand the distribution of the filler or reinforcement and other structure related phenomena like orientation and aggregation under structure, while in the case of nanocomposites, the extent of exfoliation. The distribution of the fillers used in this study is demonstrated by several SEM micrographs in Figure 2.1. Magnification is different in the micrographs because of the dissimilar size of the particles, on the one hand, and because we also wanted to show information related to local processes, on the other. According to the figure, the distribution of all fillers is homogeneous in the polymer matrix, at least as much as it is possible to judge distribution from such micrographs.

Another important aspect of structure is the orientation of anisotropic particles. According to the data presented in Table 2.1 wood flour and especially glass fibers are anisotropic, the aspect ratio of the first is 6.8, while that of the second around 300. Naturally, the attrition of the fibers takes place during processing, but they remain anisotropic and orientate during processing. A good example is offered about the orientation of the fibers in Figure 2.1c showing the arrangement of glass fibers parallel to the surface of the fracture. We must emphasize that other micrographs show vertical orientation, fiber fracture and pull out as well, which is not very surprising since orientation is determined by flow conditions and changes locally within the specimen. Nevertheless, orientation is a structure related phenomenon which must be considered during the evaluation of the results. We have not seen any traces of aggregation in the micrographs, but it is difficult to detect and must be always kept in mind in composites.

The structure of layered silicate nanocomposites is much more complicated than that of the microcomposites. The most often intercalated/exfoliated structure is claimed for them, but other structural entities, like large particles and a silicate network were also detected in many of the composites. Structure must be characterized very thoroughly with complementary techniques to have an idea about the various structural units and their relative amount. Figure 2.1d shows a micrograph taken from the fracture surface of a silicate composite prepared with sodium montmorillonite. Because of the strong interaction among the platelets of the silicate, this filler does not exfoliate practically at all. Particles of various sizes are distributed in the PA matrix and some aggregation of smaller particles can also be detected in the micrograph. As mentioned above, the structure of composites prepared with the organophilic silicate is much more complex. Gallery structure is usually characterized by X-ray diffraction, and in our composites the silicate reflection shifts towards smaller 2θ angles indicating intercalation (Figure 2.2).
2.3. Results and discussion

The results are presented in several sections. The structure of the composites is discussed in the first followed by considerations about interfacial interactions. Local deformations strongly related to the final properties of the composites are analyzed next and then the composition dependence of properties are shown in the following section. Correlations and consequences for practice are presented in the last section of the paper.

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Figure 2.1 SEM micrographs taken from the fracture surface of PA composites prepared with various fillers and reinforcements. a) glass beads, 5 vol%, b) wood fiber, 5 vol%, c) glass fiber, 5 vol%, d) NaMMT, 3 vol%, e) OMMT 3 vol%. Specimens were deformed to $2\varepsilon_y$ before fracturing.
At the same time, the appearance of the silicate reflection shows the presence of non-exfoliated tactoids and probably also of larger particles in the composite. The presence of these particles was proven by SEM, but also individual, exfoliated platelets were identified by TEM during the detailed study of nanocomposite structure. Even the formation of a silicate network could be detected by rotational viscometry. These structural entities are not shown here in order to save space, but were presented in our previous papers on the same PA nanocomposites [15]. Although SEM micrographs indicated the even distribution of the particles, we must be careful about the conclusions drawn, since microscopy might be misleading. Further information is supplied about structure by the composition dependence of properties.

![XRD traces recorded on PA/OMMT composites. Gallery structure and intercalation.](image)

**Figure 2.2**  
*Effect of composition on the XRD traces recorded on PA/OMMT composites. Gallery structure and intercalation.*

### 2.3.2. Interactions

Interactions considerably influence composite properties. They determine the local processes taking place around the inclusions during deformation, i.e. weak adhesion leads to the debonding of the components, while brittle fracture occurs in the case of
strong interactions. However, the direct determination of interfacial interactions is very difficult, if not impossible. Accordingly, various approaches are used for its estimation like the calculation of the reversible work of adhesion [20,21], the determination of debonding stress by acoustic emission experiments [18,19] or the calculation of a parameter (B) from the composition dependence of mechanical properties through the use of an appropriate model [16,17]. Parameter B expresses the relative load-bearing capacity of the filler or reinforcement and is related to interfacial adhesion.

The result of an acoustic emission experiment is shown in Figure 2.3. During the deformation of the specimen local processes are initiated around the heterogeneities, filler or fiber, some of which, like debonding, fiber fracture, pull-out generate elastic waves. These can be detected by piezoelectric sensors. The small circles in Figure 2.3 are individual signals generated by at least one local event. The figure clearly shows that signals start to appear above 1% elongation, i.e. a threshold deformation and stress can be determined, which are the characteristic values of the dominating deformation process in the given composite. The determination is difficult by the evaluation of individual signals, thus the cumulative number of signals, i.e. the total number of events, which occurred up to a given deformation, is also plotted in the figure. If debonding, the separation of the filler and the matrix at the interface, is the main deformation process, the characteristic stress is related to the interfacial adhesion of the components [19].

Figure 2.3 Results of the acoustic emission testing of a PA/WF composite containing 10 vol% of the fiber. (C) individual signals, cumulative number of signals (right axis) vs. elongation and stress (left axis) vs. elongation traces plotted as reference.
Characteristic stress values were determined and they are collected in Table 2.2. The values cover a wide range and some of them are quite surprising. The strong adhesion of NaMMT to PA is the result of the high energy of the silicate surface. Surface modification decreases surface tension thus also the interaction of the components for OMMT. The relatively small value of glass beads is quite acceptable, but the large value of wood flour and the very small adhesion of glass fibers are unexpected. The strong adhesion of wood flour to PA can be explained by the strong hydrogen bonds between the hydroxyl groups of cellulose and the amide functionality of the polymer. Only the magnitude of the value is surprising. On the other hand, glass fibers are said to be sized for PA, thus the very weak adhesion is difficult to understand and the phenomenon needs further study and considerations. Finally, we must keep in mind that the approach offers information on interfacial adhesion only if the dominating deformation process is debonding, however, other processes may also take place in our composites and dominate local deformations. Interfacial adhesion (Fa) determined in the PA/wood composites indicates that the dominating local process might not be debonding, but the fracture of the wood particles (Renner, 2010 #478) thus explaining the large value.

### Table 2.2 Parameters related to interfacial adhesion determined from the composition dependence of tensile strength and acoustic emission experiments

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Fa (mJ/m²)</th>
<th>τ₀ (MPa)</th>
<th>Parameter BT</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaMMT</td>
<td>734</td>
<td>3.3</td>
<td>13.8</td>
<td>0.995</td>
</tr>
<tr>
<td>OMMT</td>
<td>357</td>
<td>3.0</td>
<td>13.9</td>
<td>0.999</td>
</tr>
<tr>
<td>GB</td>
<td>274</td>
<td>3.8</td>
<td>3.6</td>
<td>0.943</td>
</tr>
<tr>
<td>WF</td>
<td>1316</td>
<td>3.9</td>
<td>4.4</td>
<td>0.995</td>
</tr>
<tr>
<td>GF</td>
<td>295</td>
<td>4.0</td>
<td>8.0</td>
<td>0.974</td>
</tr>
</tbody>
</table>

The other approach to estimate interfacial adhesion is the evaluation of the composition dependence of tensile yield stress or tensile strength by an appropriate model [16,17]. Plotting reduced strength against the volume fraction of the filler or reinforcement should result in a straight line the slope of which is proportional to the load carried by the second component (parameter B) and, under some conditions, related to the strength of interfacial adhesion. The tensile strength of our composites was plotted in the way dictated by the model and the resulting correlations are shown in Figure 2.4. Straight lines are obtained in most cases indeed with different slopes. The correlations are unambiguous for the macro fillers (glass beads, wood flour, glass fiber), but much less clear for the silicate composites. Both of the latter two correlations start as straight lines, but measured values deviate from the lines at larger silicate contents indicating the effect of some structural phenomenon. Aggregation, orientation, changing extent of exfoliation, the formation of a silicate network in the case of OMMT, all can occur and influence mechanical properties.
The slope of the lines was determined and the obtained values are listed in Table 2.2. They cover a wide range again, but the order of the composites is completely different from the one obtained by acoustic emission measurements. However, during the comparison of the two sets of data, we must consider that the load bearing capacity of the filler or reinforcement depends on interfacial adhesion, but also on the orientation of the particles. The effects cannot be separated, thus the unambiguous determination of interfacial adhesion is impossible in this way. It is clear that both methods successfully used for the estimation of interfacial interactions earlier have limitations and both structure and adhesion considerably influence local deformations and properties.

Figure 2.4  Composition dependence of the reduced tensile strength of PA composites. Symbols: (○) NaMMT, (□) OMMT, (△) GB, (◊) WF, (▽) GF.

2.3.3. Local deformation processes

Numerous local processes can take place in the composites prepared and studied in this project. Shear yielding and cavitation are the processes occurring in the matrix, and a number of processes related to the inclusion can also take place including debonding, fiber and particle fracture, fiber pull-out, the slipping of platelets or larger units in the silicate [22], etc. Several of these processes, like cavitation and debonding, are accompanied by volume increase, thus they can be followed by the measurement of volume strain, the increase of the volume of the specimen during deformation. The volume strain traces of the composites are presented at Figure 2.5. The amount of filler or reinforcement was 5 vol% in the composites. The traces can be divided into three sections. The first, linear part indicates the volume increase of the specimen caused by the Poisson's ratio of
the polymer being less than 0.5. Above a certain deformation the slope of the correlation increases indicating the appearance of another process, a local deformation accompanied by volume increase. Earlier studies have shown that considerable cavitation occurs in the particular PA6 polymer used in this study [23] thus we assume that the new process is cavitation. Although the increase in slope could be related to another process as well, like debonding, but we think that the different extent of volume increase is caused by dissimilar interactions, and by the fact that the particles influence the cavitation process. OMMT was shown to facilitate, while NaMMT hinder cavitation [23]. The tentative explanation is strongly corroborated by the fact that the smallest increase in volume is observed in the wood composites with the strongest interaction (see the $F_a$ value in Table 2.2). A characteristic stress value can be determined from the change of slope in the way shown in Figure 2.5, which is related to the initiation of the local process in question. The third, decreasing part of the traces result from the macroscopic yielding of the specimens caused by the mechanical strain gauge used. That part does not have physical meaning and must be ignored during evaluation.

![Volume strain traces of PA composites containing 5 vol% of the various fillers and reinforcements. Determination of the characteristic stress.](image)

As mentioned above, other local processes are accompanied by the development of elastic waves in the composite as shown by Figure 2.3. The cumulative number of signal traces are compared to each other in Figure 2.6 at 5 vol% filler content. Huge differences can be seen in the number of signals and the shape of the traces as well. The total number of signals is very large, several 10000 in the glass fiber and the wood flour containing composites, while much smaller in the other three, indicating different dominating
local processes. Debonding is clearly the dominating process in the composites containing the glass beads, while particle fracture in the wood composites as Figure 2.1a and b clearly prove. The large number of signals and SEM micrographs indicate that considerable fiber fracture occurs in the GF composites, although debonding and pull-out may also take place (see Figure 2.1c). Both particle fracture and debonding were observed in the silicate composites. The number of signals is very small in the OMMT nanocomposites, since only a few large particles are involved in processes generating sound. We may safely assume that the large variety of local processes leads to dissimilar composites properties.

![Figure 2.6](image)

*Figure 2.6 Cumulative number of signal traces of PA composites prepared with 5 vol% of the fillers. Widely differing number and composition dependence of the traces.*

The processes detected in the composites are initiated at considerably differing critical stresses as shown by Figure 2.7 in which characteristic stresses are plotted against composition. The processes detected by VOLS, presumably cavitation, is initiated at around 20 MPa stress, while acoustic emission signals appear at around 35 MPa. The yield stress and the tensile strength of the composites are much larger around 50-60 MPa. The fillers and reinforcements used in the experiments influence these characteristic stresses in different ways. It was shown earlier that in PP and PLA composites the strength of wood composites was closely related to the process detected by acoustic emission [24], i.e. the dominating local process determined the performance of the composites. Further analysis is needed to identify the local deformation process which determines properties in our PA composites.
Figure 2.7  Comparison of the characteristic stresses determined in PA6/GB composites. Symbols: (○) tensile strength, $\sigma_T$, (□) tensile yield stress, $\sigma_y$, (△) acoustic emission, $\sigma_{AE}$, (▽) volume strain, $\sigma_{VOLS}$.

2.3.4. Properties

The Young's modulus of the composites is plotted against the amount of filler or reinforcement in Figure 2.8. The comparison of micro- and nanofillers is very interesting and clearly shows the differences in their reinforcing effect. The stiffness of the composite is determined by the modulus of the components, their amount and by structure. Glass beads have large modulus, but their large size and debonding leads to moderate reinforcing effect. Wood flour has considerably smaller modulus, and the large size of the particles as well as, their debonding and/or fracture also limits reinforcement. Glass fibers increase modulus quite considerably because of their large modulus and orientation. The effect of the two clays is also very interesting and somewhat contradictory. NaMMT leads to larger modulus than glass fibers, but only in a very narrow composition range. OMMT has a somewhat smaller reinforcing effect, but in a wider range of filler contents, because of exfoliation and better dispersion. Nevertheless, the composition dependence of the stiffness of silicate composites indicate structural effects, aggregation, incomplete exfoliation, and the presence of large particles.
Tensile strength is plotted against filler content in Figure 2.9. Basically the same conclusions can be drawn from the correlation as in the case of modulus. Glass fibers reinforce PA considerably, while WF and GB hardly at all. The effect of the two silicate fillers is also more or less similar, but structural effects are much more pronounced here, as expected. Debonding is initiated very easily around the large particles of NaMMT and the probability of particle fracture also increases with increasing particle size. The exfoliation and better dispersion of OMMT leads to larger strength, but the smaller interfacial interaction caused by organophilization and structural effects lead to the decrease of strength at larger filler content.

The deformability of the composites is very important for their application as structural materials. Small elongation-at-break is usually accompanied by rigidity and brittle fracture. The deformability of the composites is plotted against filler content in Figure 2.10 in logarithmic scale to compensate for the large differences and the small values of GF and WF composites. The figure clearly shows that the large stiffness of the PA/glass fiber composites results in very small elongation-at-break values, and the deformability of the wood flour composites is only slightly larger. Interestingly, considerably larger deformations are achieved in the case of GB and the two silicates, a further advantage of the latter. The use of layered silicate nanocomposites would be very advantageous indeed, because larger stiffness is accompanied by reasonable deformability, if larger extent of exfoliation could be achieved and structure could be controlled more precisely and reproducibly in general.
Deformability usually gives some indication about fracture resistance, one expects larger impact resistance at large elongation-at-break. Fracture toughness measured by notched Charpy impact testing is plotted against filler content in Figure 2.11. Quite surprisingly, nanocomposites possess the smallest fracture resistance contrary to the indication of Figure 2.10. Debonding leads to the yielding of the matrix and relatively larger fracture toughness for the microcomposites and the fracture of the glass fibers consumes additional energy and results in the increase of fracture resistance at large fiber contents. Fracture resistance is very small for the nanocomposites at small silicate content for various reasons like strong adhesion for NaMMT and larger interface for OMMT. At larger filler content the silicates behave like microfillers as a result of aggregation and insufficient exfoliation. Uncontrolled structure is very disadvantageous after all and limits the application of layered silicate composites.

Figure 2.9  Tensile strength of PA6 composites plotted against their composition. Symbols (○) NaMMT, (□) OMMT, (△) GB, (◇) WF, (▽) GF.
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**Figure 2.10** Effect of composition on the deformability of PA composites containing various fillers and reinforcements. Symbols (○) NaMMT, (□) OMMT, (△) GB, (◇) WF, (▽) GF.

**Figure 2.11** Notched Charpy impact resistance of the composites plotted as a function of filler content. Symbols: (○) NaMMT, (□) OMMT, (△) GB, (◇) WF, (▽) GF.
2.3.5. Considerations, consequences

The analysis of local deformation processes indicated the occurrence of a number of mechanisms which influence the overall performance of the composites studied. The matrix deforms by cavitation and shear yielding, while several processes related to the filler or reinforcement also take place. The effect of the inclusions on the characteristic stresses determined by various methods varies considerably. The stress derived from volume strain measurements as well as tensile yield stress is plotted against filler content in Figure 2.12. Neither of them is influenced by the filler or reinforcement very much indicating that these processes are related to the matrix polymer. The slight differences observed indicate that the filler or reinforcement interfere with the initiation of the process somewhat, but cavitation takes place in the matrix and starts about the same stress. The same applies to yields stress as well. Yielding becomes easier in the presence of wood flour and glass beads indicating considerable extent of debonding, while the silicates increase yield stress slightly showing weak reinforcing effect, and hinting at less debonding and some particle fracture. Composites containing the glass fiber do not yield at all.

![Graph showing composition dependence of characteristic stresses related to the deformation of the matrix.](image)

**Figure 2.12** Composition dependence of characteristic stresses related to the deformation of the matrix. Tensile yield stress and volume strain associated with shear yielding and cavitation. Symbols (○) NaMMT, (□) OMMT, (△) GB, (◇) WF, (▽) GF.
Characteristic stresses determined by acoustic emission testing, on the other hand, change in a much wider range as shown by Figure 2.13. The largest stresses are recorded for glass and wood fibers indicating large extent of fiber fracture. The different inherent strength of the two fibers leads to their dissimilar reinforcing effect and strength of their composites. Both the debonding and the fracture of NaMMT particles requires relatively large stress while the debonding of glass beads and especially OMMT particles is relatively easy. These differences in the initiation stress of local deformation processes obvious influence the deformation and failure of the entire composite. The strong reinforcing effect of glass fibers is clear and justified by the large characteristic stress related to the fracture of the fiber. However, the determination of clear relationships between local processes and the performance of the composites is difficult because of the simultaneous effect of these processes, structure and interfacial interactions. Nevertheless, it is clear that the inherent characteristics of the PA matrix polymer and processes taking place in it dominate composite properties and particle related processes play a much less significant role in PA than in PP or PLA composites [24].
2.4. Conclusions

The comparison of the effect of various micro- and nanofillers on the properties of PA6 composites showed that properties can be modified in a relatively wide range. True reinforcement can be achieved with glass fibers, but the influence of all traditional fillers can be predicted with large certainty because their structure can be controlled quite well. Although layered silicate reinforce polyamide even better, but only in a very narrow composition range because of structural effects. The extent of exfoliation is not sufficiently large in polyamide/organophilized clay composites and besides individual silicate layers a number of other structural entities, i.e. tactoids, large silicate particles and possibly a silicate network, are also present in the composites. Structure cannot be controlled in the desired extent thus properties cannot be predicted and reproduced for practical applications. Numerous local deformation processes take place during the deformation of PA composites, like the cavitation and shear yielding of the matrix, as well as particle related processes. The properties of PA composites are not determined by these latter, but by those taking place in the matrix. Properties of PA composites can be adjusted in a wide range, but the routine use of layered silicates needs further efforts.

2.5. References

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2.5. References

Chapter 3

3.1. Introduction

Although the original idea of creating a large interface in the composite by the exfoliation of the silicate and thus achieving strong reinforcement at small filler content is still valid [1-18], the main problem is that a large extent of exfoliation and the control of nanocomposite structure could not be achieved practically at all. A way to reach the original goal of layered silicate nanocomposites is a more thorough study of competitive interactions prevailing among all components, the proper characterization of structure and the determination of the role of the various structural formations on the deformation, failure and properties of the composites.

Although an enormous number of papers have been published on layered silicate composites prepared from a wide variety of silicates and polymers up to now [1-6,15,16], very few of them compare the influence of the same silicate on composite structure and properties in different polymers [19,20]. Differences in the structure of the matrix polymer lead to dissimilar interactions and thus to different structure and properties. Accordingly the goal of this work was to compare interactions, structure and properties in thermoplastic polymer/layered silicate composites prepared with the same organophilic silicate, but with different matrix polymers. Special attention is paid to the analysis of structure and to the estimation of interactions, but structure-property correlations are also considered in the final section of the paper.

3.2. Experimental

3.2.1. Materials

The same organophilic silicate, Cloisite 20A (Rockwood Additives Ltd.), was used in all composites. Sodium montmorillonite is treated with distearyl-dimethyl-ammonium chloride to obtain the organophilized product (OMMT). The ion exchange capacity of the silicate is 92.6 meq/100 g, it is coated with 37.8 wt% of the surfactant resulting in 106 % surface coverage, if we calculate it from the theoretical specific surface area of the silicate (750 m²/g) or 120 % calculated from its ion exchange capacity. The layer distance of the silicate is 2.7 nm corresponding to the thickness of approximately 6 aliphatic chains [21]. The average particle size of the filler is 13.9 µm from the image analysis of SEM micrographs and 20.5 µm determined by laser light scattering (Malvern Master Sizer 2000).

Chapter 3

Competitive interactions, structure and properties in polymer/layered silicate nanocomposites

3.1. Introduction

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Composites were prepared from the OMMT in four matrices, a PP homopolymer, PLA (polylactic acid) and PA. The fourth matrix was also PP, but a functionalized polymer, maleated polypropylene (MAPP), was also added in 20 vol% (calculated for the silicate) in order to modify interactions. The most important characteristics of the polymers used are collected in Table 3.1. 2000 ppm Irganox 1010 and 2000 ppm Irgafos 168 stabilizers were added to PP based composites to prevent degradation during processing [22]. All composites contained the silicate at 0.5, 1, 1.5, 2, 3, 5 and 7 vol%. Under silicate content we always understand the amount of OMMT and not the neat, non-treated mineral.

3.2.2. Sample preparation

PLA and PA were thoroughly dried before each processing step (homogenization, injection molding); PLA at 100 °C, 300 mbar vacuum for 12 hours, while PA at 80 °C for 4 hours in an air-circulation oven. The PP, PP/MAPP and the PLA composites were prepared under similar conditions. The components were homogenized using a Brabender DSK 42/7 twin-screw compounding equipped with a filament die of 3 mm diameter at 30 rpm screw speed and at the temperature profile of 180-190-200-210 °C in the case of PP, while at 190-200-210-220 °C in the case of PLA. The granules produced in the compounding step were injection molded into standard ISO 527 1A specimen tensile bars using a Demag IntElect 550-30 machine. The temperature profile used was 40-180-190-200-210 °C and die temperature 40 °C, holding pressure 600 bar and holding time 35 s in the case of PP, while 450 bar and 35 s in the case of PLA. PA composites were processed by using a Berstorff ZE 34 Basic twin screw extruder at 60-210-225-230-230 °C and 50 rpm, while injection molding was done using the same Demag machine as above with the temperature profile of 40-235-240-250-260 °C at the injection rate of 50 mm/s. The temperature of the mold was 60 °C, while holding pressure and time were 350 bar and 20 s, respectively.

3.2.3. Characterization

The morphology of the composites was characterized by various techniques. Transmission electron micrographs were taken from ultrathin sections prepared with a Leica EM FC6 apparatus by a Tecnai G2 Twin microscope (LB6, 200 kV). SEM micrographs were recorded using a Jeol JSM 6380 LA apparatus on fracture surfaces created by the cryogenic fracture of neat and deformed samples. XRD traces were recorded on the composites using a Phillips PW 1830/PW 1050 equipment with CuKα radiation at 40 kV and 35 mA anode excitation. The possible formation of a silicate network was checked by rotational viscometry using a Paar Physica USD 200 apparatus at 280 °C (PA), 190 °C (PP and PP/MAPP) and 180 °C (PLA) in oscillatory mode in the frequency range of 0.1-600 1/sec on discs with 25 mm diameter and 0.5 mm thickness in the parallel plate arrangement. The amplitude of the deformation was 5 %, which was in the linear elastic region checked by an amplitude sweep.
3.2. Experimental

Polymer, Type, Producer, Stiffness (GPa), \( M_n \) (g/mol), \( M_n/M_M \), MFI (g/10 min), Density (g/cm³)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Type</th>
<th>Producer, Location</th>
<th>Stiffness (GPa)</th>
<th>( M_n ) (g/mol)</th>
<th>( M_n/M_M )</th>
<th>MFI (g/10 min)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Tipplen H649F</td>
<td>Mol, Hungary</td>
<td>1.29</td>
<td>68900</td>
<td>4.4</td>
<td>2.77 ± 0.03</td>
<td>0.90</td>
</tr>
<tr>
<td>MAPP</td>
<td>Orevac CA</td>
<td>Arkema, France</td>
<td>0.88</td>
<td>25000</td>
<td>8.6</td>
<td>125.2 ± 2.4</td>
<td>0.90</td>
</tr>
<tr>
<td>PLA</td>
<td>Ingeo 4032 D</td>
<td>Nature Works, USA</td>
<td>3.12</td>
<td>88500</td>
<td>1.8</td>
<td>3.73 ± 0.19</td>
<td>1.24</td>
</tr>
<tr>
<td>PA</td>
<td>Domamid 27</td>
<td>Domo Chem., Belgium</td>
<td>1.09</td>
<td>39600a</td>
<td>–</td>
<td>20.0 ± 2.0</td>
<td>1.14</td>
</tr>
</tbody>
</table>

a) \( M_v \), intrinsic viscosity, in conc. sulfuric acid, at 25 °C, \( a=0.78, K=3.32 \times 10^{-2} \text{cm}^3/\text{g} \)
b) 230 °C/2.16 kg
c) 190 °C/2.16 kg
Mechanical properties were characterized by tensile testing using an Instron 5566 apparatus. Tensile modulus was determined at 0.5 mm/min cross-head speed and 115 mm gauge length, while other tensile characteristics were measured at 5 mm/min speed. All tensile bars were conditioned in an atmosphere of 50 % relative humidity (RH) and 23 °C for 2 days before testing. PLA specimens were stored for four weeks before testing to allow physical ageing to take place. Acoustic emission (AE) signals were recorded and volume strain (VOLS) of the samples was determined by similar methods and equipment as described in Chapter 2.

Interactions were estimated quantitatively by various approaches. The reversible work of adhesion was calculated from surface tensions determined by inverse gas chromatography for the silicate [21] and by contact angle measurements for the polymers. The effective load bearing capacity of the silicate was estimated from the composition dependence of tensile yield stress by an appropriate model [23,24]. Debonding stress [25] and a quantity characterizing interfacial adhesion was also derived from the results of acoustic emission experiments [26].

3.3. Results and discussion

The results of the experiments are presented and discussed in several sections. The composition dependence of mechanical properties is compared first for the four matrices then structure and local deformation processes are analyzed next. A separate section is dedicated to interactions and then correlations between structure and properties are discussed in the last section together with relevance to practice.

3.3.1. Properties

One of the main advantages, if not the main advantage, of layered silicate nanocomposites is the assumed large reinforcement obtained with a small amount of filler. Reinforcement means the increase of stiffness or strength, or both. The absolute increase in stiffness is not very impressive in our composites, modulus increases from 1.29 GPa to 1.31 GPa upon the addition of 7 vol% silicate to PP, while it changes from 1.09 GPa to 2.75 GPa in PA. Stiffness as large as 10 GPa can be achieved in PP reinforced with carbon fibers [27]. The results obtained show that the basic idea does not work and the goal of large reinforcement is not achieved in our case. However, we are interested more in interactions and relative changes and these are different across the four matrices used.

The relative modulus of the four composites is plotted against silicate content in Figure 3.1. Stiffness increases in all four cases, but in different extent. Although dissimilar relative increases were expected before the experiments, the order of the composites is somewhat surprising. The extent of reinforcement depends on the stiffness of the matrix and much less on homogeneity or interactions. The considerable increase of stiffness upon the introduction of the MAPP coupling agent and the small values obtained for PLA indicate dissimilar interfacial adhesion and/or different extent of exfoliation in the four cases.

Properties measured at larger deformations are influenced much more by these
factors, i.e. structure and interactions, than stiffness. The relative yield stresses of the four composites are plotted as a function of OMMT content in Figure 3.2. The relative order of the four composites remained the same as in the case of stiffness, but the differences are much larger. True reinforcement is achieved in PA, while yield stress decreases considerably for PLA and PP. Better adhesion in the PP/MAPP matrix resulted in a considerable increase of yield stress compared to neat PP. The reinforcing effect of any filler or reinforcement is difficult to judge from the absolute value of yield stress or even from the relative value related to the matrix polymer, since the effect of the effective matrix cross section must be considered [23,24,28] and matrix characteristics also influence reinforcement. Nevertheless, we can establish unambiguously that the different chemical structures of the matrix polymers studied result in dissimilar properties, presumably as an effect of different composite structures and interactions.

The deformability of the composites is presented in Figure 3.3 as a function of composition. Elongation-at-break decreases with increasing silicate content in all cases, as expected. However, the actual values cover a wide range from very small to reasonable deformability. Improved interfacial adhesion results in very small deformability in the PP/MAPP composites and the small values obtained for PLA are more or less expected. The relatively large elongations measured in the PA composites are rather surprising especially in view of the fact that the largest reinforcement, both in stiffness and yield stress, was achieved in this polymer. Large stiffness usually leads to small deformability and fracture resistance. All mechanical properties measured indicate considerable differences among composites prepared with the four matrices probably because of dissimilar structure, interactions and possibly due to the influence of local deformation processes.

![Figure 3.1](image)

**Figure 3.1** Relative modulus of polymer/silicate composites plotted as a function of OMMT content. Symbols: (○) PP, (●) PP/MAPP, (△) PLA, (□) PA.
Chapter 3

Figure 3.2  *Effect of silicate content on the relative tensile yield stress of composites.*  
*Symbols: (○) PP, (●) PP/MAPP, (△) PLA, (□) PA.*

Figure 3.3  *Dependence of the relative elongation-at-break of polymer/OMMT composites on silicate content.*  
*Symbols: (○) PP, (●) PP/MAPP, (△) PLA, (□) PA.*
3.3.2. Structure

At the dawn of nanocomposite research all composites containing an organophilized layered silicate were claimed to have exfoliated structure [29-32]. Since more detailed investigations showed that this is not true, structure changed to exfoliated/intercalated instead [5,16,33], but the complexity of structure was still largely ignored. The ultimate proof of exfoliation was practically always a TEM micrograph showing individual silicate platelets. However, usually a few plates can be detected practically in every composite, thus it is better to look for other evidence as well. Above a certain extent of exfoliation individual platelets form a silicate network, which can be detected quite well by melt rheology. Cole-Cole plots of the components of complex viscosity yield a regular or somewhat distorted arc, if the material possesses a single relaxation time, or a narrow distribution of relaxation times. The Cole-Cole plot of composites is also more or less a regular arc, when the second component is homogeneously dispersed in a matrix, but it strongly deviates from the arc if additional structural formations appear in the melt resulting in relaxation processes with two or more separate relaxation times [34-36]. The Cole-Cole plots of the composites are shown in Figure 3.4.

![Cole-Cole plots (η'' vs. η') of selected polymer/organophilized silicate composites. OMMT content: 7 vol%. Symbols: (○) PP, (●) PP/MAPP, (△) PLA, (□) PA.](image)

The correlation corresponds to a perfect arc indeed for PP and also for PLA, i.e. for polymers in which reinforcement was the weakest. The addition of the MAPP coupling agent distorts the arc considerably and a completely different correlation is obtained for PA indicating dissimilar structure. The extent of deviation corresponds to the order
observed in mechanical properties, on the one hand, while indicates the possible formation of a silicate network, i.e. considerable extent of exfoliation, on the other. Extensive exfoliation and the presence of silicate layers are demonstrated quite well by Figure 3.5 showing the TEM micrograph of a PA composite.

![TEM micrograph recorded on a PA/OMMT composite containing 3 vol% silicate. Individual silicate layers tactoids and the possibility of network formation.](image)

Figure 3.5

Complete exfoliation obviously cannot be expected in our composites, but tactoids, seen also in Figure 3.5, as well as larger particles must be also present. The XRD traces presented in Figure 3.6 clearly confirm this assumption and show the presence of ordered silicate structure. The first peak observed in the XRD pattern is characteristic for silicate stacks (layer distance, regularity), while the second is just an overtone, thus we do not discuss it further. The comparison of the XRD patterns to that of the neat OMMT indicates some shift in the position of the silicate reflection the extent of which is the largest in PA and much smaller in the other three polymers. Quite surprisingly the regularity in the stacking of the platelets increased considerably during homogenization in PLA, the peak became much sharper and overtones more intensive. The reason for the larger order is unclear and needs further investigation.
Although the appearance of the silicate reflection in the XRD patterns proves the presence of tactoids and particles, it does not tell anything about their amount. In order to obtain a more quantitative estimate, the silicate peaks were integrated [37]. Integration was done in the Origin 8.5 software. A baseline was fitted to the XRD traces taking into account the change in background noise with decreasing 2θ degree. Then a Lorentzian function was fitted to the peak and the area under it was integrated. The peak area obtained is plotted against silicate content in Figure 3.7. Although intensity is influenced by a number of factors like orientation and regularity, the quantitative comparison of the intensity of the silicate reflection indicates that the extent of exfoliation, or structural changes at least, is the largest in PA and very similar in the other three composites. The small effect of MAPP is somewhat surprising since earlier results indicated that the coupling agent assists exfoliation indeed [37].

![XRD traces of polymer/OMMT composites containing 5 vol% silicate.](image)

**Figure 3.6**  *XRD traces of polymer/OMMT composites containing 5 vol% silicate.*
The presence of larger particles is rarely checked in layered silicate composites, although it may influence local deformation processes and ultimately the overall properties of the composites considerably. As the SEM micrographs presented in Figure 3.8 show, smaller or larger particles are present in all composites. The composites were deformed up to twice their yield strain, $2\varepsilon_y$, before recording the micrographs. Besides proving the presence of the particles, the micrographs offer additional information as well. The fracture of a large particle occurred in PP as shown by Figure 3.8a. The size of the particle occupying the center of Figure 3.8b is smaller and the orientation of smaller entities around it indicate that the addition of MAPP changes structure indeed. Finally apart from the one large particle seen in Figure 3.8c, the structure of the PA composite seems to be quite homogeneous. The two micrographs presented in Figure 3.8b and c indicate that besides particle fracture, the debonding of larger particles also takes place during deformation, i.e. particle related local deformation processes occur which must influence the properties of the composites.

![Figure 3.7](image)

**Figure 3.7** Correlation between the peak area of the silicate reflection and OMMT content. Symbols: (○) PP, (●) PP/MAPP, (△) PLA, (□) PA.
The presence of larger particles is rarely checked in layered silicate composites, although it may influence local deformation processes and ultimately the overall properties of the composites considerably. As the SEM micrographs presented in Figure 3.8 show, smaller or larger particles are present in all composites. The composites were deformed up to twice their yield strain, $2\varepsilon_y$, before recording the micrographs. Besides proving the presence of the particles, the micrographs offer additional information as well. The fracture of a large particle occurred in PP as shown by Figure 3.8a. The size of the particle occupying the center of Figure 3.8b is smaller and the orientation of smaller entities around it indicate that the addition of MAPP changes structure indeed. Finally apart from the one large particle seen in Figure 3.8c, the structure of the PA composite seems to be quite homogeneous. The two micrographs presented in Figure 3.8b and c indicate that besides particle fracture, the debonding of larger particles also takes place during deformation, i.e. particle related local deformation processes occur which must influence the properties of the composites.

![Figure 3.8](image)

**Figure 3.8** SEM micrographs showing large particles in polymer/OMMT composites. Silicate content: a), c) and d) 2 vol%, b) 3 vol%. Specimens were deformed to $2\varepsilon_y$ before fracturing and recording the micrographs.
3.3.3. Local processes

Because of their heterogeneous structure stress distribution is inhomogeneous in composites, thus local deformations occur which depend on the elastic properties of the components, on structure and interactions. These local processes were shown to determine the final properties of composites before [38]. The micrographs presented in Figure 3.8 prove that local processes take place also in the layered silicate composites discussed here. Some local processes can be followed well by acoustic emission testing. Burst like processes like particle fracture or debonding generate elastic waves which can be detected by piezoelectric sensors. The result of such a test is shown in Figure 3.9. Small circles indicate individual events (signals, hits) which were detected during a tensile test. The signals appear above a certain deformation threshold and most of the events occur in a limited range of deformation. The stress vs. strain trace is also plotted in the figure as reference. Although the distribution of signals supplies valuable information about the local process initiating it, it is difficult to evaluate it, thus the cumulative number of signals is also plotted in the figure. This confirms that most of the signals are evolved above a threshold deformation and stress and that the trace goes to saturation. Usually such traces are obtained when debonding or particle fracture is the dominating local deformation processes. Plotting the cumulative number of signals against deformation allows the determination of a characteristic deformation and stress value as shown in Figure 3.9.

Figure 3.9  Acoustic emission testing of a PP/OMMT composite. Silicate content: 5 vol%. (○) individual acoustic events. Continuous lines are stress vs. strain traces plotted as reference (left axis, red line) and the cumulative number of signals vs. strain correlation (right axis, blue line).
The cumulative number of signal traces are compared to each other in Figure 3.10 for the four composites all of them containing 5 vol% silicate. The traces are very similar, but the number of detected signals differs considerably. A relatively large number of signals are detected in PP and PLA, although this latter fails at small deformation because the large stiffness of the matrix is further enhanced by the presence of the silicate. MAPP changes structure and interfacial adhesion. Smaller particles do not fracture and debonding is more difficult at stronger interfacial adhesion, thus less signals are detected. We assume that the debonding of a few particles yield acoustic events in PA, in accordance with the largest reinforcement and most homogeneous structure of the composite prepared from this polymer (see Figure 3.8 c).

![Figure 3.10](image)

**Figure 3.10** *Comparison of the cumulative number of signal vs. strain traces for composites prepared with various matrix polymers. Silicate content: 5 vol%.*

Some of the local processes occurring during the deformation of composites, like debonding and cavitation, are accompanied by volume increase which can be followed by the measurement of volume strain. Other processes, like particle fracture or the shear yielding of the matrix occur at constant volume. The volume strain measured during the deformation of a PLA composite is presented in Figure 3.11 together with that of the neat matrix polymer as comparison. The initial increase of volume is caused by the Poisson's ratio of the polymer being different from 0.5, but the steeper increase above 2.5 % linear elongation is the result of a local process. Several processes may initiate volume increase, as mentioned above, among others debonding, crazing and cavitation. Since SEM micrographs showed debonding in most composites, it would be the obvious selection as the source of volume increase. However, a detailed microscopic study showed considerable cavitation of the matrix both in PLA (see Figure 3.12) and in PA composites thus it may contribute or even dominate volume increase.
composites thus it may contribute or even dominate volume increase.

![Graph]

**Figure 3.11** Volume strain of a PLA/OMMT composite. Silicate content is 2 vol% (—). The correlation obtained for the matrix polymer (---) is shown for comparison. The corresponding stress vs. strain traces are also plotted as reference.

![SEM micrograph]

**Figure 3.12** SEM micrograph taken from the fracture surface of a PLA/OMMT composite containing 2 vol% silicate. Extensive cavitation of the matrix.
Unfortunately, volume increase could not be measured in PP composites since the mechanical strain gauge used initiated the macroscopic yielding of the specimens. Nevertheless, we can conclude that a number of local processes take place during the deformation of our composites, which may determine their macroscopic properties.

3.3.4. Interactions

The results presented above clearly show that the structure of the composites is different and these differences are reflected in their properties. Since the chemical structure of the four matrices differs considerably from each other we may safely assume that also their interaction with the silicate is dissimilar. The degree of exfoliation is determined by thermodynamic and kinetic factors, thus surface properties and interactions must be analyzed to explain structural differences. Parameters related to interactions are listed in Table 3.2. The surface tension of the polymers appears in column one. The smallest surface tension was measured for PP, as expected. The surface tension of the other two polymers is larger because of the polar groups in their structures and we may assume that PA can form the strongest interactions. The surface tension of MAPP was measured as 34.5 mJ/m², but because of its reactivity, it may develop even chemical bonds with some of the components of the composite [39]. We must pay special attention to the surface tension of the organophilic montmorillonite. The non-treated silicate has a very high surface energy [21] (~780 mJ/m²), but organophilization decreases it to the same level as the polymers used in this study. Decreased surface energy has the benefit of weaker adhesion among the silicate layers facilitating exfoliation, but also weaker interaction with the matrix polymer. The balance of these competitive interactions, which are of the same order of magnitude, determines the extent of exfoliation. The results also indicate that the interaction among the silicate layers is still stronger than matrix/filler interactions shown by the comparison of \( W_{AB} = 132.6 \text{ mJ/m}^2 \) for the silicate layers compared to that of the PA/OMMT composite which is 108.6 mJ/m².

Table 3.2  Quantities related to interfacial adhesion in polymer/OMMT nanocomposites determined by various approaches

<table>
<thead>
<tr>
<th>Component</th>
<th>( \gamma_s^a ) (mJ/m²)</th>
<th>( W_{AB} ) (mJ/m²)</th>
<th>( F_a ) (mJ/m²)</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>33.7</td>
<td>76.4</td>
<td>158 ± 40</td>
<td>1.5</td>
</tr>
<tr>
<td>PP/MAPP</td>
<td>–</td>
<td>–</td>
<td>198 ± 32</td>
<td>3.5</td>
</tr>
<tr>
<td>PLA</td>
<td>43.5</td>
<td>95.0</td>
<td>292 ± 49</td>
<td>1.2</td>
</tr>
<tr>
<td>PA</td>
<td>46.5</td>
<td>108.6</td>
<td>357 ± 298</td>
<td>4.5</td>
</tr>
</tbody>
</table>

* a) The surface tension of OMMT is 66.3 mJ/m² and that of MAPP is 34.5 mJ/m².
The direct determination of the strength of matrix/filler adhesion is difficult, if not impossible, thus we can only estimate it with various indirect methods. The easiest is the calculation of the reversible work of adhesion \( W_{AB} \) from the surface tension of the components

\[
W_{AB} = 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} + 2\left(\gamma_1^p \gamma_2^p\right)^{1/2}
\]

where \( p \) and \( d \) stands for the dispersion and polar components of the surface tension \( (\gamma) \) of components 1 and 2, respectively. Work of adhesions reflect the relations shown by surface tensions; the strongest matrix/silicate interaction forms in PA and the weakest in PP. The relatively strong interaction predicted for PLA is somewhat surprising, especially if we consider the results of mechanical testing shown in Figure 3.1 and 3.2.

The reversible work of adhesion approach is relatively simple. However, it ignores specific interactions, and the determination of surface tensions is not very easy either. Further information can be obtained about interactions from acoustic emission experiments. If debonding is the dominating deformation mechanism, the separation of the matrix/filler interface depends on several factors including interfacial adhesion, i.e.

\[
\sigma^D = -C_1 \sigma^T + C_2 \left(\frac{E F_a}{R}\right)^{1/2}
\]

where \( \sigma^D \) and \( \sigma^T \) are debonding and thermal stresses, respectively, \( E \) the Young's modulus of the matrix, \( R \) the radius of the particles and \( F_a \) interfacial adhesion. \( C_1 \) and \( C_2 \) are geometric constants related to the debonding process. If we know them, we can calculate \( F_a \), since the rest of the variables are usually known [26]. The values calculated from characteristic stress values determined by acoustic emission are listed in column four of Table 3.2. The results confirm the previously established order, the strongest interaction develops in PA and the weakest in PP. The relatively large value obtained for PLA is somewhat surprising as well as the smaller value obtained for the PP/MAPP matrix. The drawback of the approach is that the fracture of particles also gives acoustic signals and this may bias the evaluation of the results. On the other hand, we may assume that debonding also occurs as shown in Figure 3.8b and c and that smaller particles do not break, but debond thus the values presented in Table 3.2 give some indication about interfacial adhesion.

If debonding is the main local deformation process, the strength of interaction can be estimated also from the composition dependence of tensile yield stress by an appropriate model

\[
\sigma_y = \sigma_{y_0} \frac{1 - \varphi}{1 + 2.5 \varphi} \exp(B \varphi)
\]

where \( \sigma_y \) and \( \sigma_{y_0} \) are the tensile yield stress of the composite and the matrix, respectively, \( \varphi \) is the volume fraction of the silicate and \( B \) is related to its relative load-bearing capacity, i.e. to the extent of reinforcement, which depends among other factors also on interfacial interaction. \( B \) parameters determined from the tensile yield stress of the composites are listed in column five of Table 3.2. The results show that the strongest interactions develop in PA and the weakest in PLA in this case. The values obtained for the other two matrices
are in between, but deviate somewhat from the other two predictions. We must be aware of the fact that two factors determine the value of $B$, the extent of exfoliation through the contact surface between the silicate and the polymer and the strength of interfacial interactions [23,24]. Moreover, $B$ is influenced also by the corresponding property of the matrix, smaller values are obtained in stiffer and stronger matrices. In spite of the difficulties in evaluation and in taking into account all factors, the message of the results is clear: interactions are competitive, they are different in the various polymers and determine structure as well as properties.

3.3.5. Discussion, correlations

The properties of the composites are determined by their structure and this latter is mainly controlled by competitive interactions. Several local deformation processes occur during the deformation of the composites both in the matrix and around larger entities of the silicate (stacks, particles). The ultimate properties of the composites are determined by the combined effect of these factors. The relationship of various processes can be seen reasonably well if we compare the composition dependence of characteristic stresses as shown by Figure 3.13 for PA.

![Figure 3.13](image_url)  
**Figure 3.13**  Dependence of the characteristic stresses of PA/OMMT composites on silicate content. Symbols: (▼) VOLs, volume strain, (△) AE, acoustic emission, (□) yield stress, (○) tensile strength.
The increase of volume is initiated at relatively small stresses. The related process was identified earlier as cavitation [40]. Particle fracture and/or debonding starts at slightly larger stress as shown by the characteristic stress determined by the acoustic emission measurement. Tensile yield stress and strength are much larger indicating that local processes do not influence these later. Interactions determine the extent of exfoliation but composite properties are dominated mainly by matrix characteristics and not by interactions or structure.

The role of local processes as well as interactions is completely different in PLA (Figure 3.14). Acoustic emission events are initiated at small stresses and because of weak interactions it can be mainly debonding and some particle fracture. Volume strain initiates yielding and this latter is close to the fracture of the polymer. Particle related processes are not very important in this polymer either. Although volume strain could not be measured in PP the relationship of the rest of the characteristic quantities indicate that particle related processes are much more important in this polymer both at poor and good adhesion, i.e. with and without the MAPP coupling agent. This statement is especially valid for neat PP, since improved adhesion results in very small deformations (see Figure 3.3).

![Figure 3.14](image)

**Figure 3.14** Characteristic stress values of PLA/OMMT composites plotted against silicate content. Symbols: (/vnd) VOLS, volume strain, (vs) AE, acoustic emission, (vs) yield stress, (vs) tensile strength.
The analysis of local processes showed that all composites have some acoustic activity and according to Figure 3.10 it is different in the various matrices. We assumed that these processes are related to the number of non-exfoliated structural entities, mainly to relatively large particles. This assumption is strongly corroborated by Figure 3.15 showing the correlation of XRD intensity of the silicate peak and the number of acoustic signals detected up to the yielding of the specimen. The correlations are relatively close in all cases and the differences among the polymers are obvious. Although acoustic activity depends on a number of factors, it is clear that large particles are present in all of the composites and they initiate local deformation processes. Depending on the characteristics of the matrix, these processes may lead to the failure of the composite (PP).

![Figure 3.15](image)

**Figure 3.15** Correlation between the cumulative number of acoustic signals and the area under the silicate peak in the XRD pattern of polymer/OMMT composites. Symbols: (○) PP, (●) PP/MAPP, (△) PLA, (□) PA.

The strength of interactions is crucial for exfoliation, but it influences local processes as well. PLA proved to be contradictory in many respects. Relatively strong interactions were estimated by two methods, while yield stress and parameters derived from it contradicted this. We mentioned that parameter $B$ depends on the extent of exfoliation, but also on the characteristics of the matrix. The relationship between this parameter and matrix yield stress is plotted against each other in Figure 3.16 for a series of polymer/zeolite composites as reference. The results obtained for the investigated four sets of composites are also plotted in the figure. Most of the points fit the general tendency quite well, only the PA composite deviates more significantly, its performance is better than the average. This deviation certainly results from larger extent of exfoliation and stronger
interactions. PLA fits the general line thus the larger adhesion estimated from AE measurements is definitely caused by the larger strength of this matrix. Although the structure of the polymer/silicate composites studied in this work is complex and the relationships among interactions, structure and properties are complicated we can clearly establish the role of competitive interactions in the determination of the extent of exfoliation and macroscopic properties.

![Figure 3.16](image-url)  
**Figure 3.16** Dependence of the load bearing capacity of the silicate (parameter $B_y$) on the yield stress of the matrix; (○) polymer/zeolite composites used as reference.

### 3.4. Conclusions

The comparison of polymer/OMMT composites prepared with four matrices of different chemical structure showed that competitive interactions among silicate layers and between the silicate and the polymer determine the extent of exfoliation and structure generally. The morphology of the composites is complicated, various structural entities can be present in them. Exfoliation is never complete, besides individual silicate layers, the composite can contain a silicate network, stacks of silicate plates and larger particles in various amounts. Several local deformation processes can take place around these structural entities as well as in the matrix. The dominating process depends on interactions, and on the size and amount of the heterogeneities. The main particle related processes are particle fracture and debonding, while cavitation takes place in the polymer, at least in PA and PLA matrices. The macroscopic properties of layered silicate composites are determined by the balance of the extent of exfoliation and interfacial adhesion that
Figure 3.16

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3.4. Conclusions

3.5. References

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Chapter 4

4.1. Introduction

The dispersion of an active component in a matrix or the controlled release of a substance into a medium are major issues in several areas and applications. Accordingly, many combinations of materials are explored both as supports or carriers as well as active components. A variety of materials and assemblies can be used as carriers like liposomes, polymer micelles and nanoparticles, nanogels, dendrites, silica or metal nanoparticles. Halloysite is a naturally occurring mineral, which is available both in platelet-like and tubular form as described in the review paper of Joussein et al. [1]. Numerous attempts have been made to use halloysite nanotubes as carriers for all kinds of bioactive molecules including drugs [2-14]. However, besides medical applications, halloysite nanotubes are used as supports in other areas as well. Shchukin et al. [15,16] developed an anticorrosion agent in which halloysite nanotubes contain the inhibitor that is released in a controlled way during a certain period of time. Fu et al. [17] used halloysite as a carrier for N-isopropyl-N'-p-phenylenediamine antioxidant to increase the stability of styrene-butadiene rubber.

Polyolefins usually contain a phenolic antioxidant as primary stabilizer. In the past decade, however, some concerns emerged on their possible negative effect on human health [18]. Natural antioxidants could be ideal candidates to replace synthetic phenolic stabilizers. Quercetin, a natural plant derived flavonoid, proved to be a very efficient melt stabilizer in polyethylene (PE) [19] however, it has some drawbacks as well. Its melting temperature is 316 °C, thus it does not melt under the normal processing conditions of PE, it has extremely limited solubility, and it gives the polymer a very strong yellow color. The use of a support or a carrier material to disperse quercetin homogeneously in PE seemed to be an obvious solution to these problems and halloysite nanotube were selected for the purpose.

A detailed description of actual and potential application of halloysite nanotubes is given in the review paper of Yuan et al. [20]. Most of these applications require a detailed knowledge of halloysite morphology and surface properties, but the mineral is rarely characterized in detail in spite of the fact that Yuan et al. [20] call the attention to the importance of proper characterization in their excellent review paper. Particle characteristics, surface area, pore size and volume, as well as surface energy are rarely determined, although they must influence both the adsorption and release of active molecules.

References

Chapter 4

Adsorption of an active molecule on the surface of halloysite for controlled release application: interaction, orientation, consequences

4.1. Introduction

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As mentioned above halloysite seemed to be an obvious choice as carrier material and possible controlled release effect could be an additional bonus. However, the adsorption and release of an active molecule from the surface depends on a large number of factors including the characteristics of the halloysite and those of the surrounding medium. The goal of this study was to determine the interactions among the halloysite and quercetin and identify the location of the active molecule on or inside the filler, if possible. An attempt was made to determine the amount of adsorbed quercetin, as well as the kinetics of adsorption. Preliminary calculations and modelling were carried out to estimate the arrangement of quercetin molecules on the surface of the mineral and to predict possible consequences.

4.2. Experimental

The quercetin used in the study was obtained from Sigma-Aldrich, USA and used as received. Its molecular weight is 302.24 g/mol, melting temperature 316 °C and purity >95 %; its chemical formula is presented in Scheme 4.1.

Scheme 4.1 The chemical structure of quercetin.

The halloysite nanotubes (Dragonite XR) were supplied by Applied Minerals, USA. The source of the mineral is the Dragon mine located in the Tintic mining district in Utah, USA The morphology of the mineral was characterized by scanning (SEM) and transmission electron microscopy (TEM, FEI Morgagni 268D). SEM indicated the aggregation of the tubes to relatively large particles (Figure 4.1). The average size of the particles was determined by a Horiba Partica LA950 V2 particle size analyzer and proved to be 6.5 μm. The specific surface area of the tubes, pore size and volume were determined by nitrogen adsorption using a NOVA2000 (Quantachrome, USA) apparatus. The measurements were done at -195 °C after evacuating the sample at 120 °C for 24 hours down to 10^-5 Hgmm. The dispersion component of surface tension was determined by inverse gas chromatography (IGC). The filler was agglomerated with water and the 250-400 μm fraction was used for the packing of the column. The dispersion component of surface tension was determined by the injection of n-alkanes at various temperatures between 160 and 300 °C because of the high surface energy of the mineral.
The adsorption kinetics of quercetin onto the halloysite nanotubes was studied in suspension. Quercetin was dissolved in ethanol to prepare a solution of 0.03-2.00 g/dm³ concentration. Halloysite was added subsequently and sonicated for 60 min, evacuated at 300 mbar pressure and then sonicated again for 15 min to remove the air from the tubes. The halloysite content of the dispersion was 10 g/dm³ in each case. After predetermined adsorption times the slurry was centrifuged and the concentration of quercetin in the solution was determined by UV-VIS spectroscopy from the intensity of the adsorption peak appearing at 374 nm. The adsorption of quercetin was determined also by a dissolution method [21,22] described more in detail elsewhere [23]. During the discussion of the results the quercetin content of the samples is presented in wt%, i.e. the amount of quercetin related to the weight of the halloysite. This unit allows the comparison of all results on the same scale including those of the adsorption experiments and the ones obtained on dry halloysite samples.

The interaction of quercetin with halloysite was studied by Fourier transform infrared spectroscopy (FTIR). Measurements were done both in transmission and in diffuse reflectance (DRIFT) mode. Potassium bromide pastilles containing ~0.4 wt% halloysite were prepared for the first technique, while dried powder was used in the second. The spectra were recorded in 16 scans by 2 cm⁻¹ resolution in both cases. Quercetin adsorption was followed also by X-ray photoelectron spectroscopy (XPS). The spectra were recorded using a Thermo Scientific K-Alpha (Thermo Fisher Scientific, UK) spectrometer equipped with a micro-focused, monochromatic AlKa X-ray source (1486.6 eV). An X-ray beam of 400 µm size was used at 6 mA and 12 kV. The spectra were acquired in the constant analyzer energy mode with the pass energy of 200 eV for the survey. Narrow regions were collected using the snapshot acquisition mode (150 eV pass energy), enabling rapid collection of data (5 s per region). Charge compensation was achieved with the system flood gun that provides low energy electrons (~0 eV) and low energy argon ions (20 eV) from a single source. The argon partial pressure was 2x10⁻⁷ mbar in the analysis chamber. The Thermo Scientific Avantage software, version 5.948 (Thermo Fisher Scientific, UK), was used for digital acquisition and data processing. Spectral calibration was determined by using the automated calibration routine and the internal Au, Ag and Cu standards supplied with the K-Alpha system. Surface compositions (in atomic %) were determined by the consideration of the integrated peak areas of the detected atoms and the respective sensitivity factors. The fractional concentration of a particular element A was computed using Equation 4.1

\[
A(\%) = \frac{I_A / s_A}{\sum (I_n / s_n)} 100
\]  

where \( I_n \) and \( s_n \) are the integrated peak areas and the Scofield sensitivity factors, respectively, corrected for the analyzer transmission. The possible intercalation of quercetin into the interlayer space was studied by X-ray diffraction (XRD). The patterns were recorded using a Phillips PW 1830 equipment with CuKα radiation at 40 kV and 35 mA in reflection mode.
The theoretical amount of quercetin which can be introduced into the voids within the tubes was estimated from pore volumes determined in different ways. Preliminary molecular modelling was carried out to estimate the strength of quercetin/halloysite interaction and the arrangement of the molecules on the surface of halloysite. Since accurate experimental geometry for halloysite nanotubes is not available, theoretical investigations were performed using the kaolinite clay mineral of similar structure as a model system. The lattice parameters and atomic positions determined by low-temperature neutron powder diffraction by [24] were used in the calculations. The Mercury [25] package was used for the construction of the crystal structures from the experimental parameters. The size of the monolayer model was ~15x25 Å and free valences were replaced by hydrogen atoms. The geometry optimization of quercetin was carried out at the density functional theory (DFT) level using the M06-2X [26] functional and the 6-31++G** [27] basis set. Subsequently 50-50 initial structures were generated randomly placing the quercetin molecule on both sides of the crystal. In order to check the orientation of the quercetin molecule on the surfaces calculations were done with 25 parallel and 25 perpendicular initial orientations in both cases. The geometry optimization of the complexes were performed by molecular mechanics (MM) using the universal force field (UFF) [28] freezing all atomic positions in the crystal. The Gaussian 09 [29] package was used for the MM and DFT calculations.

4.3. Results and discussion

The results of the experiments are discussed in several sections. Halloysite characteristics will be presented first, followed by the results obtained in the study of adsorption kinetics. The interactions between the two components are discussed next followed by considerations about the possible location of quercetin on or within the halloysite layers. The surface structure of coated halloysite is considered subsequently including possible consequences for practice.

4.3.1. Halloysite characteristics

The use of halloysite nanotubes both as controlled release support and as adsorbent requires their thorough characterization. Competitive interactions determine the amount of released material, the optimum and/or maximum amount of active component used for coating, and the rate of release. The surface energy of the mineral determines the strength of interaction, while its specific surface area as well as pore volume the adsorbed amount. However, halloysite nanotubes are rarely characterized in detail and many of the characteristics mentioned above are never determined. FTIR or UV-VIS spectroscopy are often used to follow the adsorption of a certain molecule [10,13,30], TEM to demonstrate tubular structure [12,30], zeta potential and pH [4,30] are determined occasionally, but specific surface area and pore volume [30] are rarely measured, and practically no attempt is made to determine surface energy.
Because of the high energy of their surface, halloysite nanotubes are expected to aggregate (Figure 4.1.). These aggregates could be separated reasonably well by ultrasonic treatment. Particle size analysis of the mineral indicated an average particle size of 6.5 µm. The tubular structure of the anisotropic particles is clearly shown by TEM (Figure 4.2.)

**Figure 4.1** *Particle structure of aggregated halloysite nanotubes; a SEM micrograph*

Besides particle characteristics, the surface area and pore structure are also very important for the intended application. According to the nitrogen adsorption measurements the specific surface area of the mineral is 57 m$^2$/g. A surface area was calculated also from the average dimensions of the tubes and 49 m$^2$/g was obtained in this way. The good agreement of the two values indicates the accessibility of the total surface area, at least by nitrogen. BET measurements yielded the total pore volume (0.181 cm$^3$/g) and the volume of the micropores (0.023 cm$^3$/g) of halloysite as well. The volume inside the tubes was calculated also from tube geometry and a value of 0.039 g/cm$^3$ was obtained. This value is close to that of the pores and might determine the amount of the active molecules which can be adsorbed by halloysite, at least if the majority of the compound is loaded within the tubes.
Layered silicates often can accommodate guest molecules among their layers. Good examples are montmorillonites and layered double hydroxides [3,31,32]. Accordingly, the theoretical possibility exists that halloysite can also adsorb quercetin within its layered structure. The layer distance of our mineral determined by XRD is 0.7 nm, somewhat smaller than that of montmorillonite which is around 1 nm. Although halloysite is regarded as a non-swelling clay, some sources claim the intercalation of urea [33,34] and small molecular weight substances within the layers [1].

**Figure 4.2** TEM micrograph taken from individual halloysite nanotubes.

IGC yielded 278 mJ/m² for the dispersion component of surface tension and >1000 mJ/m² for its polar component. This latter number must be treated with the utmost care because of the technical difficulties involved in their determination. The composition and structure of the external and internal surfaces of halloysite is dissimilar, the internal surface is very similar to gibbsite, while the external one consists of silicon dioxide. Infinite dilution IGC measures the energy of the most active sites and the values do not give information about the overall energy of the two surfaces. Only additional experiments may decide the question and give information about the location of quercetin on or inside the halloysite tubes.
4.3.2. Adsorption

Quercetin was adsorbed onto the surface of halloysite from ethanol solution. Under such conditions adsorption is a competitive process, both the active molecule and the solvent competes for active sites on the surface of the mineral. Quercetin has multiple -OH groups which can interact with the surface, but ethanol is also expected to form strong secondary bonds or H-bridges with it. The amount of adsorbed quercetin is plotted against the concentration of the added quercetin in Figure 4.3. The most active sites are occupied first; the amount of bonded quercetin increases linearly with the amount of added quercetin and practically all antioxidant molecules adsorb on the surface of the mineral. Adsorption continues with increasing concentration at larger quercetin amounts as well, but with a smaller slope. The change in slope indicates an energetically heterogeneous surface and possible multilayer coverage.

![Figure 4.3](image)

The amount of adsorbed quercetin plotted against that of the added stabilizer. Symbols: (□) 0, (○) 1, (△) 2, (▽) 4, (◇) 10, (▲) 20 days.

The time dependence, i.e. the kinetics, of adsorption is presented in Figure 4.4. In agreement with the conclusions drawn in the previous paragraph, adsorption is fast initially and slows down later. At small solution concentrations the adsorption isotherm goes to saturation, but increases continuously at larger concentrations. This kinetics was observed above 2 wt% quercetin content, i.e. at 3, 5, 7, 10, 15 and 20 wt%. In the case of simple physisorption one would expect a simple correlation going towards saturation just like at or below 2 wt% quercetin content (see Figure 4.4). Such a behavior was observed practically by all the groups using halloysite as an adsorbent [35-39]. However, both the concentration of the active component in the solution and the amount of halloysite in the slurry was smaller in the reported cases than in ours. Solution concen-
trations ranged between 0.03 and 0.3 g/dm$^3$ with the most frequent value of 0.05 g/dm$^3$ or less [36,37,39,40], while halloysite content changed between 1 and 8 g/dm$^3$ with the usual value of 1 g/dm$^3$ [36,37,39,40]. In our experiments the corresponding concentrations of the solutions were 0.03-2.00 g/dm$^3$ and uniformly 10 g/dm$^3$ for the suspension. Moreover, most of the kinetic studies were carried out in water solution previously. One may safely assume and the results strongly support the explanation that the considerable polarity of the active molecule used in this study, its relatively small solubility in ethanol, the large concentrations used and the energetically heterogeneous surface of halloysite lead to the observed adsorption kinetics and to multilayer coverage.

![Figure 4.4](image)

Figure 4.4  The time dependence of quercetin adsorption from ethanol solution at various quercetin concentrations. Symbols: (□) 0.3, (○) 0.7, (∆) 1.0, (▼) 2.0, (◇) 3.0, (<) 5.0 wt% quercetin related to the amount of halloysite.

4.3.3. Interactions

The adsorption isotherms presented above prove that quercetin molecules adsorb on the high energy surface of halloysite. The amount adsorbed is determined by competitive processes, by the relative strength of competing specific interactions. The competition is demonstrated well by Figure 4.5 comparing the amount of quercetin adsorbed from solution and that remaining on the surface after a dissolution process [23]. In this latter, the surface of the mineral is coated with increasing amounts of the active molecule and then the surplus, non-bonded compound is dissolved with an appropriate solvent, ethanol in this case. The comparison of the two correlations show that larger amount remains on the surface in the dissolution experiment than adsorbs from solution. In the latter case quercetin and solvent molecules compete for active sites and the ad-
sorption of the solvent prevents that of the probe molecule. All active sites are occupied by quercetin molecules in the dissolution experiment and strong interaction with the surface prevent their dissolution and replacement by the solvent.

Interactions are often followed by FTIR spectroscopy [34,40-42]. The overall DRIFT spectrum of quercetin, the neat halloysite and that of some coated nanotubes are shown in Figure 4.6. Quite a few peaks of quercetin and the halloysite overlap with each other, but characteristic peaks can be distinguished which do not interfere. The bonds assigned to the surface (3698 cm\(^{-1}\)) and lattice (3629 cm\(^{-1}\)) hydroxyl groups of the halloysite and the skeleton vibration of the aromatic rings of quercetin (1518 cm\(^{-1}\)) were used in further analysis. In Figure 4.7 the relative intensity of this latter is plotted against the amount of quercetin used for treatment. The two hydroxyl vibrations of halloysite were used as references in the evaluation. The non-linear correlation probably results from the simultaneous effect of the numerous factors (particle size, porosity, sample preparation conditions, etc.) influencing the intensity of DRIFT absorption. The two sets of data agree excellently indicating that quercetin does not intercalate among halloysite layers. In the case of intercalation, the interaction of surface hydroxyl groups with quercetin would result in the shift of the corresponding vibration and also in a decrease of its intensity as shown by several sources [34,40,41]. In spite of some claims [41], lattice hydroxyl groups are not available for interaction. Although surface hydroxyl groups are located also on the internal surface of the tubes and interact freely with any probe molecule, their number is small compared to the total number of such -OH groups and thus their interaction does not influence the position or intensity of the corresponding vibration.

![Figure 4.5](image.png)

**Figure 4.5** Effect of competitive interactions on the adsorption and dissolution of quercetin on or from the surface of halloysite. Symbol: (□) adsorption, (○) dissolution.
The analysis of halloysite vibrations indicated the lack of intercalation, but did not give information about interactions. The spectra of halloysite samples coated with different amounts of quercetin are presented in Figure 4.8 in the range of the aromatic skeleton vibration of the probe molecule.

Figure 4.6 Overall DRIFT spectra of quercetin, halloysite and nanotubes coated with various amounts of quercetin.

Figure 4.7 Change in the relative intensity of the aromatic skeleton vibration of quercetin (1518 cm\(^{-1}\)) plotted against the amount of quercetin used for treatment. Surface and lattice hydroxyl vibrations were used as reference bands: (●) surface hydroxyl, 3698 cm\(^{-1}\), (○) lattice hydroxyl, 3629 cm\(^{-1}\).
The analysis of halloysite vibrations indicated the lack of intercalation, but did not give information about interactions. The spectra of halloysite samples coated with different amounts of quercetin are presented in Figure 4.8 in the range of the aromatic skeleton vibration of the probe molecule.

**Figure 4.8**  Shift in the aromatic skeleton vibration of quercetin (1518 cm\(^{-1}\)) as an effect of interaction with the halloysite surface. Effect of surface loading.

The comparison of the spectra clearly shows that the band shifts towards larger wavenumbers with increasing coating and its intensity increases at the same time. The shift exceeds 30 cm\(^{-1}\) wavenumber indicating the strong interaction of the components. Tan et al. [42] observed a shift towards smaller wavenumbers of ibuprofen adsorbed on the surface of halloysite, which was explained with the formation of hydrogen bonds between the carboxyl groups of the compound itself. The hydroxyl groups of quercetin can and do interact with each other in a similar way, shown also by the high melting temperature of the compound. However, the fact that the observed shift decreases with increasing quercetin loading and approaches the value of neat quercetin clearly proves
that the downward shift is a result of quercetin/halloysite interaction. This latter is very strong, stronger than the one developing among quercetin molecules. The composition dependence of the shift discussed above is shown much better in Figure 4.9 in which the position of the vibration appearing at 1518 cm\(^{-1}\) in the spectrum of neat quercetin is plotted against the amount of the active molecule used for treatment. The S shaped correlation shows a threshold or critical concentration and decreasing shift with increasing coating as mentioned above.

One may safely assume that the band shifts considerably as an effect of interaction with the active sites of the highest energy, but less and less as the strength of interaction decreases and a multilayer forms. The results presented here corroborate those obtained in the adsorption and dissolution experiments indicating the existence of an energetically heterogeneous halloysite surface, strong interactions and multilayer coverage.

![Figure 4.9](image)

**Figure 4.9**  *Position of the aromatic skeleton vibration of quercetin plotted against the amount of quercetin added.*

### 4.3.4 Location

Controlled release from devices containing nanotubes is based on the assumption that the probe molecules are located inside the tubes and they diffuse slowly into the surrounding medium. Unfortunately very few evidence is presented in the literature which unambiguously confirms this assumption. Several possibilities exist for the location of the probe molecule, it can be located on the external or internal surfaces, on both of them, or it can be even intercalated into the interlamellar space.
Several papers show that in spite of the fact that halloysite is a non-swelling clay, small molecules can enter the interlamellar space. Inorganic salts, alcohols, DMSO, formamide, acetamide [1], etc. were shown to intercalate into halloysite, but molecules much larger than water and compounds with benzene rings cannot penetrate among the lamellae. The analysis of FTIR spectra indicated the absence of intercalation (Figure 4.7). The penetration of molecules into the interlamellar space results in an increase of interlayer distance, which can be monitored by X-ray diffraction. Overall XRD traces recorded between 4 an 40° 20 angles are presented in Figure 4.10a for the halloysite nanotubes, quercetin and a halloysite sample loaded with 12 wt% quercetin. The comparison of the traces reveals that unlike in other cases [42,43] quercetin is adsorbed onto halloysite only in the amorphous form and it does not intercalate into the interlamellar space. However, intercalation is difficult to determine unambiguously from the overall traces, thus several XRD patterns are presented in Figure 4.10b in the range of interest, between 4 and 20°. The characteristic reflection of halloysite at 12° 20 angle does not shift at all confirming earlier conclusion about the lack of intercalation. Accordingly, quercetin must be adsorbed on either or both surfaces of the halloysite nanotubes.

Because of its large penetration depth (~10 µm), FTIR spectroscopy cannot differentiate between the external and internal surfaces of halloysite. XPS, on the other hand, has an escape depth of a few nanometers (<10 nm) thus it probes only the external surface of the mineral. Apart from contaminations, halloysite does not contain carbon atoms thus the determination of the intensity of the C1s peak at 285 eV in the XPS spectrum makes possible the analysis of the adsorption of quercetin. The carbon content of the samples is plotted against the amount of quercetin used for treatment in Figure 4.11. The expected increase in carbon content can be clearly seen in the figure. A very similar correlation is obtained as in Figure 4.9, but for a different reason. At small quercetin contents only the surface contamination is seen, the amount of quercetin is small and does not increase with increasing coverage. Apparently, quercetin is located inside the tubes until a critical concentration is reached, at which the tubes are saturated and the active molecules appear also on the external surface. The saturation tendency observed is a result of multilayer coverage, saturation is reached when the thickness of the layer equals or exceeds escape depth. The results and considerations presented above clearly show that quercetin does not penetrate into the interlayer space, but at small coverage it is located within the tubes and then appears also on the external surface. This result also implies that surface energy is larger inside the tubes than outside that supports our conclusion about the energetically heterogeneous surface and explains the characteristics of quercetin adsorption from solution.
Figure 4.10  a) Overall XRD traces of halloysite, quercetin and a halloysite sample loaded with 12 wt% quercetin. b) XRD patterns of neat halloysite and those recorded on nanotubes coated with different amounts of quercetin showing the lack of intercalation.
Figure 4.10  Overall XRD traces of halloysite, quercetin and a halloysite sample loaded with 12 wt% quercetin.

b) XRD patterns of neat halloysite and those recorded on nanotubes coated with different amounts of quercetin showing the lack of intercalation.

Figure 4.11  Dependence of the carbon content of halloysite on the amount of quercetin added.

4.3.5. Surface structure, consequences

The final issues to be considered are the arrangement of quercetin molecules on the surface of halloysite, critical concentrations and consequences for practice. Surfactants were shown to arrange on the surface of clays in different ways depending on their molecular structure and surface coverage [31,44]. At small surface coverage the molecules orientate parallel to the surface, while arrange vertically at larger amounts. Quercetin is a fairly planar molecule (see Scheme 4.1) with a considerable number of evenly distributed functional groups thus one can expect it to orientate parallel to the surface. Preliminary molecular modelling confirmed the assumption and yielded the arrangement shown in Figure 4.12. Maybe not very easy to see, but quercetin is attached to the surface at several points simultaneously. During geometry optimization all molecules oriented initially perpendicularly to the surface turned into parallel position, and energetically deeper complexes were obtained when quercetin was placed on the proton-rich [AlOx(OH)y] side of the crystal. Consequently, the results of the theoretical investigations indicate that the adsorption of the quercetin molecule is favored on the AlOx(OH)y side of the crystal, inside the tubes, and in a parallel position to the surface.
Characteristic concentrations can be derived from the results of various measurements. The amount of quercetin needed for complete coverage can be obtained from the FTIR measurements (see Figure 4.9) and the value obtained is 4.5 wt%. XPS detects the filling of the tubes and the appearance of quercetin on the external surface of the nanotubes; the corresponding concentration is 3.5 wt%. Earlier dissolution measurements yielded the irreversibly bonded quercetin (0.8 wt%) and the maximum amount which cannot be dissolved from the surface with ethanol (4.0 wt%) [23]. Finally, the amount of quercetin necessary to fill the pores, i.e. the voids inside the tubes, was calculated from the density of the antioxidant and the value obtained was 4.1 wt%. The agreement of all these values is surprisingly good indicating a critical concentration of around 4.0 wt%. Below this value quercetin is located mostly inside the halloysite tubes and it is strongly bonded to the surface. As a consequence, its dissolution or diffusion into the very apolar PE matrix is not probable, stabilization and controlled release effect cannot be expected. Obviously, the critical concentration depends both on the guest molecule and the medium in question.

4.4. Conclusions

In order to check the possible use of halloysite nanotubes as a controlled release natural antioxidant device, the mineral was thoroughly characterized with various techniques including the determination of particle and tube morphology, specific surface area, pore size and volume, as well as surface energy. The tubular structure of individual particles was confirmed and BET measurements showed a relatively large specific surface area. The high surface energy determined by IGC predicted strong adsorption of the active molecule, quercetin, on the surface of halloysite and difficult release as a consequence. FTIR spectroscopy confirmed strong interaction, an energetically heterogeneous surface and the development of multilayer coverage at large loadings. FTIR and XRD experiments proved the complete lack of intercalation and showed that below 3.5 wt% quercetin loading most of the molecules are located within the tubes. Molecular modelling of the surface indicated the parallel orientation of quercetin molecules.

Figure 4.12 Predicted arrangement of a quercetin molecule on the surface of halloysite; result of molecular modelling.
with the surface. Critical concentrations derived from various measurements agreed well with each other further confirming that up to about 4.0 wt% loading, quercetin is bonded very strongly to the halloysite surface. As a consequence, the dissolution of the active molecules is very difficult or impossible, especially into apolar media like PE, thus neither stabilization nor controlled release effect can be expected below that concentration.

4.5. References

Chapter 5

5.1. Introduction

The results related to the adsorption of the active, antioxidant molecule on the surface of halloysite indicated strong adhesion and predicted difficult release in apolar media. However, above the critical concentration controlled release can be expected because some of the stabilizer is loaded inside the halloysite nanotubes. In order to check the possible use of halloysite nanotubes as support and controlled release device for the stabilization of PE, we studied the dissolution of the active molecule, quercetin, from their surface. The effect of the surrounding media on the characteristic concentrations related to the adsorption and desorption of quercetin were determined in eight solvents in order to predict the dissolution of the stabilizer in PE. Preliminary stabilization experiments were carried out and are reported here to check the stabilization efficiency of quercetin adsorbed on halloysite and its possible controlled release behavior.

5.2. Experimental

Stabilization experiments were carried out with the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow index of the powder: 0.32 g/10 min, nominal density: 0.947 g/cm³) polymerized by a Phillips catalyst. The additive-free polymer powder was provided by the MOL Group, Hungary.

The active component, quercetin, was loaded onto the surface of the tubes from ethanol solutions of increasing concentrations. The halloysite content of the suspension was kept at 10 g/dm³ in all experiments. The suspension was treated with ultrasound for 60 min to separate the tubes and then evacuated to remove air from within the tubes. After evacuation the suspension was agitated with ultrasound for another 15 min and then ethanol was removed by evaporation. The samples were kept in a vacuum oven at room temperature overnight. The amount of adsorbed quercetin was determined by thermogravimetry (TGA). The correlation between the nominal and measured quercetin content of the tubes is presented in Figure 5.1. The agreement between the two quantities is reasonable, especially if we consider the complicated procedure to cover halloysite with the target molecule.

Eight solvents with different characteristics were used to dissolve surplus quercetin from the surface of the nanotubes. Their purity exceeded 90% in each case and they were used as received. Various quantities were used to characterize the polarity and possible interaction of the solvents with quercetin. The Hildebrand solubility parameter ($\delta$), dielectric permittivity ($\varepsilon$), dipole moment ($\mu$) characterize polarity, polarizability and interaction in general terms, while the donor (DN) and acceptor numbers (AN) of...
Chapter 5

Competitive interactions and controlled release of a natural antioxidant from halloysite nanotubes

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5.2. Experimental

Stabilization experiments were carried out with the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow index of the powder: 0.32 g/10 min, nominal density: 0.947 g/cm³) polymerized by a Phillips catalyst. The additive-free polymer powder was provided by the MOL Group, Hungary.

The active component, quercetin, was loaded onto the surface of the tubes from ethanol solutions of increasing concentrations. The halloysite content of the suspension was kept at 10 g/dm³ in all experiments. The suspension was treated with ultrasound for 60 min to separate the tubes and then evacuated to remove air from within the tubes. After evacuation the suspension was agitated with ultrasound for another 15 min and then ethanol was removed by evaporation. The samples were kept in a vacuum oven at room temperature overnight. The amount of adsorbed quercetin was determined by thermogravimetry (TGA). The correlation between the nominal and measured quercetin content of the tubes is presented in Figure 5.1. The agreement between the two quantities is reasonable, especially if we consider the complicated procedure to cover halloysite with the target molecule.

Eight solvents with different characteristics were used to dissolve surplus quercetin from the surface of the nanotubes. Their purity exceeded 90 % in each case and they were used as received. Various quantities were used to characterize the polarity and possible interaction of the solvents with quercetin. The Hildebrand solubility parameter ($\delta$), dielectric permittivity ($\varepsilon$), dipole moment ($\mu$) characterize polarity, polarizability and interaction in general terms, while the donor ($DN$) and acceptor numbers ($AN^*$) of

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Fowkes indicate the tendency for specific interactions. The characteristics of the solvents are listed in Table 5.1. The coated filler was put into a vial containing the selected solvent, sealed and vigorously stirred for 24 hours. The suspension was centrifuged and then the concentration of quercetin in the solution was determined by UV-VIS spectroscopy with the measurement of the intensity of the absorption peak appearing at 374 nm.

Preliminary stabilization experiments were carried out with PE samples homogenized in a Brabender W 50 EHT internal mixer. The PE powder and the additives were mixed first in a mechanical blender for 20 s and then the blend was introduced into the mixer. Processing was carried out at 250 °C and 50 rpm for 10 min. The obtained material was compression molded into 1 mm thick plates at 190 °C and 180 kN using a Fontijne SRA 100 equipment and the plates were placed into an oven at 100 °C and aged for 5 and 10 days. Stability was characterized by the oxygen induction time (OIT) measured at 180 °C in oxygen.

![Figure 5.1](image)

**Figure 5.1**  Correlation between the nominal and measured quercetin content of coated halloysite nanotubes.
Correlation between the nominal and measured quercetin content of controlled release from halloysite nanotubes. However, above the critical concentration controlled release can be expected on the surface of halloysite indicated strong adhesion and predicted difficult release in apolar surroundings. The effect of the surrounding media on the characteristic concentration of quercetin was determined in eight solvents with different characteristics used to dissolve surplus quercetin. After evacuation the suspension was agitated with ultrasound for another 15 min and centrifuged for 60 min to separate the tubes and then evacuated to remove air from within the tubes. The amount of adsorbed quercetin was determined by thermogravimetry (TGA). The correlation between the nominal and measured quercetin content of the tubes is presented in Figure 5.1. The agreement between the two quantities determined by TGA and interaction in general terms, while the donor (DN) and acceptor number (AN*) of quercetin were determined by the solvent properties.

### Table 5.1 Properties of the solvents used in the dissolution experiments and the characteristic concentrations determined

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\rho^a$ (g/cm$^3$)</th>
<th>$\delta$ (MPa)$^{1/2}$</th>
<th>$\mu$ (D)</th>
<th>$\varepsilon$</th>
<th>$DN$ (kcal/mol)</th>
<th>$AN^*$ (kcal/mol)</th>
<th>Characteristic concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>0.2</td>
<td>19.0</td>
<td>1.04</td>
<td>4.80</td>
<td>0</td>
<td>5.4</td>
<td>c$_{100}$</td>
</tr>
<tr>
<td>Diethyl-ether</td>
<td>0.2</td>
<td>15.1</td>
<td>1.15</td>
<td>4.33</td>
<td>19.2</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Ethyl-acetate</td>
<td>0.9</td>
<td>18.6</td>
<td>1.78</td>
<td>6.08</td>
<td>17.1</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Butanol</td>
<td>1.2</td>
<td>23.3</td>
<td>1.66</td>
<td>17.84</td>
<td>–</td>
<td>9.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Methyl-ethyl-ketone</td>
<td>6.0</td>
<td>19.0</td>
<td>2.78</td>
<td>18.56</td>
<td>–</td>
<td>–</td>
<td>1.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11.0</td>
<td>26.0</td>
<td>1.69</td>
<td>25.30</td>
<td>20.0</td>
<td>10.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Acetone</td>
<td>18.0</td>
<td>20.2</td>
<td>2.88</td>
<td>21.01</td>
<td>17.0</td>
<td>2.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>40.0</td>
<td>18.6</td>
<td>1.75</td>
<td>7.52</td>
<td>20.0</td>
<td>0.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

a) Solubility of quercetin in the solvent
5.3. Results and discussion

The results are discussed in several sections. The dissolution of quercetin from the surface of halloysite is presented first together with the characteristic concentrations obtained. Competitive interactions are considered in the next section, followed by the discussion of correlations and consequences for practice.

5.3.1. Dissolution

The dissolution technique introduced by Papirer [1] and adapted later by Fekete [2] is a very simple, but efficient approach to study the adsorption of various substances onto the most diverse surfaces. Up to now the method was mainly used for the study of the surface coating of mineral fillers with surfactants. The method consists of the coverage of the filler with increasing amounts of a surfactant or other active molecule followed by the dissolution of the surplus, not bonded material from the surface with an appropriate solvent. Strong interaction prevents the dissolution of the active molecules at small concentrations, below monolayer coverage, but more and more of the compound is dissolved as the amount used for treatment increases and multilayer coverage forms. In Figure 5.2 the concentration of quercetin dissolved in butanol is plotted against the amount used for treatment. The figure demonstrates well the procedure and the effect of surface coverage. Quercetin concentration is zero in the solution at small amounts used for treatment, all the molecules remain adsorbed on the surface. With increasing coverage quercetin appears in the solution first and then its concentration increases linearly, all additional amount added is dissolved in this range. Figure 5.2 shows two sets of data obtained after 24 and 85 hours of stirring. Dissolved amounts are practically the same proving that prolonged time does not lead to additional dissolution. All subsequent dissolution experiments were carried out for 24 h, as a consequence.

The results of dissolution experiments are plotted in a different way in Figure 5.3. The amount of bonded quercetin is plotted against the quantity used for treatment. The two series shown were determined in two solvents, in butanol and ethyl-acetate. The obtained dissolution correlations indicate the physisorption of quercetin on the surface of the halloysite; both correlations tend towards a saturation value. Two characteristic quantities can be determined from such adsorption isotherms. $c_{100}$ is the proportionally bonded additive when all the material used for treatment remains on the surface and nothing is dissolved. The other characteristic concentration is $c_{\text{max}}$, the maximum amount of the compound used for treatment that remains on the surface without dissolution. The comparison of the two dissolution correlations presented in Figure 5.3 clearly indicates differences in the solvation power of the two solvents, butanol is more effective than ethyl-acetate in dissolving the active substance from the surface. Both $c_{100}$ and $c_{\text{max}}$ are smaller in butanol than in the other solvent, ethyl-acetate.
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**Figure 5.2** Dissolved quercetin plotted against the amount used for treatment. Effect of the time of dissolution; (○) 24 h, (□) 85 h.

**Figure 5.3** Typical dissolution curves presenting the amount of bonded quercetin as a function of the amount used for coating. Effect of solvent characteristics; (○) butanol, (□) ethyl-acetate.
Characteristic quantities determined with the eight solvents are compiled in Table 5.1 together with characteristics which are related to their polarity and dissolution strength. \(c_{100}\) values change between 0.8 and 2.2 wt% related to the filler, with an average value of 1.5 wt%. The dependence of \(c_{100}\) on solvent characteristics differs from earlier experience [3]. During the treatment of CaCO\(_3\) with stearic acid \(c_{100}\) was constant, practically independent of the solvent used. \(c_{\text{max}}\) values, on the other hand, changed in a relatively wide range in that case, and we see much larger variation in this characteristic also for the halloysite/quercetin pair. \(c_{\text{max}}\) varies between 3.1 and 6.5 wt%, a twofold increase with changing solvent characteristics. The difference indicates the significance of competitive interactions and the influence of the surrounding medium, which is of importance also for the intended application.

5.3.2. Competitive interactions

As mentioned above, the dissolution correlations clearly prove that quercetin is physisorbed on the surface of halloysite. This statement is further corroborated by the fact that characteristic concentrations determined by competitive interactions acting during dissolution depend on solvent characteristics; chemisorption would result in a continuously increasing amount of bonded quercetin. Quercetin interacts with the surface of the halloysite, but also with the solvent, while this latter also adsorbs on the surface of the filler. Since the surface energy of halloysite is very large, quercetin is adsorbed very strongly to it, the solvent can interact only with free surface or try to replace quercetin, which becomes easier with increasing solvent power. The fact that such an exchange may occur is shown by the effect of solvent characteristics on \(c_{100}\) and \(c_{\text{max}}\).

In an attempt to express the effect of the solvent on the characteristic concentrations in quantitative terms, we plotted them against the properties listed in Table 5.1. In Figure 5.4 the characteristic concentrations are presented as a function of the solubility of quercetin in the solvents. The two correlations are very similar that is quite interesting and difficult to explain. A minimum appears on the \(c_{\text{max}}\) vs. solubility correlation around 5 g/dm\(^3\). Large amounts of quercetin remain on the surface of halloysite at small solubility, because the interaction between the solvent and the active molecule is not very strong, interaction with the filler is preferred. The slight increase observed at large solubility is more difficult to understand. Specific interactions and the actual concentration of quercetin on the surface and in the solution may play a role here. Preferential interactions must be influenced by the presence of all components as shown by Karasz [4] in copolymers and polymer blends.
Chapter 5

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Solubility parameter ($\delta$), dielectric permittivity ($\varepsilon$) and dipole moment ($\mu$) were used for the characterization of the solvents. Although the scatter of the points is rather large, a clear tendency could be observed for all three correlations; characteristic concentrations decrease with the increasing value of the variable in question. We calculated the solubility parameter of quercetin by using the group contribution of van Krevelen and Hoftyzer [5] and obtained the value of 26 MPa$^{1/2}$. The solubility parameter of the solvents ranges from 15 to 26 and characteristic concentrations decrease continuously as their solubility parameter increases. Since all the correlations are very similar, we present here only the one obtained between $c_{100}$, $c_{\text{max}}$ and the dielectric constant of the solvents (Figure 5.5). We must note here that we plotted characteristic concentrations also against the Hansen solubility parameter in order to account for specific interactions. We arrived practically to the same correlation as shown in Figure 5.5 thus we refrain from its presentation here. As Figure 5.5 shows stronger effect and larger scatter is observed for $c_{\text{max}}$, but the same tendency prevails as for $c_{100}$. Obviously larger polarity and polarizability increases the solubility of quercetin in the solvents and dissolves it from the surface of halloysite.

Figure 5.4  Correlation between the characteristic concentrations and the solubility of quercetin in the various solvents; (○) $c_{100}$, (□) $c_{\text{max}}$. 

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Figure 5.5  Characteristic concentrations plotted against the dielectric constant of the solvents used for dissolution; (○) $c_{100}$, (□) $c_{\text{max}}$.

The characteristics of the solvents discussed above do not reflect specific interactions between the various compounds. These can be expressed much more adequately by the donor and acceptor numbers of Riddles and Fowkes [6,7]. Characteristic concentrations are plotted against the donor ($DN$) and corrected acceptor ($AN^*$) numbers in Figure 5.6. The scatter of the points is significant, but some conclusions can be drawn from the figure, nevertheless. Characteristics values seem to be smaller at both ends of the range, at large $DN$ and $AN^*$ values indicating that both acceptor and donor characteristics help dissolution. This conclusion is further confirmed by the fact that no points are situated in the middle of the range, since quercetin could not be dissolved in such solvents in sufficient amounts to carry out the experiments. These results also indicate that the dissolution of quercetin from the surface of halloysite must be very difficult in PE, a completely apolar polymer.
5.3.3. Discussion, consequences

The results above indicated that halloysite can be covered with a large amount of quercetin (see Figure 5.1). Dissolution experiments, on the other hand, showed that a part of the active molecules is adsorbed very strongly onto the surface and cannot be dissolved from it (Figure 5.2). Obviously the alignment of the molecules on the surface and surface coverage are of large importance, if we want to use the material combination as controlled release stabilizer in polyethylene. Since quercetin is a rather planar molecule (see Scheme 4.1), one would assume that it is arranged parallel to the surface of the mineral and molecular modeling using the Gaussian 09 package confirmed this assumption as it was demonstrated in Chapter 4. Accepting parallel arrangement, the surface coverage of halloysite was calculated both from the \( c_{100} \) and the \( c_{max} \) values. A surface need of 0.81 nm\(^2\) was assumed for the quercetin molecule and the surface area obtained by nitrogen adsorption was used in the calculations. The results are summarized in Table 5.2. Surface coverages calculated from the \( c_{100} \) value, i.e. from the amount proportionally bonded to the surface are much smaller than 100 %, indicating an energetically heterogeneous surface and a loose arrangement of the molecules on it. Large free surfaces are available at these quercetin concentrations. Values derived from \( c_{max} \) are close to or slightly larger than 100 % surface coverage. Obviously partial multi-layers remain on the surface of halloysite only if the solvation power of the solvent is small, its interaction with quercetin is weak.
### Table 5.2 Surface coverage of the halloysite with quercetin at the characteristic concentrations derived from the dissolution experiments

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$c_{100}$ (wt%)</th>
<th>Surface coverage (%)</th>
<th>$c_{\text{max}}$ (wt%)</th>
<th>Surface coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>2.2</td>
<td>62</td>
<td>6.5</td>
<td>184</td>
</tr>
<tr>
<td>Diethyl-ether</td>
<td>1.4</td>
<td>40</td>
<td>5.8</td>
<td>164</td>
</tr>
<tr>
<td>Ethyl-acetate</td>
<td>2.0</td>
<td>57</td>
<td>4.7</td>
<td>133</td>
</tr>
<tr>
<td>Butanol</td>
<td>1.1</td>
<td>31</td>
<td>3.7</td>
<td>105</td>
</tr>
<tr>
<td>Methyl-ethyl-ketone</td>
<td>1.2</td>
<td>34</td>
<td>3.1</td>
<td>88</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.8</td>
<td>23</td>
<td>4.0</td>
<td>113</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.4</td>
<td>40</td>
<td>5.2</td>
<td>147</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>1.5</td>
<td>42</td>
<td>4.5</td>
<td>127</td>
</tr>
</tbody>
</table>

Smaller than 100 % surface coverage raises also the question of the location of the active molecule on the surface. The chemical composition of halloysite is different inside the tubes and on the outer surface. In the inside, the surface corresponds to kaolinite containing aluminum oxide hydroxide moieties, while the external surface of the tube consist of silicon dioxide units. Some sources claim that molecules can penetrate also into the interlamellar space [8-11]. The majority of the groups using halloysite as carrier material for active molecules assume that these latter are located within the tubes and released from there to achieve prolonged effect [12-24]. As described in Chapter 4, detailed experiments proved more or less unambiguously that quercetin molecules cannot penetrate into the gallery space of halloysite and up to a critical concentration, which is approximately 4 wt% they are located within the tubes.

Preliminary stabilization studies were carried out in order to check, if the desired controlled release effect can be achieved with the halloysite/quercetin combination. Contrary to the work of Fu et al. [25], we used only 50 and 250 ppm quercetin. At the very large concentrations applied by Fu [25] stabilization effect and possible controlled release are difficult to determine and they are not advantageous from the economical point of view either. Quercetin was adsorbed onto the surface of the halloysite tubes in different amounts, homogenized with polyethylene at 0.33 wt% halloysite content and the residual stability of the polymer was determined after oven ageing. Oxygen induction time is plotted as a function of ageing time in Figure 5.7 at 50 and 250 ppm quercetin content corresponding to 1.5 and 7.5 wt% loading of the additive on the halloysite. The solubility parameter of PE is 17 MPa$^{1/2}$ [26], while that of quercetin is around 26 MPa$^{1/2}$. The large difference indicates almost complete immiscibility of quercetin with PE. If we compare the characteristic concentrations determined with solvents of small $\delta$ to those used for treatment, we can see that 1.5 wt% quercetin loading is around or below the $c_{100}$ value expected for PE, while the second, i.e. 7.5 wt% is definitely larger.
than \(c_{\text{max}}\). This relation of concentrations forecasts no dissolution of the stabilizer into PE at 50 ppm additive content, thus no stabilizing effect, while reasonable stabilization is expected at 250 ppm.

![Figure 5.7](image)

**Figure 5.7** Effect of ageing time and the amount of quercetin adsorbed on the surface of halloysite on the residual stability of PE; (□) 50 ppm quercetin, separately dispersed, (△) 50 ppm quercetin, adsorbed, (●) 250 ppm quercetin, adsorbed

Two sets of data are plotted in Figure 5.7 at 50 ppm quercetin content. The components, i.e. quercetin and halloysite, were added to polyethylene separately in one case, while quercetin was adsorbed onto the mineral, in the other. The time dependence of stability is completely different in the two cases. Relatively large stability is obtained initially in the first, indicating the stabilization efficiency of the additive, while practically none in the second showing that quercetin adsorbed below the \(c_{100}\) level is attached strongly to the surface of the halloysite and cannot stabilize the polymer. Stability remains very small throughout the time span of the experiment. At 250 ppm adsorbed quercetin, stability is considerably larger at the beginning of ageing and does not decrease much with ageing time. We must point it out here, though, that the absolute value of stability is very small, because of the high temperature and long processing time used in these preliminary experiments. The effect and behavior of the stabilizer must be confirmed with further experiments. Nevertheless, these results indicate that quercetin can be dissolved from the surface of halloysite only at concentrations larger than \(c_{100}\) in polyethylene and the time dependence presented in Figure 5.7 may indicate that a large amount of quercetin is located within the tubes and is released slowly with time.
5.4. Conclusions

Quercetin is a very efficient natural antioxidant for PE [27], but its poor solubility and high melting temperature limits its application. The use of halloysite nanotubes as a support or carrier material seemed to be an obvious solution for the problem. Contrary to most works in this area the halloysite nanotubes used as potential carrier material for a controlled release stabilizer in polyethylene were thoroughly characterized with several techniques. Specific surface area, pore volume and surface energy determine the adsorption of the active molecule on the surface of the mineral. The high surface energy of the halloysite results in strong bonding of the additive onto the surface. Dissolution experiments carried out for the determination of the effect of solvent characteristics on the amount of irreversibly bonded quercetin proved that adsorption and dissolution depend on competitive interactions prevailing in the system. Solvents with low polarity dissolve only surplus quercetin adsorbed in multilayers. Polyethylene does not contain functional groups, thus the polymer forms weak interactions with every substance; quercetin dissolves into it from the halloysite surface only above a critical surface coverage. Preliminary stabilization experiments confirmed that strong adhesion prevents dissolution and results in limited stabilization efficiency. At larger adsorbed amounts better stability and extended effect were measured indicating dissolution and controlled release. Further experiments are needed for the verification of controlled release action.

5.5. References

5. Van Krevelen, D. W., Te Nijenhuis, K., *Properties of polymers: Their correlation with chemical structure; Their numerical estimation and prediction from additive group contributions*, Elsevier: Amsterdam (2009)
Quercetin is a very efficient natural antioxidant for PE [27], but its poor solubility limits its practical application. Strategies, Syntheses, Characterization and Applications

Chapter 5

Controlled release from halloysite nanotubes


Long term stabilization of PE by the controlled release of a natural antioxidant from halloysite nanotubes

6.1. Introduction

As mentioned in Chapter 5, most polyethylene products are routinely stabilized by the combination of a synthetic phenolic antioxidant and a secondary, processing stabilizer, usually a phosphorous compound. Stabilization in this way is the current state of the art and an accepted technology used at industrial level thus in the last few decades very little attention was paid to the development of new stabilizers. As a consequence, no alternatives are available to replace traditional hindered phenolic antioxidants in spite of the fact that some time ago concerns emerged about the potential health and environmental hazard of these compounds [1].

A large number of natural compounds proved to be beneficial as antioxidants for the human health and these materials might present an obvious solution to replace synthetic antioxidants. Although the number of potential natural compounds which might be used as antioxidant in polymers is very large, only several of them have been studied in stabilization experiments [2-20]. Most of the natural compounds studied as polymer stabilizers up to now have several advantages. Besides being natural, they are also very efficient, quercetin, for example, protected PE against degradation during processing already at 50 ppm additive content. However, natural antioxidants, have some drawbacks as well. In the case of quercetin the melting temperature of the compound is 316 °C, thus it does not melt under the normal processing conditions of PE, it is very polar resulting in extremely limited solubility in PE, and it gives the polymer a very strong yellow color. The use of a support or a carrier material to disperse quercetin homogeneously in PE might solve at least some of these problems.

Halloysite nanotubes offer an obvious choice for a carrier or support material. It is a naturally occurring mineral, which is mined in acceptable purity and used for various purposes including the controlled release of active substances, mainly drugs [21-33]. Besides the solution of separation problems and water treatment [34-37], halloysite nanotubes were used as carrier material for a stabilizer as well [38,39]. Fu et al. [39] used halloysite as carrier for N-isopropyl-N'-p-phenylenediamine antioxidant to increase the stability of styrene-butadiene rubber. The approach resulted in improved homogeneity and stability, but at rather large, 2-3 wt%, antioxidant content. The analysis of the adsorption and release kinetics of quercetin from the nanotubes allowed us to draw conclusions about competitive interactions and their role in the release of the stabilizer into polyethylene [40]. Preliminary stabilization experiments were carried out to check the stabilization efficiency of quercetin adsorbed on halloysite [40]. Since the results of the experiments were promising, the decision was made to carry out a more thorough study to determine the efficiency of quercetin adsorbed on halloysite support as stabilizer and the...
Chapter 6

Long term stabilization of PE by the controlled release of a natural antioxidant from halloysite nanotubes

6.1. Introduction

As mentioned in Chapter 5, most polyethylene products are routinely stabilized by the combination of a synthetic phenolic antioxidant and a secondary, processing stabilizer, usually a phosphorous compound. Stabilization in this way is the current state of the art and an accepted technology used at industrial level thus in the last few decades very little attention was paid to the development of new stabilizers. As a consequence, no alternatives are available to replace traditional hindered phenolic antioxidants in spite of the fact that some time ago concerns emerged about the potential health and environmental hazard of these compounds [1].

A large number of natural compounds proved to be beneficial as antioxidants for the human health and these materials might present an obvious solution to replace synthetic antioxidants. Although the number of potential natural compounds which might be used as antioxidant in polymers is very large, only several of them have been studied in stabilization experiments [2-20]. Most of the natural compounds studied as polymer stabilizers up to now have several advantages. Besides being natural, they are also very efficient, quercetin, for example, protected PE against degradation during processing already at 50 ppm additive content. However, natural antioxidants, have some drawbacks as well. In the case of quercetin the melting temperature of the compound is 316 °C, thus it does not melt under the normal processing conditions of PE, it is very polar resulting in extremely limited solubility in PE, and it gives the polymer a very strong yellow color. The use of a support or a carrier material to disperse quercetin homogeneously in PE might solve at least some of these problems.

Halloysite nanotubes offer an obvious choice for a carrier or support material. It is a naturally occurring mineral, which is mined in acceptable purity and used for various purposes including the controlled release of active substances, mainly drugs [21-33]. Besides the solution of separation problems and water treatment [34-37], halloysite nanotubes were used as carrier material for a stabilizer as well [38,39]. Fu et al. [39] used halloysite as carrier for N-isopropyl-N'-p-phenylenediamine antioxidant to increase the stability of styrene-butadiene rubber. The approach resulted in improved homogeneity and stability, but at rather large, 2-3 wt%, antioxidant content. The analysis of the adsorption and release kinetics of quercetin from the nanotubes allowed us to draw conclusions about competitive interactions and their role in the release of the stabilizer into polyethylene [40]. Preliminary stabilization experiments were carried out to check the stabilization efficiency of quercetin adsorbed on halloysite [40]. Since the results of the experiments were promising, the decision was made to carry out a more thorough study to determine the efficiency of quercetin adsorbed on halloysite support as stabilizer and the

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6Hári, J., Sárközi, M., Földes, E., Pukánszky, B. submitted to Polymer Degradation and Stability
possible controlled release action of the device. The most important results are presented in this chapter together with consideration about consequences for practice.

6.2. Experimental

6.2.1. Materials

The polymer used in the experiments was the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow rate: 0.3 g/10 min at 190 °C, 2.16 kg; nominal density: 0.947 g/cm³) polymerized by a Phillips catalyst. The additive free polymer powder was provided by Mol NyRt., Hungary. The halloysite nanotubes (Dragonite XR) were supplied by Applied Minerals, USA. Quercetin (95 %) was purchased from Sigma-Aldrich. Irrespective of its form, the antioxidant was added to the polymer in 250, 500, 750 and 1000 ppm, to study the effect of additive content on stability. Reference compounds contained 500 ppm quercetin. 1000 ppm Sandostab PEPQ (PEPQ, Clariant) phosphonite secondary stabilizer was also added to each polyethylene sample.

6.2.2. Sample preparation

Quercetin, was loaded onto the surface of the tubes from ethanol solution. The quercetin content of the pretreated halloysite was 7.4, 15.2, 21.2 and 30.3 wt%. The halloysite content of the suspension was kept at 10 g/dm³ in all treatments. The suspension was treated with ultrasound for 60 min to separate the tubes and then evacuated to remove air from within the tubes. After evacuation the suspension was agitated with ultrasound for another 15 min and then ethanol was removed by evaporation. The samples were kept in a vacuum oven at room temperature overnight. The amount of adsorbed quercetin was determined by thermogravimetry (TGA).

The polymer and the additives were homogenized in a high speed mixer. The dry blend was processed and pelletized at 50 rpm speed and 260 °C barrel temperatures using a Rheomex S ¾” type single screw extruder attached to a Haake Rheocord EU 10V driving unit. For further studies, films of about 100 µm thickness were compression molded at 190 °C and 5 min using a Fontijne SRA 100 machine.

Besides the polyethylene compounds containing the halloysite nanotubes pre-treated with quercetin (P, Q/H) several reference compounds were also prepared (Table 6.1.). Polyethylene not containing any additive was also extruded (PE), as well a compound stabilized only with the phosphonite secondary stabilizer (P). The effect of halloysite on stabilization was checked by the preparation of a compound not containing the mineral, but only the two stabilizers (P, Q), while the effect of pretreatment was compared to the simultaneous addition of the components (P, Q, H). The abbreviations in the parentheses will be used in figures to differentiate the compounds and facilitate understanding.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>PE</th>
<th>content (w/w%)</th>
<th>PE</th>
<th>PQ</th>
<th>content (ppm)</th>
<th>Halloysite content (w/w PE %)</th>
<th>Quercetin content (ppm)</th>
<th>Composition of Q/H (mQ/mHNT %)</th>
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<tr>
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<td>-</td>
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<td>-</td>
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</tbody>
</table>
1.2. Experimental

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### Table 6.1. Composition of the samples.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>PE content (w/w%)</th>
<th>PEPQ content (ppm)</th>
<th>Halloysite content (w/wPE%)</th>
<th>Quercetin content (ppm)</th>
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</tr>
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<tr>
<td>500-P, Q/H</td>
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<td>0.33</td>
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<tr>
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<td>0.33</td>
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<td>1000-P, Q/H</td>
<td>99.67</td>
<td>0.33</td>
<td>1000</td>
<td>30.3</td>
<td></td>
</tr>
</tbody>
</table>

6.2.3. Characterization

The halloysite was characterized very thoroughly by several methods as it was described in Chapters 4 and 5. The morphology of the mineral was studied by electron microscopy (SEM, TEM). The average size of the particles was determined by laser light scattering method. The specific surface area of the tubes, pore size and volume were determined by nitrogen adsorption and the surface tension was determined by inverse gas chromatography (IGC).

The melt flow rate (MFR) of the polymer was determined according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load using a Göttfert MPS-D MFR tester. Residual thermo-oxidative stability was characterized by the oxidation induction time (OIT) measured at 180 °C in oxygen atmosphere with constant, 20 ml/h flow rate in open aluminum pans using a Perkin Elmer DSC 2 apparatus. The functional groups of polyethylene were determined by FTIR spectroscopy on the 100 µm thick compression molded films in transmission mode using a Tensor 27 (Bruker) spectrophotometer. Five parallel measurements were carried out on each sample between 4000 and 400 cm⁻¹ wavelengths at 2 cm⁻¹ resolution by 16 scans. FTIR spectroscopy was used also for the determination of residual PEPQ content. The color of the samples was described by the yellowness index (YI) and the optical L⁺ parameter measured on a Hunterlab Colourquest 45/0 apparatus. Accelerated ageing was done in an air circulation oven (Memmert UFE 600) at 100
°C for 5 and 10 days. The homogeneity of the samples was checked by optical microscopy on 5 µm thick slices cut from the samples with an ultramicrotome. Micrographs were recorded using a Keyence VHX 5000 digital optical microscope.

6.3. Results and discussion

The results of the study are reported in several sections. The characteristics of the active halloysite nanotubes containing the stabilizer are discussed first and then the stabilization efficiency of the device is described in the next section. Long term stabilization and controlled release are presented in the last section of the paper together with some discussion on practical consequences.

6.3.1. Characterization of active nanotubes

The detailed study of the release characteristics of the quercetin/halloysite complex has shown that numerous factors must be considered, which are often partially or completely neglected. Very few attempts are made to determine the surface energy of the nanotubes, their pore size and volume although these determine both the amount of active molecules accommodated inside the tubes as well as the kinetics and amount of released material. The detailed characterization of halloysite nanotubes showed that their average length is 203 ± 119 nm, external diameter 50 ± 23 nm and internal diameter 15 ± 6 nm accompanied by a pore volume of 0.039 cm³/g. The specific surface area determined by nitrogen adsorption is 57 nm²/g. The surface energy of halloysite is very high, the dispersion component of surface tension is 278 mJ/m², while a value larger than 1000 mJ/m² was obtained for the polar component. Detailed investigations (see Chapter 4.) showed that the energy of the internal and external surfaces is different, the energy is larger inside the tubes leading to preferential adsorption. The critical concentration of adsorption inside the tubes is around 4 wt% quercetin, below this amount all the active molecules are located within the tubes, as it was presented in Chapter 4. The strong surface energy results in strong adhesion and slow or no release at all below this concentration, especially into an apolar medium like the polyethylene matrix used in these experiments.

Based on the results obtained in the previous stage of the research, quercetin was adsorbed on the surface of halloysite in amounts exceeding this critical value (4 wt%) considerably. The active nanotubes were characterized by FTIR spectroscopy. The spectra of selected compositions, some of them from the previous study, are presented in Figure 6.1. The spectra of the halloysite tubes and that of quercetin are also included as reference. The spectra clearly show that at and below 3 wt% quercetin content, the absorption bands of the active molecule do not appear in the spectrum, because of the very strong adhesion of this latter by the internal surface of halloysite.
Chapter 6

At larger concentrations the characteristic vibrations of quercetin can be detected in the spectrum, in which the main peaks of the mineral and the stabilizer are seen simultaneously.

![Figure 6.1](image-url)

**Figure 6.1**  *Fourier-transform infrared spectra of halloysite (H), quercetin (Q) and halloysite nanotubes loaded with different amounts of the natural antioxidant.*

Preferential and very strong adhesion of quercetin within the tubes is demonstrated even better by the correlation between the intensity of the vibration appearing at 1563 cm\(^{-1}\) and the amount of quercetin adsorbed on the surface of the tubes. As the correlation presented in Figure 6.2 shows, the intensity of the band belonging to the aromatic skeleton vibration of quercetin is basically zero below 4 wt% quercetin content and increases only above this amount. The results prove the preferential adsorption of quercetin inside the tubes and predict smaller stabilization efficiency below this level.
6.3.2 Processing stability

Quercetin proved to be a very efficient processing stabilizer in an earlier study [18]. It protected the polymer against degradation already at very small additive contents. In Phillips polyethylene processing stabilization is mainly about the prevention of the formation of long chain branches through the radical reactions of chain-end vinyl groups. The vinyl group content of our polymer is plotted against quercetin content in Figure 6.3. Unfortunately halloysite also absorbs in the region of the vinyl groups, thus to facilitate comparison halloysite absorption was deducted from the spectra. All samples have the same vinyl content which allow the drawing of several conclusions. The stabilizer package used in the experiments protects the polymer efficiently at all quercetin contents. The secondary stabilizer plays an important role in stabilization, since vinyl content does not decrease during extrusion even when it is used as the only stabilizer. The interaction of quercetin and PEPQ is important in stabilization.

Figure 6.2 Changes in the intensity of the characteristic absorption band of quercetin at 1563 cm⁻¹ wavelength (skeleton vibration of the aromatic rings) plotted as a function of the amount of quercetin adsorbed on the halloysite nanotubes. Symbols: (○) previous measurements, (●) this work.
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The consumption of the secondary antioxidant demonstrates this interaction well. The amount of residual PEPQ is plotted against quercetin content in Figure 6.4. Considerable amount of PEPQ is consumed during extrusion when the primary stabilizer, quercetin is absent, while the levels are much higher when the combination of the two stabilizers is used. The level of remaining PEPQ is basically the same independently of the amount of quercetin added. The form of addition does not influence significantly PEPQ consumption, maybe the separate introduction of the three components (quercetin, PEPQ, halloysite) leads to somewhat smaller residual secondary antioxidant content. The large consumption might be the result of competitive interactions and adsorption of the two additives on the surface of the mineral, but this tentative explanation needs further study and proof.

Changes in the viscosity of the polymer indicate very sensitively the possible formation of long chain branches, i.e. degradation during processing. The MFR of the samples is plotted against quercetin content in Figure 6.5. Strong increase is observed in the viscosity of the neat polymer not containing any stabilizer. The secondary stabilizer protects the polymer quite efficiently even when it is applied alone, as indicated already by its vinyl group content. It is interesting to note that MFR is even larger in the presence of the halloysite (P, H). The increase probably does not result from the primary effect of the mineral, since the combination of the phosphorous antioxidant and quercetin without any halloysite leads to the same viscosity as in the presence of the mineral. The observation
is interesting, but an unambiguous explanation needs further study. However, the results clearly show that the combination of quercetin and PEPQ efficiently protects the polymer against degradation during processing independently of the form of addition (adsorbed, separately introduced) and halloysite does not influence viscosity at the amount used.

As mentioned in the introductory part, one of the disadvantages of quercetin as stabilizer is its strong yellow color; one hoped for less discoloration when quercetin is adsorbed inside the halloysite tubes. The effect of quercetin content on the color of the polymer is presented in Figure 6.6. According to the results, the discoloration effect is very strong and independent of the homogenization technique; all compounds containing quercetin have a very strong yellow color. We must consider here, however, that quercetin was added always above the critical level of 4 wt%, since below this concentration the stabilizer would not have been active. Obviously weaker color and efficient stabilization cannot be achieved at the same time, and quercetin can be used only in applications in which color is not an issue.

![Graph showing the dependence of residual PEPQ on quercetin content and homogenization technique.](image)

**Figure 6.4** Dependence of the amount of residual PEPQ on the quercetin content of PE and on the technique of homogenization. Symbols: (▼) P; (△) P, Q; (●) P, H; (■) P, Q, H; (○) P, Q/H.
Chapter 6

130

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**Figure 6.5** Differences in the MFR of the polymer as a function of quercetin content and homogenization technology. Symbols: (□) PE; (△) P; (△) P, Q; (◆) P, H; (■) P, Q; (★) P, Q/H; (●) P, Q/H.

**Figure 6.6** Correlation between the yellowness index of the PE compounds studied and quercetin content. Symbols: (▽) P; (△) P, Q; (◆) P, H; (■) P, Q, H; (●) P, Q/H.
Residual stability is an important characteristic of PE compounds in long term applications, like pipes or automotive parts. The OIT of the compounds measured at 180 °C in oxygen is plotted as a function of quercetin content in Figure 6.7. The correlation is different from those presented in previous figures. Vinyl group content, residual PEPQ, MFR or color practically did not change with increasing quercetin content, while OIT depends considerably on it. In fact, 250 ppm adsorbed quercetin does not render the polymer sufficiently stable, stability reaches acceptable levels only above this additive concentration. Both the presence of the halloysite and adsorption seem to decrease stabilization efficiency under the conditions of the OIT test. Separate addition of the three components increases residual stability and considerably larger value is obtained when the polymer does not contain the halloysite tubes. Obviously further experiments must be carried out to verify these results, a single composition is not sufficient for drawing unambiguous conclusions, but the results are rather unexpected and not very favorable for long term stabilization.

![Figure 6.7](image)

**Figure 6.7**  Increasing residual stability (OIT) of PE with increasing quercetin content. Effect of homogenization technology. Symbols: (▽) P; (△) P, Q; (◆) P, H; (■) P, Q, H; (●) P, Q/H.

### 6.3.3. Long term stabilization, controlled release

Long term stability is an important requirement in a number of applications including the automotive industry. The efficiency of stabilizer packages under such conditions can be checked by accelerated ageing. The results of this test are presented in Figure 6.8, in which residual stability is plotted against quercetin content. The correlation is very similar to that shown in Figure 6.7. Compounds not containing the primary antioxidant,
Chapter 6

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Figure 6.7 Increasing residual stability (OIT) of PE with increasing quercetin content. Effect of homogenization technology. Symbols: () P; (P, Q) P, Q; (P, H) P, H; (P, Q, H) P, Q, H; (P, Q/H) P, Q/H; (P, Q) 0 day, (P, Q) 5 days, (P, Q) 10 days ageing.

Long term stabilization by controlled release

Long-term stability is an important requirement in a number of applications including the automotive industry. The efficiency of stabilizer packages under such conditions can be checked by accelerated ageing. The results of this test are presented in Figure 6.8, in which residual stability is plotted against quercetin content. The correlation is very similar to that shown in Figure 6.7. Compounds not containing the primary antioxidant, quercetin, do not have any stability, while OIT increases more or less proportionally with quercetin content. The correlation is not linear, at least not at small quercetin content, showing the effect of the halloysite carrier on stability, as mentioned above. The absence of the halloysite, or the separate addition of the components leads to increased residual stability, while increased ageing time decreases stability as expected. Information about the time dependence of ageing or controlled release cannot be drawn from the figure in this representation.

Figure 6.8 Effect of quercetin content and accelerated ageing on the residual stability of PE compounds. Symbols:

- () P; (P, H) P, H; (P, Q, H) P, Q, H; (P, Q/H) P, Q/H; (P, Q) 0 day,
- (P, Q) 5 days,
- (P, Q) 10 days ageing.

Residual stability is plotted against ageing time in Figure 6.9 and the representation is much more informative about the time dependence of ageing. Compounds which do not contain quercetin have very limited stability, which further decreases during ageing, however, the differences are not significant. 500 ppm quercetin renders the polymer sufficiently stable and the comparison of the technique of addition indicates considerable differences exceeding 30 min. The presence of halloysite obviously decreases the efficiency of the additive package quite substantially. The most efficient is the quercetin/PEPQ combination without halloysite. The mineral obviously adsorbs the additives on its high energy surface even from the melt. Since adsorption is competitive, both quercetin and PEPQ is attached to the surface, thus more quercetin remains in the polymer
and stability decreases somewhat less than in the third case, when quercetin is absorbed prior to the test, in a separate step. Moreover, the adsorption of the polymer cannot be excluded either, although it develops much weaker interactions with halloysite than the two additives. The compounds containing quercetin adsorbed on the halloysite carrier possesses the smallest residual stability; adsorption apparently decreases the activity of the stabilizer, hinders its diffusion and/or reactions.

Figure 6.9  The influence of ageing time and homogenization technology on the residual stability of PE compounds. Symbols: (▽) P; (△) P, Q; (◆) P, H; (■) P, Q, H; (●) P, Q/H. Quercetin content was 500 ppm.

The presence of the halloysite carrier seems to be disadvantageous for stabilization. On the other hand, the slope of the correlations indicates slightly decreased ageing rate in compounds containing halloysite. The slope seems to change inversely with stabilizing efficiency; stabilizer consumption, i.e. ageing, is the fastest in the absence of the halloysite nanotubes and the slowest for the pretreated mineral. The effect of addition technology on ageing is demonstrated well by Figure 6.10 in which the change of OIT is plotted as a function of ageing time. The reference is the OIT of the samples before ageing. A slight increase can be seen in stability at short ageing time, which can be explained by the dissolution of surplus stabilizer at the high temperature of ageing, but OIT decreases sharply at the longer ageing time.
The decrease is the largest for the quercetin/PEPQ combination, in the absence of halloysite, while the smallest for the compound containing the pretreated mineral. Apparently, degradation is slower in the presence of halloysite and some controlled release is achieved indeed in agreement with the experience of Fu and Lvov [39].

**Figure 6.10**  
*Effect of ageing time on the extent of OIT change compared to the non-aged sample. Symbols: (△) Q; (■) Q, H; (●) Q/H.*

Although not directly related to stability, it is interesting to follow the change of the color of the samples during ageing (Figure 6.11). Color decreases with ageing time, which might be surprising at first, but was explained with the consumption of quercetin having a stronger discoloration effect than its degradation product. The color of the compound containing the quercetin/PEPQ combination without halloysite and that of the one into which the three additives were added separately decreases considerably slower than that of the third compound containing the pretreated controlled device. Apparently the release of well dispersed quercetin from the surface of the carrier results in more reactions, larger decrease in color and larger stability. In spite of the smaller absolute value of stability, decreased rate of ageing is gained through the use of the controlled release device prepared from halloysite nanotubes.
6.4. Conclusions

The natural antioxidant, quercetin, used in these experiments is a very efficient stabilizer for polyethylene. In the presence of a phosphonite secondary stabilizer it protects the polymer against degradation during processing already at 50 ppm concentration and renders it stable during use at 250 ppm. Since its solubility in PE is very limited, it forms a separate phase at very small concentration. The use of a halloysite nanotube support results in more homogeneous dispersion and facilitates dissolution to the polymer. Because of the high energy of the halloysite surface, the stabilizer adheres to it very strongly and does not dissolve in polyethylene below a critical concentration. Only stabilizer added above this amount, which is around 4 wt% calculated for the halloysite, stabilizes the polymer resulting in a loss of active additive. Nevertheless, the melt stabilization efficiency of quercetin does not decrease in the presence of the halloysite support. The efficiency of long term stabilization decreases somewhat, but halloysite nanotubes pretreated with the stabilizer possess controlled release function, ageing is slower in their presence than with separately dispersed components or in the absence of the halloysite. It is a question of decision if controlled release and slower ageing are compensated by the loss of efficiency and smaller OIT in long term use.
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6.5. References

Chapter 6

Chapter 7

Summary

The interest in layered silicate nanocomposites ebbed somewhat in recent years, because of the difficulties encountered during their preparation and study, and also because the expected breakthrough in their application has not been achieved yet. Our group gained extensive experience in this field and the results obtained pointed out the most important factors determining the structure and properties of layered silicate nanocomposites, as well as the most relevant questions which have not been answered yet. A thorough literature research has revealed that very few or practically no studies have been carried out to compare nano reinforcements to traditional fillers and that nanofillers have not been tested in different matrices either. As a consequence, we set up two projects to fill the void and supply information on these basic questions. The tendency in publications on nanocomposites clearly indicated that the interest of the researchers turned from layered silicates towards other nanofillers, since better progress and larger success was expected with carbon nanotubes, graphene, or other nanofillers. To follow the trend and in accordance with the need which emerged in another research area of the group, we set out to explore the possible use of halloysite nanotubes as controlled release devices in the stabilization of polyethylene. However, before launching the stabilization experiments we had to get acquainted with the new nanofiller, characterize it very thoroughly and study the interaction of the stabilizer with the tubes in detail. Only after collecting the necessary basic information could we start to use the nanodevice for stabilization. This Thesis reports the route and progress on this road and the most important results that were achieved during the work. Although we summarized the most important results at the end of each chapter, we briefly repeat them here to give a concise overview. At the end of this chapter we compile our most important new findings in a few thesis points.

The comparison of the effect of various micro- and nanofillers on the properties of PA6 composites showed that these latter can be modified in a relatively wide range. True reinforcement can be achieved with glass fibers, but the influence of all traditional fillers can be predicted with large certainty because their structure can be controlled quite well. Although layered silicates reinforce polyamide even better than glass fibers, but only in a very narrow composition range because of structural effects. The extent of exfoliation is not sufficiently large in polyamide/organophilized clay composites and besides individual silicate layers a number of other structural entities are also present in the composite. Structure cannot be controlled in the desired extent thus properties cannot be predicted and reproduced for practical applications. Numerous local deformation processes take place during the deformation of PA composites, the cavitation and shear yielding of the matrix, but also particle related processes. The properties of PA composites are not determined by these latter, but by those taking place in the matrix. Properties of PA composites can be adjusted in a wide range, but the routine use of layered silicates needs further efforts.
The comparison of polymer/organophilic montmorillonite composites prepared with four matrices of different chemical structures showed that competitive interactions among silicate layers and between the silicate and the polymer determine the extent of exfoliation and structure generally. The morphology of the composites is complicated, various structural entities can be present in them. Exfoliation is never complete and besides individual silicate layers, the composite can contain a silicate network, stacks of silicate plates and larger particles in various amounts. Several local deformation processes can take place around these structural entities as well as in the matrix. The dominating process depends on interactions, and on the size and amount of the heterogeneities. The main particle related processes are particle fracture and debonding, while cavitation takes place in the polymer, at least in PA and PLA matrices. The macroscopic properties of layered silicate composites are determined by the balance of the extent of exfoliation and interfacial adhesion that decreases upon organophilization. Increased reinforcement and improved composite properties can be achieved only by the proper control of all interactions prevailing in the composite.

In order to check the possible use of halloysite nanotubes as a controlled release natural antioxidant device, the mineral was thoroughly characterized with various techniques including the determination of particle and tube morphology, specific surface area, pore size and volume, as well as surface energy. The tubular structure of individual particles was confirmed and BET measurements showed a relatively large specific surface area. The high surface energy determined by IGC predicted strong adsorption of the active molecule, quercetin, on the surface of halloysite and difficult release as a consequence. Quercetin is a very efficient natural antioxidant for PE, but its poor solubility and high melting temperature limits its application. The use of halloysite nanotubes as a support or carrier material seemed to be an obvious solution for the problem. FTIR spectroscopy confirmed strong interactions, an energetically heterogeneous surface and the development of multilayer coverage at large loadings. FTIR and XRD experiments proved the complete lack of intercalation and showed that below 3.5 wt% quercetin loading most of the molecules are located within the tubes. Molecular modelling of the surface indicated the parallel orientation of quercetin molecules with the surface. Critical concentrations derived from various measurements agreed well with each other further confirming that up to about 4.0 wt% loading, quercetin is bonded very strongly to the halloysite surface. As a consequence, the dissolution of the active molecules is very difficult or impossible, especially into apolar media like PE, thus neither stabilization nor controlled release effect can be expected below that concentration.

Specific surface area, pore volume and surface energy determine the adsorption of an active molecule on the surface of halloysite nanotubes. As the previous study has shown, the high surface energy of the mineral results in the strong bonding of the additive onto the surface. Dissolution experiments carried out for the determination of the effect of solvent characteristics on the amount of irreversibly bonded quercetin proved that adsorption and dissolution depend on competitive interactions prevailing in the system. Solvents with low polarity dissolve only surplus quercetin adsorbed in multilayers. Polyethylene does not contain functional groups, thus the polymer forms weak interactions with every substance; quercetin dissolves into it from the halloysite surface only above the critical surface coverage. Preliminary stabilization experiments confirmed that strong ad-
hension prevents dissolution and results in limited stabilization efficiency. At larger adsorbed amounts better stability and extended effect were measured indicating dissolution and controlled release.

The natural antioxidant, quercetin, used in the experiments is a very efficient stabilizer for polyethylene; in the presence of a phosphonite secondary stabilizer it protects the polymer against degradation during processing already at 50 ppm concentration and renders it stable during use at 250 ppm. Since its solubility in PE is very limited, it forms a separate phase at very small concentration. The use of a halloysite nanotube support resulted in its more homogeneous dispersion and easier dissolution into the polymer. Since only stabilizer added above the critical concentration stabilizes the polymer, the use of the halloysite support results in the loss of the active additive. However, the melt stabilization efficiency of quercetin does not decrease in the presence of the halloysite support. The efficiency of long term stabilization decreases somewhat, but halloysite nanotubes pretreated with the stabilizer possess controlled release function, ageing is slower in their presence than with separately dispersed components or in the absence of halloysite. It is a question of decision if controlled release and slower ageing are compensated by the loss of efficiency and smaller OIT in long term use.

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

1. With the help of direct comparative measurements we could prove for the first time that although layered silicates reinforce polyamide even better than traditional glass fibers, they do this only in a very narrow composition range because of structural effects. The extent of exfoliation is not sufficiently large in polyamide/organophilized clay composites and besides individual silicate layers a number of other structural entities are also present in the composite leading to a very complicated structure (Chapter 2).

2. The same experiments showed that numerous local deformation processes take place during the loading of PA composites, the cavitation and shear yielding of the matrix, as well as particle related processes. The properties of PA composites are not determined by these latter, but by those taking place in the matrix (Chapter 2).

3. The comparison of the structure and properties of polymer/organophilic montmorillonite composites prepared with matrices of different chemical structures showed that competitive interactions among silicate layers and between the silicate and the polymer determine the extent of exfoliation and structure generally. As a consequence, the macroscopic properties of layered silicate composites are determined by the balance of the extent of exfoliation and interfacial adhesion that decreases upon organophilization (Chapter 3).

4. Although considerable effort is done to use halloysite nanotubes as carrier material for the preparation of controlled release devices, very few attempts are made to characterize the filler properly. Contrary to the general approach we characterized our halloysite nanotubes in detail and proved that it possesses an energetically
heterogeneous surface, enters with the probe molecule, quercetin, into strong interaction leading to the development of multilayer coverage at large loadings (Chapter 4).

5. Structural investigations proved the complete lack of intercalation of quercetin into the galleries of the silicate and showed that below a critical concentration most of the probe molecules are located within the tubes with parallel orientation to the surface. Below this critical concentration the adhesion of the probe molecules to the surface is very strong and they do not dissolve easily into the surrounding matrix (Chapter 4).

6. With the help of preliminary stabilization experiments we confirmed that strong adhesion prevents dissolution and results in limited stabilization efficiency. At larger adsorbed amounts better stability and extended effect were measured indicating dissolution and controlled release (Chapter 5).

7. A more detailed stabilization study showed that the melt stabilization efficiency of quercetin does not decrease in the presence of the halloysite support and halloysite nanotubes pretreated with the stabilizer possess controlled release function, ageing is slower in their presence than with separately dispersed components or in the absence of the halloysite (Chapter 6).
List of symbols

\( \gamma_f \) surface tension of the filler (mJ/m\(^2\))
\( \gamma_m \) surface tension of the matrix (mJ/m\(^2\))
\( \gamma_{mf} \) interfacial tension (mJ/m\(^2\))
\( \gamma_d, \gamma_p \) dispersion and polar component of surface tension (mJ/m\(^2\))
\( \delta \) Hildebrand solubility parameter (MPa)\(^{1/2}\)
\( \varepsilon \) dielectric permittivity (F/m)
\( \varepsilon_y \) yield strain (%)
\( \eta', \eta'' \) real and imaginary part of complex viscosity (Pas)
\( \mu \) dipole moment (D)
\( \rho_f \) density (kg/m\(^3\))
\( \sigma_d, \sigma^T \) debonding and thermal stresses (MPa)
\( \sigma_y \) tensile yield strength of composite (MPa)
\( \sigma_yo \) tensile yield strength of matrix (MPa)
\( \sigma_{yi} \) tensile yield strength of interphase (MPa)
\( \varphi \) volume fraction
\( A_f \) specific surface area of filler
\( AN^* \) acceptor number (kcal/mol)
\( B \) parameter, load bearing capacity of the filler
\( c_{100}, c_{\text{max}} \) characteristic concentrations (%)
\( C_1, C_2 \) geometric constants
\( \text{CEC} \) cation exchange capacity (meq/100g)
\( DN \) donor number (kcal/mol)
\( E \) Young's modulus (GPa)
\( F_a \) interfacial adhesion (mJ/m\(^2\))
\( G', G'' \) storage and loss moduli (Pa)
\( I_n \) integrated peak area
\( l \) thickness of interface (nm)
\( M_p, M_w \) number average, weight average molecular weight
\( M_v \) average molecular weight determined by the measurement of intrinsic viscosity
\( R \) radius of the particle
\( s \) solubility (g/cm\(^3\))
\( s_n \) Scofield sensitivity factor
\( S_{mf} \) wettability (mJ/m\(^2\))
\( W_{AB} \) reversible work of adhesion (mJ/m\(^2\))
List of symbols

Abbreviations

BET specific surface area measurement according to the Brunauer-Emmett-Teller theory
CaCO₃ calcium carbonate
CNT carbon nanotube
CPCIMMT montmorillonite coated with N-cetyl-pyridinium chloride
DFT density functional theory
DRIFT diffuse reflectance Fourier-transform infrared spectroscopy
DSC differential scanning calorimetry
EMI electromagnetic interference
FTIR Fourier-transform infrared spectroscopy
HDT heat deflection temperature
IGC inverse gas chromatography
LB₆ Lanthanum hexaboride
LDH layered double hydroxide
LDPE low density polyethylene
LED light-emitting diode
MAPP maleic anhydride grafted polypropylene
MFR melt flow rate (g/10 min)
MM molecular mechanics
MMT montmorillonite
MWCNT multiwalled carbon nanotube
NaMMT sodium montmorillonite
NMR nuclear magnetic resonance
OIT oxygen induction time
OMMT organophilized montmorillonite
PA polyamide
PA6 polycaprolactam
PE polyethylene
PhoMMT montmorillonite coated with trihexyl-tetradecyl-phosphonium chloride
PLA poly(lactic acid)
POSS polyhedral oligomeric silsesquioxane
PP polypropylene
PS polystyrene
PVT pressure-volume-temperature correlation
SiO₂ silicon dioxide, silica
SEM scanning electron microscopy
TiO₂ titanium dioxide
TEM transmission electron microscopy
TGA thermogravimetry
UFF universal force field
UV-Vis ultraviolet-visible spectroscopy
VOLS volume strain measurement
XPS X-ray photoelectron spectroscopy
XRD X-ray diffraction

Acknowledgements

First of all I would like to thank my supervisor Béla Pukánszky for his attention, patience and relentless support of my studies. I appreciate very much his guidance towards a more scientific way of thinking. I should also thank Mihály Kállay the head of the Department of Physical Chemistry and Material Science for his support during my Ph.D work. I am grateful to Enikő Földes, Ramóna Carmen Bende, Ildikó Erdősné-Fazekas, Eszter Drotár and István Sajó for their help with various measurements and calculations and to my students for the work we did together. I should also thank the Slovak Academy of Sciences especially Mária Omastová and Matej Mičušík for their help and assistance. I am grateful to my friends and colleagues at the Department of Physical Chemistry and Material Science and at the Laboratory of Plastics and Rubber Technology of the Budapest University of Technology and Economics, as well as at the Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences for their help and for the pleasant atmosphere they created. I also appreciate the financial support of the National Scientific Research Fund of Hungary (OTKA Grant No K 108934, K101124, K 120039 and PD 112489). The research work has been part of the BME R + D + I project supported by the grant TÁMOP 4.2.1/B-09/1/ KMR-2010-0002. At last but not the least, I should like to thank my wife, my family and my friends especially to Károly Renner for their encouragement, love and continuous support in reaching my goals.
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List of publications

Papers used for the preparation of the Thesis
(IF: impact factor, IC: independent citation)


Other publications


**Conference presentations**


Nyilatkozat

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


Hári József