Polymer/layered silicate nanocomposites: structure formation, interactions and deformation mechanisms

Ph. D. Thesis

by

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2011
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Chapter 1

Introduction

The interest in nanotechnology has been increasing continuously in recent years and it includes all kinds of polymer composites containing nano-sized fillers or reinforcements [1]. Layered silicate nanocomposites are one class of these materials containing finely dispersed silicate particles [2-6]. The results of the Toyota group [7-9] called the attention to the potentials of these materials and intensive research has been going on in this field since then. These materials are claimed to have advantageous properties compared to microcomposites containing traditional fillers. The extremely large interface created by the evenly distributed nano-sized particles is expected to lead to strong reinforcement at relatively small filler content making possible the production of strong and light parts. Several examples, mainly on polyamide nanocomposites, are often cited in the literature, which indicate that these expectations can be fulfilled and the composites show large improvement in stiffness, strength and heat deflection temperature compared to the neat matrix polymer [9,10]. On the other hand, in spite of the excellent properties of some of these nanocomposites, their application is limited, and the industry is still waiting for the major breakthrough in this technology. Nanocomposites prepared with matrices other than polyamide possess moderate properties at most and in some cases the incorporation of the silicate into the polymer leads to considerable deterioration of performance [3,11-14]. The reasons for the inferior performance are not always known, they must lay in our limited knowledge about the preparation and structure-property relationships of these materials. Issues which need much more attention are definitely structure and interfacial interactions.

In any composite, the conditions of considerable reinforcement and good properties are the homogeneous distribution of the reinforcing component, large aspect ratio, orientation and good adhesion. Unfortunately, these conditions are rarely fulfilled in layered silicate nanocomposites thus the inferior performance should not be surprising. The structure of layered silicate nanocomposites is usually oversimplified and the formation of partially intercalated/exfoliated structure is claimed in most cases [3-6,15-17]. However, a more detailed study on a wider length scale proved that the structure of nanocomposites is more complicated than expected, besides tactoids and individual layers also large particles and a silicate network may be present in the composite [18-20]. Quantitative characterization of the complex structure of these composites is badly needed, but rarely done. Similarly, compared to the basic idea behind nanocomposites, interfacial interactions are treated rather superficially, the available information is limited and very often contradictory. Very little unambiguous information exists about the various competitive interactions of the coated silicate surface, the size and characteristics of the uncoated area, the strength of interfacial adhesion, the thickness and properties of the interphase formed and their relationship to the macroscopic properties of the nanocomposites.
Layered silicate nanocomposites seemed to be interesting materials because of their potentials, but also because of the contradictions and unsolved questions related to them. The Laboratory of Plastics and Rubber Technology have longstanding traditions in studying heterogeneous polymer systems and a large experience has been obtained in this field during the years. It seemed to be obvious to study layered silicate nanocomposites already many years ago. The work started almost a decade ago and led to several publications and two PhD theses [21,22]. We got acquainted with clays, their structure, modification and behavior in the first thesis and identified the problems related to the preparation and structure of layered silicate nanocomposites [13,23-26]. Experiments on PP, PVC and PA6 nanocomposites pointed out general aspects which proved to be independent of the matrix used like the complicated structure containing various structural units, partial exfoliation, the importance of interactions, extent of exfoliation, etc. Polypropylene was used as matrix in the second thesis which focused on more specific questions like the proper characterization of structure, possible interactions, extent of exfoliation, etc [19,27-30]. This thesis also pointed out several contradictions and unsolved questions and the route to follow in further studies. The present thesis builds on this experience. It focuses on issues neglected in our preceding studies, like the kinetics of exfoliation, stability, the type of surface modification, interphase formation and deformation mechanism. Most of the results presented here extended our knowledge on layered silicate nanocomposites, but also pointed out the necessity for further work and efforts in the quest of producing composites meeting the expectations more closely.

1.1. Nanocomposites

Nanocomposites can be classified in many ways; 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 (SiO$_2$), TiO$_2$, calcium carbonate (CaCO$_3$) or polyhedral oligomeric silsesquioxane (POSS); nanotubes and fibers are small in two dimensions, but can be micrometer long. Nanoreinforcements with only one dimension in the nanometer range can be achieved by platelets, usually single silicate layers. Montmorillonite or hectorite is used the most often as reinforcement, but some groups try to disperse also nano-sized graphite platelets in polymers.

Most of the layered silicates used belong to the general family of so-called 2:1 layered silicates. Their crystal structure consists of layers made up of two silica tetrahedra fused to an edge-shared octahedral sheet of either alumina or magnesia (see Fig. 1.1) [6]. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. The negative surface charge of the silicate layers is compensated by solvated cations in the space confined between two layers, called also the gallery. In order to decrease the interaction of the layers and increase their gallery distance, inorganic cations are exchanged to organic ones, mostly by ammonium cations with one or more long aliphatic tails [31,32]. Larger distance and weaker forces are expected to facilitate exfoliation and help the distribution of the layers in the polymer.
1.2. Nanocomposite structure

The homogeneous dispersion of nanoparticles is the primary condition of the preparation of nanocomposites with acceptable properties. Parallel alignment of the reinforcement with the external load, as well as good adhesion are further conditions to be met, if the particles are anisotropic (layered silicates, nanotubes) and the composite is used in load-bearing application. Moreover, extensive exfoliation is a further requirement in layered silicate nanocomposites [12,33-37], which is often difficult to achieve, since the kinetics of exfoliation depends on many factors and the structure formed in the process is usually quite complicated as discussed in this section.

1.2.1. Particle structure

The existence of original clay particles, either uncoated sodium montmorillonite (NaMMT), or organophilized silicate (OMMT), is hardly ever mentioned in studies on nanocomposites [38-40]. 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 (WAXS) measurements and transmission electron microscopy (TEM) are used for the characterization of the composites and those do not detect the presence of large particles.

**Figure 1.1** Crystalline structure of montmorillonite [6].
However, a more detailed study on a wider length scale proved that the structure of nanocomposites is more complicated than expected, besides tactoids and individual layers also large particles may be present in the composite. SEM micrographs clearly show the particulate structure of PP/OMMT composites [19]. Large particles are dispersed in PP in the PP/OMMT composite not containing any functionalized polymer and also the interfaces are rather distinct; the wetting and/or adhesion of the components seem to be rather poor (see Fig. 1.2a). It also proved that nanocomposite cannot be prepared from a neat PP and an organophilic silicate; limited intercalation may take place in such composites at most.

In order to facilitate exfoliation a coupling agent, usually maleic anhydride or acrylic acid grafted PP (MAPP or AAPP) is added to the combination of PP and organophilized montmorillonite [41-48]. The presence of MAPP clearly changes the morphology (Fig. 1.2b). The introduction of a functionalized polymer decreases the size of the original particles and the interfaces are much less distinct than in the previous case. Both the changing particle size and the modification of the interface indicate that MAPP helps to break down particles and modifies interfacial interactions. Nevertheless, it can be safely stated that complete exfoliation has not been achieved, and clay particles in the length scale of microns are also present in these composite. Their amount and size must strongly influence all properties.

**Figure 1.2** SEM micrographs taken from the etched surface of PP nanocomposites containing 2 vol% organophilic montmorillonite. a) PP/OMMT, b) PP/OMMT/MAPP(20 vol%).

### 1.2.2. Surface modification, gallery structure

In most cases not neat sodium montmorillonite, but organically modified silicate is used for the preparation of polymer/layered silicate nanocomposites. Solvated inorganic cations located in the galleries of layered silicates are exchanged to organic cations of long chain amines in order to separate the layers [31,32]. Increased gallery distance and decreased surface energy should lead to easier exfoliation. As a consequence, the amount of surfactant located in the galleries and the orientation of the mole-
cules should influence the structure and properties of layered silicate/polymer nano-
composites significantly.

The gallery distance of silicates is routinely determined by WAXS. Layer dis-
tance is inversely proportional to the position of the silicate reflection recorded at low
2θ angles. Several studies were carried out to investigate the effect of the type and
amount of the surfactant on exfoliation and on the properties of composites [37,49-51],
but relatively little attention is paid to the gallery structure of the original organophi-
lized MMT. Reichert et al. [37] found in PP/OMMT composites that large extent of
exfoliation cannot be achieved if the length of the aliphatic chain is equal or less than 8
carbon atoms; large, micron sized particles were found in the composite in these cases.
Better dispersion was obtained at chain lengths of 12-18 carbon atoms, but the function-
ality of the coupling agent used (MAPP) also influenced exfoliation. Fornes et al. [49]
investigated the effect of the amount and type of surfactant used for organophilization,
i.e. gallery structure, on the structure and properties of PA nanocomposites in detail.
They showed that surfactants with two long tails are less advantageous than those hav-
ing 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. Similarly, Vaia
[51] has shown that gallery structure strongly influences intercalation in PS nanocom-
posites. Contrary to Fornes et al. [49], he found that head groups do not influence inter-
calation and two long aliphatic chains are more advantageous than one. These contra-
dictions clearly prove that unambiguous, general correlations have not been established
yet among the gallery structure of the silicate, interactions and composite properties.

1.2.3. Exfoliation

Exfoliation is usually studied by TEM, which is able to detect also individual
silicate layers [52]. Very few publications present micrographs in which only individual
silicate layers are dispersed in the polymer for any matrix and especially for PP.Usu-
ally, intercalated stacks or tactoids with a range of gallery distances form in the compos-
ites 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 [49,53], but this
can be achieved only with the proper selection of components and processing condi-
tions.

A variety of structural units were detected in PP/MMT composites [19]. Two
micrographs are presented in Fig. 1.3, which demonstrate the wide scale of structures
found in PP/OMMT/MAPP composites. A very large and compact clay particle is
shown in Fig. 1.3a detected in a composite with 3 vol% silicate and 20 vol% MAPP
content. Obviously disintegration and intercalation are at the preliminary stages for this
particle. Nevertheless, it possesses a relatively wide range of gallery distances. A looser
structure is presented in Fig. 1.3b. Besides larger layer distance, the stacks contain
smaller number of platelets and more individual layers can be detected in the micro-
graph. The structure observed in the TEM micrographs obviously depends on composi-
tion, but also on sampling, i.e. on the choice of the location from which the slice was taken. Processing conditions were the same in both cases.

![TEM micrographs](image)

**Figure 1.3** TEM micrographs taken from PP/OMMT/MAPP nanocomposites. 
*a* 3 vol% silicate, 20 vol% MAPP, *b* 2 vol% silicate, 30 vol% MAPP.

The evidence presented above proves that a wide range of structural units are present in PP/silicate composites, but also in other composites; similar structures were detected in polyamide/montmorillonite (PA/MMT) composites as well [20]. The surface area of the various units differs considerably and they undergo various micromechanical deformation processes during deformation. One or more type of structural formations may determine the micro- and macromechanical deformation processes and thus the properties of the composites, as shown in PA nanocomposites [20]. The extent of exfoliation and the developed structure depends on interactions, but the adhesion of the dominating unit to the matrix polymer is crucial for the determination of composite properties.

1.2.4. Silicate network

TEM definitely confirmed the presence of individual silicate layers in PP nanocomposites containing also MAPP. Exfoliated silicate platelets were shown to interact with each other in water suspension and the type as well as the extent of interaction depended on the pH of the water and on the amount of clay [54]. Face-to-face in-
interaction leads to aggregation, while edge-to-face orientation results in the formation of a silicate network structure. Both phenomena have been observed also in polymer composites [16,37,55].

Although quite a few papers mention the formation and existence of such a network as a possibility [37,42,56-61], relatively few papers focus on the determination of the conditions, which would yield such structures or on the characterization of the network itself [57,60]. The formation of the network is usually detected by TEM [37,57,58] or by the analysis of the results of rheological measurements, from the linear viscoelastic properties of nanocomposite melts [42,56,59]. TEM micrographs published are usually not very convincing, but the low frequency range of complex viscosity or $G'$, as well as the appearance of a yield stress clearly indicate considerable changes in the structure of the melt, and in all probability refer to the formation of a silicate network [62]. In PVDF/clay/PMMA composites, Moussaif and Groeninckx [61] observed a considerable increase of storage modulus in the low frequency range with increasing intercalation and/or exfoliation, and explained the phenomenon with the formation of a silicate network. They also found that network formation increases stiffness considerably in the rubbery plateau region.

Although TEM cannot and does not supply unambiguous proof for the formation of the silicate network, large extent of exfoliation occurs at very small silicate and large MAPP content, and occasionally overlapping of the silicate layers may be observed as a result as shown in Fig. 1.4 [19]. In spite of the convincing micrograph, TEM alone does not prove the formation of the silicate network, but together with rheology it may supply sufficient evidence for it. Moreover, such micrographs offer indirect evidence that considerable exfoliation takes place during the processing of these materials, since only highly exfoliated stacks or individual layers may form the network. Exfoliation and network formation obviously depend on component properties, composition and processing conditions.

As mentioned above, the presence of the silicate network is usually detected by the increase of storage modulus and complex viscosity with decreasing frequency, in the small frequency range of the spectrum [62]. Earlier studies of materials in which internal processes are accompanied by the loss of energy (dielectric polarization, mechanical deformation) showed that plotting the two components of dynamic viscoelastic characteristics (dielectric permittivity, viscosity, modulus) against each other yields an arc-shaped curve if the process can be described with a single relaxation time (Cole-Cole plot) [63,64]. If the material possesses a relaxation time spectrum, the arc transforms to a semicircle or a skewed semicircle [64,65]. If more than one process with different relaxation times occur simultaneously, the so called Cole-Cole plot is further modified; i.e. a new semicircle or a tail appears [66,67]. The formation of a network structure leads to the increase of the elastic component of modulus and viscosity, and the network obviously deforms with different relaxation times than the homogeneous melt, thus we expect a correlation deviating from a semicircle in the above mentioned representation.

The Cole-Cole plots of composites containing 2 vol% silicate and various amounts of MAPP are shown in Fig. 1.5. The deviation from a skewed semicircle is
clearly visible at large MAPP contents. The change in the shape of the plots indicates the appearance of a new relaxation process, probably the formation of the silicate network. The critical MAPP content, at which this change occurs is relative large, it is around 20 vol%, since relatively large degree of exfoliation is needed to form the network at this silicate content. The change in shape depends on MAPP and silicate content. Not only does the shape of the traces change, but the absolute value of viscosity also increases considerably with silicate content. Larger number of silicate particles increase the probability and the efficiency of exfoliation and promote the formation of the silicate network.

Figure 1.4 Interaction of silicate layers at small clay (0.5 vol%) and large (60 vol%) MAPP content; possible network formation of the silicate sheets.

1.3. Nanocomposite preparation

Many ways and approaches have been published on the preparation of layered silicate nanocomposites. The methods can be classified in different ways and because of the overlapping of techniques the classification will be always arbitrary. The two most often cited reviews on nanocomposites, that of Alexandre and Dubois [3] and the one written by Sinha Ray and Okamoto [4], also differ somewhat in their classification of nanocomposite preparation. Alexandre and Dubois [3] defined four categories: exfoliation-adsorption, which is the solvent assisted mixing of the components, in situ intercalative polymerization, melt intercalation and template synthesis, in which the silicate is
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usually formed by sol-gel technology. Mostly double-layered hydroxide nanocomposites are prepared in this way. On the other hand, Sinha Ray and Okamoto [4] define only three categories: the intercalation of polymer or pre-polymer from solution, in situ intercalative polymerization, and melt intercalation. Our classification is more similar to this second approach and discusses solvent assisted methods, in situ polymerization and melt compounding. Since the last technique is used overwhelmingly for the preparation of polyolefin/layered silicate composites, we pay our attention mostly to it. The combination of monomers, polymers, solvents and other compounds, as well as the type and modification of the silicate used are practically unlimited.

![Image](image-url)

**Figure 1.5** Cole-Cole plots obtained for PP/OMMT/MAPP nanocomposites at 2.0 vol% clay and various MAPP contents. Symbols: (○) 0, (□) 10, (△) 20, (▽) 30, (◇) 40, (★) 50 vol% MAPP.

### 1.3.1 In situ polymerization

This technique consists of intercalating a monomer or a prepolymer into the galleries of the silicate and then initiating polymerization by heat or radiation. The initiator or catalyst can be diffused into the galleries of the silicate or fixed through cationic exchange to the layers before swelling them by the monomer. The method can be used for the production of thermoplastic or thermostet composites. Mostly epoxy [68,69], polyurethane [70,71] and polyester [72,73] composites were prepared in the latter class with this method. Methyl methacrylate [74-76] and styrene [77,78] are the most often used monomers for the preparation of thermoplastic nanocomposites by this approach, but many other monomers have been tried as well [79]. The polymerization
itself can be done in bulk [70-73,80], solution [78], emulsion [76,77,79] or suspension [77]. Occasionally solvents are used to assist the intercalation of the monomer into the galleries of the silicate even when suspension or emulsion polymerization is used. The technique and the conditions depend very much on the components. The key factor is the separation of the silicate into individual layers and the prevention of their aggregation after the completion of polymerization. The preparation of the composites in aqueous media is relatively easy, since layered silicates exfoliate in water. Accordingly, composites can be efficiently produced from sodium montmorillonite, but solvents and other swelling agents must be used when organophilic silicates are used in the process.

Polyolefin composites cannot be very easily produced by in situ polymerization. Most of the catalysts used for polyolefins are extremely sensitive to water and polar compounds. Even organophilized silicates contain some water, which can destroy the catalyst, but the surfactants used for organophilization were also reported to interact with it [81]. Nevertheless, several attempts were made to prepare PP and PE nanocomposites by using metallocene [81], palladium [82] or Ziegler type catalysts [83].

1.3.2. Solution mixing

In situ polymerization has the advantage that monomers diffuse into the galleries of the silicate more efficiently than high molecular mass polymers. The use of monomers and occasionally solvents offers the additional possibility of adjusting the competitive interactions among the components in a way, which makes possible intercalation and hopefully results in exfoliation. Polymerization involves chemical reactions. Solution mixing tries to apply the same principles, but without the difficulties of initiation or catalysis reactions, which are very sensitive to numerous factors as mentioned above.

Many attempts have been made to prepare polymer/layered silicate nanocomposites by solution blending. Water soluble polymers, like poly(ethylene oxide), poly(vinyl alcohol), poly(vinylpyrrolidone) and poly(acrylic acide) can be used with high efficiency in this approach. Neat, unmodified layered silicates exfoliate relatively easily and almost quantitatively in water, thus the mixing of the solution made from the polymer with the slurry of the silicate is relatively easy. Unfortunately, the result of competitive interactions is rather difficult to predict. Occasionally homogeneous, stable colloidal distribution of the silicate layers prevails in the mixture [84] and a good quality film can be prepared under mild drying conditions. On the other hand, reaggregation of the silicate layers may also occur like in poly(vinylpyrrolidone) [85] and poly(ethylene oxide) [84]. Organic solvents must be applied when the polymer does not dissolve in water. Usually organophilic silicates are used as reinforcements in such cases. Nanocomposites can be prepared with a wide variety of solvents.

Polyolefin nanocomposites are rarely prepared with this technology for reasons which are easy to understand. Polyolefins are usually difficult to dissolve in any solvent, the dissolution must be done at high temperatures creating technical problems, and the polarity of the solvent is not sufficiently high to induce complete exfoliation.
1.3.3. Melt compounding

Previous sections have shown that the degree of exfoliation depends on competitive interactions, on the properties of the components and on preparation conditions. A high degree or complete exfoliation is very difficult to achieve even when in situ polymerization or solution mixing is used; the result often does not justify the complications related to these methods. No one should be surprised, as a consequence that the large majority of polymer/layered silicate nanocomposites are produced by melt compounding. The technique is simple, all available equipment can be used for processing, and composites can be prepared from practically every thermoplastic polymer. Among others, layered nanocomposites were prepared by this route from styrenic polymers [86,87], natural rubber [88], polyamide [12,89-93] and very many from polyolefins, especially from polypropylene [94-98]. The approach is especially useful for polyolefins, since either the in situ polymerization or the solution blending techniques are overly complicated for these polymers. The equipment used for the production of the composites also covers a wide range from two-roll mill [95] and internal mixer [96-98] to twin-screw extruder [90,94]. Further processing to specimens or a final product can be also done by any technology like compression [95] or injection molding [93,94,96], or extrusion [89].

The results presented in the two previous sections indicated that the extent of exfoliation is influenced by many factors and the prediction of the final result is extremely difficult. The controversy related to the various factors is demonstrated well by the contradictory results of several groups [49,51]. The same controversy applies to the effect of processing conditions. Poisson et al. [89] found that processing conditions did not influence significantly the studied properties of single- and multilayer blown films prepared from PA6/nanoclay composites. Yilmazer and Ozden [99] came practically to the same conclusion. On the other hand, Fornes et al. [90] found that the molecular mass of PA6 used for the preparation of nanocomposites influenced considerably exfoliation; better exfoliation was achieved with the polymer of larger molecular mass. They explained this result by the larger shear stresses developing during the processing of this polymer compared to its small molecular mass counterpart. Wang et al. [98] came practically to the same conclusion when they found that the temperature of mixing must be adjusted according to the viscosity of the composite in order to achieve sufficiently high shear stresses leading to acceptable degree of exfoliation. Artzi et al. [100] showed changes in the structure and properties of ethylene vinyl alcohol copolymer/OMMT nanocomposites as a function of mixing time, i.e. processing conditions. Because of these controversial conclusions, we analyze a few results obtained on the effect of processing conditions on nanocomposite structure in the next paragraph.

The most thorough study on the effect of processing conditions on silicate exfoliation and dispersion was carried out by Paul and co-workers [101-103]. In their first two studies [101,102] the authors compared the effect of various processing equipment and conditions on the dispersion of two organophilic silicates with different surface modifications at 5 wt% silicate content in a PA6 matrix. The equipment used included a co-rotating intermeshing, a counter-rotating intermeshing and a counter-rotating non-intermeshing machine. They studied the effect of different screw configu-
rations offering dissimilar levels of shearing from high, through medium to low. They found that the degree of exfoliation depends both on clay treatment and on processing conditions. Both the level of shear and residence time influenced the structure and properties of the composites. Residence time increases exfoliation generally, but both back mixing and shear intensity have an optimum. A series of very thorough experiments were done by Lertwimolnun and Vergnes [62,104,105] on the effect of processing conditions on the structure and properties of PP/layered silicate nanocomposites. They found that the rate of processing, as well as the amount of MAPP considerably modify structure and properties. They came to the conclusion that the extent of exfoliation characterized by the yield stress of flow depends strongly on the conditions of processing.

From the results presented above we may conclude that processing conditions considerably influence the structure of polyolefin nanocomposites. Although the proper selection of processing conditions may increase the extent of exfoliation considerably, complete exfoliation rarely occurs in polyolefin and especially in PP composites. As a consequence, we may conclude again that competitive interactions of the components must be always considered, if we want to achieve large extent of exfoliation and good properties.

1.4. Interfacial interactions

Polymer/layered silicate nanocomposites are expected to have very large interfaces, which supposed to generate their exceptional properties. The specific surface area of totally exfoliated silicates is around 750 m\(^2\)/g, thus the surface characteristics of the silicates, interactions and interphase formation must influence composite properties considerably.

1.4.1. Surface characteristics of silicates

Layered silicate nanocomposites can be rarely prepared from neat, unmodified silicates like sodium montmorillonite. Only water soluble polymers can intercalate into the galleries of NaMMT, thus organophilic silicates are used practically always for the preparation of nanocomposites in other matrices. This is especially valid for polyolefin nanocomposites, although attempts are made occasionally to use neat sodium montmorillonite and improve dispersion by selecting appropriate processing technology [106-108]. Organophilization changes drastically the surface free energy of the silicate, which in view of the extremely large interface supposedly forming, must influence properties significantly. However, in spite of its importance, organophilization and its effect is usually treated in very general terms and the surface characteristics of silicates are rarely investigated in detail.

The majority of papers published on polymer/layered silicate nanocomposites containing an organophilic 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 [3-5,37]. Unfortunately, this explanation does not agree with the fact that nanocomposite cannot be prepared from organophilic silicates and PP without an additional compatibilizer, although both are hydrophobic [37,43,109]. 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 interfaces) [5,34]. 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 not true. Organophilization decreases the surface free energy of the silicates leading to the decrease of the strength of interaction between the filler and the polymer [110]. The interaction of the silicate and the polymer, both neat and organophilic silicates, is an adsorption process. The strength of adsorption can be characterized by the reversible work of adhesion [111,112], which considerably decreases upon treatment with an organic substance. These considerations are strongly supported by the fact that organophilic silicates cannot be exfoliated in PP, as mentioned above, although both are hydrophobic and apolar.

Besides the orientation of surfactant molecules in the galleries, the amount used for organophilization is also important in the determination of surface characteristics and behavior. A small amount does not cover the entire surface, leaves high energy surface uncovered and results in large surface tension, while excessive amounts may dissolve or disperse in the polymer leading to inferior properties. The relative area covered by the surfactant depends on the ion exchange capacity of the silicate and on the chain length of the surfactant. For montmorillonite, about 70 % of the silicate surface is covered when the length of the alkyl chain of the alkylammonium ion is less than 16 carbon atom; the rest of the surface is free [31]. As a consequence, the surface of organophilic silicate contains three areas with considerably differing activities. The energy of the ionic centers is relatively high as well as that of the free silicate surface, while the surface covered by the alkyl chains has low surface tension. Accordingly various interactions may develop in a composite system, all of which influence exfoliation, structure and properties.

1.4.2. Interactions

In particulate filled composites particle/particle interactions induce aggregation, while matrix/filler interaction leads to the development of an interphase with properties different from those of both components [113,114]. Similarly to structure, interactions are more complicated in layered silicate nanocomposites than in filled composites. The silicate, the considerable amount of surfactant used and the polymer may interact in various extents and ways. Silicate particles and platelets may aggregate, the polymer may dissolve the surfactant and even chemical reactions may take place in the composite during homogenization.

Just like in all heterogeneous polymer systems interactions play a crucial role also in the determination of the structure and properties of layered silicate nanocomposites. However, various approaches have been developed in the latter systems and even
the terminology is more confused because of the nanometer dimensions of the particles. Interactions as well as their relative role are also somewhat more complicated in nano-composites, because of the larger number of components, e.g. PP/layered silicate nano-composites usually consist of at least four components: polymer, silicate, surfactant and a compatibilizer.

The interaction of the silicate layers must be overcome to achieve exfoliation [115]. Referring to the book of Theng [116] Alexandre and Dubois [3] claim that the forces which hold the stacks together are relatively weak and the intercalation of small molecules is easy. However, experience shows that the forces among silicate platelets are so strong in the polymer melt that the high shear of processing often cannot separate them even if the silicate is treated with a surfactant. Organophilization separates the layers and decreases the forces between them. Ion exchange capacity, surface coverage and layer distance determine the forces acting among the silicate platelets [115] and these factors must be optimized to achieve exfoliation.

The interactions in layered silicate PA nanocomposites were analyzed by molecular dynamics modeling by Sikdar at al. [117] and 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. Further interactions develop between the polymer and the silicate, 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 interaction and finally the properties of the composites.

Solvents [118], other additives [119] and compatibilizers [41-48] are often added to nanocomposites to assist intercalation and exfoliation). These may enter into competitive interactions with any of the components. It is less probable that functional groups of these compounds interact with the aliphatic chain of the surfactant, but they may adsorb on the silicate surface. The interaction of polar substances with organically modified silicates was shown by Jordan [31] and Lagally [32] a long time ago, who proved that the use of a mixture of apolar and polar solvents can lead to considerable swelling of organophilic clays. However, the functional groups of the compatibilizer may interact with the head group of the surfactant, or even react chemically with it [27]. Such interactions may remove the surfactant from the silicate surface and create a completely new composite with different structure and even composition. Finally, the compatibilizer must also interact with the polymer to assist stress transfer from the matrix to the silicate. Quite a few of the interactions listed above are ignored, but definitely not investigated in sufficient detail.

The chemical structure of the components of layered silicate nanocomposites is assumed to be constant in most cases. Occasionally, questions are raised about the thermal stability of the surfactant under the conditions of melt intercalation or processing. In most cases when stability is checked experimentally, no changes are found in the
chemical structure of the surfactant. Evidence of chemical transformation or degradation and resulting changes in properties are rarely found in published papers [120,121]. Other chemical reactions are not even considered, although some of the components of layered silicate nanocomposites are rather reactive.

1.5. Interphase formation and properties

The formation of an interphase in heterogeneous polymers is a well accepted fact [113,114,122,123]. Some authors claim that the interphase determines the properties of composites or blends [124,125]. Even if that is not the case, interphase volume, thickness and characteristics considerably influence composite properties. Nevertheless, much controversy surrounds the interphase, because its detection is difficult both with direct and indirect methods. Simulation and extraction experiments indicated the formation of an interphase of a few nanometer thickness in particulate filled thermoplastic composites [126-128]. Thicknesses deduced from mechanical properties proved to be much larger since the extent of deformation also influences the apparent thickness of the interphase. Most information indicates that a hard interphase forms in particulate filled and fiber reinforced composites [113,129] and very often the formation of an interphase with graded properties is assumed in various models and calculations [130,131]. The importance of the interphase is shown by the increasing number of models which include it as a separate phase [132-134].

Large interfaces and a considerable interphase volume should form in composites containing fillers or reinforcements with dimensions in the nanometer range. The interphase, if it has properties different from those of both components, should change composite properties considerably. The importance of the interphase was emphasized in composites containing spherical nanoparticles [135], but interphase formation has not been mentioned yet practically at all in layered silicate nanocomposites. It is also quite surprising that the formation of an interphase and its properties are not considered even when polymeric compatibilizers are added to the composite, which are assumed to interact strongly with the silicate [41,42]. In such cases an interphase should definitely form between the silicate surface and the matrix.

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, which occurs quite frequently. Spectroscopy cannot see changes in properties in the absence of chemical reactions. The only possibility for the detection and analysis of an interphase is to follow changes in molecular mobility by nuclear magnetic resonance spectroscopy (NMR) [136], dielectric spectroscopy [136] or by changes in the dynamic mechanical spectra of the composites. The latter do not show much change in most cases. However, NMR and dielectric spectroscopy indicated an increase in the mobility of polymers confined in the galleries of layered silicates and the appearance a second, lower glass transition temperature for the interphase than for the bulk material [136]. These observations raise some doubts about the thermodynamic model calculations based on the confinement and restricted mobility of polymer chains, on the one hand, and forecast the formation of a soft interphase, on the
other. This latter could explain the less then 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 their mobility.

The results and conclusions described in the previous paragraph are contradicted by the measurements and calculations of Utracki et al. [137-139]. The authors prepared various polymer/layered silicate nanocomposites, determined their PVT behavior and applied the Simha-Somcynsky [140] equation of state for the determination of the free (hole) fraction of the materials. The model could be applied only if the adsorption of the polymer was assumed on the clay surface resulting in clay platelets covered by a 6 nm layer of solid like matrix and an interphase of 100-120 nm thickness with changing properties. The results showed that free volume decreases by 4 to 16% depending on the system studied. Adsorption and the decrease of free volume indicate the formation of a hard interphase. Unfortunately, none of the parameters derived from the model correlated with the actual mechanical properties of the composites.

Since only contradictory information and very little experimental evidence are available about interphase formation and properties in layered silicate nanocomposites, we may speculate somewhat about possible scenarios, based on the interactions discussed in previous sections. A hard interface with good adhesion must form if the polymer directly interacts with the silicate surface. This should lead to restricted movement of the polymer, to increased glass transition temperature, stiffness and strength. Considerable reinforcement can be expected only in this case. The polymer may interact also with the surfactant in several ways. If we accept the scheme presented by Vaia [51,141], i.e. the commingling of the surfactant with the polymer, then basically a polymer blend forms inside the galleries. Naturally the structure and properties of the blend depend on miscibility, but small molecular mass compounds always dissolve in some extent in polymers. Since the aliphatic chains of the surfactant are usually amorphous and very mobile with a glass transition temperature below room temperature, the mobility of the polymer should increase resulting in the formation of a soft interphase. The consequences of a soft interphase have been mentioned above. Finally, a further possibility is that the surfactant and the polymer are immiscible and surfactant molecules lay parallel to the surface of the silicate. In this case the polymer interacts mainly with the surfactant by weak dispersion forces, interfacial adhesion becomes weak and loose, relatively soft interlayer forms again. Possibly other scenarios could be also created, but we do not want to speculate further. However, all these considerations indicate that much more attention must be dedicated to the study of interphase formation and to its effect on composite properties than before.

1.6. Micromechanical deformation processes

In previous sections we pointed out several factors, which are largely neglected, but definitely not considered thoroughly enough in the determination of the behavior of polymer/layered silicate nanocomposites. Certain aspects of structure are ignored, interactions are treated in general terms, and stiffness is considered as the most
important property in the majority of the papers. However, micromechanical deformations are similarly important and practically no attention is paid to them. Layered silicate nanocomposites are heterogeneous polymer systems. In such materials stress concentration develops around the heterogeneities under the effect of external load. Local stress maximums initiate local deformation processes and the dominating mechanism determines the final properties of the composites.

Although the knowledge of micromechanical deformation processes is crucial for the successful application of these materials, very few attempts have been made to study them in detail. Kim et al. [142] investigated the deformation behavior of PA/silicate nanocomposites and based on TEM microscopy they proposed a scheme for the deformation and failure mechanism. The model of the authors consists of several processes including the deformation and fracture of clay particles or tactoids, which indicates that intercalation was not complete in their case. Lefebvre et al. [143] measured the volume strain of PA nanocomposite samples during deformation. They determined the various components of strain by a detailed analysis and concluded that besides elastic deformation, considerable debonding and plastic flow also takes place during the elongation of the samples. These experiments [142,143] indicate that both the structure and the deformation mechanism of PA nanocomposites might be more complex than often indicated in the literature.

The deformation of polymer/layered silicate composites may be dominated either by that of the matrix or by processes related to the reinforcement. The possibilities for the deformation of the matrix are relatively few and simple. The polymer may deform by shear yielding, but its cracking or fracture may also take place. Voiding, or cavitation, was shown to occur during the deformation of neat polyamide [144]. Much larger is the number of possible deformation processes related to the reinforcement, to the silicate in our case. According to the above mentioned model of Kim et al. [142] fracture or peeling off the silicate layers and the slipping of individual layers or stacks may occur during deformation. If we allow also for the presence of larger entities, and this is definitely 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. [143]. Basically all silicate related processes depend on interaction, both on the forces acting among the layers and on matrix/filler adhesion. As a consequence, the quality of organophilization, i.e. the type and amount of the surfactant used, is expected to influence the mechanism of deformation and the properties of the composites considerably.

The analysis of micromechanical deformation processes in PA6/layered silicate composites by volume strain and acoustic emission measurements showed that elastic deformation and shear yielding dominate during the elongation of these materials [20]. The matrix polymer and the composites deform according to different mechanisms. Sound is emitted by cavitation in the former, while sound emitting processes are 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 the particles. Matrix/silicate adhesion seems to be strong, debonding rarely takes place, and volume increase is initiated primarily by particle failure. The type and amount of the surfactant
used for organophilization plays an important role in the determination of deformation processes and properties, since it influences both matrix/filler interaction and the internal adhesion of silicate particles.

1.7. Open questions, goals

The literature survey presented in previous sections of this chapter proved that numerous questions related to layered silicate nanocomposites are open or not studied in detail. Already the crucial and relatively basic question of structure is not treated sufficiently thoroughly, the picture is oversimplified, unjust assumptions are made and important factors are neglected. Published papers and our own research alike proved that we must always consider at least four structural elements in these composites: large particles, tactoids, silicate platelets and a possible silicate network. Moreover, these structural units can be present in all matrices, although their relative amount depends on the properties of the matrix and the silicate, on composition, processing conditions and on some other factors. Thorough quantitative characterization of structure is essential for the understanding of structure-property correlations. Similarly important is the question of interactions. As mentioned above numerous interactions, even chemical reactions, compete with each other and influence structure formation. Similarly to traditional microcomposites, the development of an interphase must be assumed also in these materials, but very little is known about the existence and properties of the interphase.

One factor determining these interactions is the type and amount of the surfactant used for organophilization. Ammonium compounds are used the most frequently for treatment in spite of their disadvantages. Only a few attempts are made to use other principles or compounds for the separation and homogenous dispersion of the silicate, like dipole-dipole interactions and phosphonium salts. One of the major disadvantages of ammonium salts is their limited thermal stability. Some polymers, like polyamides, are processed at relatively high temperatures and long chain ammonium salts decompose at these temperatures. Although such decomposition had been documented several times, it is thought not to influence composite structure or properties. Even less attention is paid to the stability of the polymer used as matrix. Thermal stability of composites is usually studied by thermal gravimetry (TGA) and based on such measurements often improved dimensional and thermal stability is claimed compared to the neat polymer. However, the thermal or thermo-oxidative degradation of the polymer might influence structure formation and lead to the deterioration of composite properties. Although many other contradictions or open questions may be mentioned, finally we call attention here only to the mechanism of deformation and its relation to macroscopic properties. Only a very limited number of papers deal with this issue in spite of the fact that in heterogeneous polymer systems deformation and failure mechanism is usually related to the heterogeneities present, thus the type, size, amount and properties of the structural units in layered silicate nanocomposites must have profound effect on deformation and failure.

Besides these open questions the goals and scope of this Thesis was determined also by other factors. One of them was the set of unfinished topics and small projects remaining from earlier studies. For example we studied the kinetics of exfoliation in
several series of experiments, but never summarized the results to draw general conclusions from them. Another factor was a cooperation started recently with a Belgian group preparing silicates modified with a phosphonium salt. We agreed with them to start a project in which we study the possible benefits of such a modification. However, the major goal of the thesis was to extend our knowledge about layered silicate nanocomposites even further to advance towards the preparation of composites with properties corresponding to expectations.

1.8. Scope

The number of open questions listed in the previous section is quite large. We could not hope to address them all in the course of this PhD work. This would have been impossible for many reasons including theoretical and technical obstacles as well as the lack of time and capacity. Focusing on a few well defined questions allowed us to study them more thoroughly, to draw general conclusions and reveal the role of important factors not considered before. Unfortunately or fortunately the results occasionally opened up new questions and pointed out new problems, but this often happens in research. As mentioned above, this Thesis is a direct continuation of previous work, builds on the experience obtained earlier, even uses materials prepared previously and evaluates or reevaluates results obtained on them in order to answer open questions and resolve contradictions. Since the work consists of different subprojects, the various materials, sample preparation and measurement techniques used could not be united reasonably into a single experimental section. We could have saved space by compiling the details of certain techniques used practically in all projects, like wide angle diffraction, in a section, but it seemed to be more reasonable to summarize experimental details individually in each chapter. In spite of the diversity of the materials and techniques used, the work in the Thesis offers the possibility to contemplate most important questions related to layered silicate nanocomposites and allowed us drawing important general conclusions, which are summarized in the last chapter.

As the literature survey presented in Section 1.3.3 proved, the kinetics of particle break down and exfoliation partially determines the structure of the nanocomposites and thus their final properties. Kinetics depends on many factors including component properties and processing conditions. Organophilic silicates were dispersed efficiently in PA and PVOH without compatibilizers, but limited exfoliation was achieved in polyolefins. Obviously, the polarity of the matrix, i.e. interactions is a crucial factor in exfoliation and structure formation, but other factors, like the molecular mass of the matrix and processing conditions, also influence them. We investigated these questions and report the results in Chapter 2. The measurements were done in three series. Composites were prepared from organophilic montmorillonite and polypropylene in the first without the use of coupling agent. A functionalized polymer, maleated PP, was used as coupling agent in the other two series. Rather surprisingly, the structure of the composites changed also in the absence of the coupling agent accentuating the effect of other factors than interactions. However, the results also indicated that parallel to changes in the structure of the composites other processes, mainly the degradation of the polymer may also take place. The possible degradation of polypropylene and the effect of the
components on it were investigated in a subsequent study. The results are reported in Chapter 3 of the Thesis. The results of the kinetic studies indicated that both the silicate and the coupling agent influence stability. Accordingly, an experimental design was created exploring the effect of these two components and their possible interaction on the stability of PP/layered silicate nanocomposites. The results proved that thermal stability is an important and practically relevant issue, which must be considered also during the commercial production of nanocomposite parts.

Another important question which is not studied in sufficient detail relates to the interactions developing in nanocomposites. Most layered silicate nanocomposites contain at least three components which must be considered in this respect: the polymer, the clay and the surfactant. Often additional components are added to the composite to assist exfoliation or modify interactions like the functionalized polymer in PP or PE composites. Most components contain more than one functional group. Thus we must consider the amide and the aliphatic section in polyamides, the ions, the silicate and the hydroxyl groups in silicates, or the head and tail groups of the surfactant. The situation is further complicated by the spontaneous formation of an interphase, which occurs in all composites. The amount and properties of such an interphase considerably influence, occasionally determine the properties and the performance of the material. In Chapter 4 we report an attempt to estimate the properties of an interphase formed spontaneously in PP/layered silicate composites. A model developed earlier was used in the calculations, which showed that an interphase forms indeed, but the determination of its properties is difficult because of the simultaneous change of structure.

Polypropylene was used as matrix in most of our studies. However, the apolar character of the polymer limits exfoliation, while the presence of an additional component, the coupling agent, complicates evaluation. In order to simplify composition and achieve a large extent of exfoliation we selected a different matrix, polyamide 6, for the study of the effect of the type of surfactant on exfoliation and structure in our next project. This selection was further influenced and directed by the cooperation with a Belgian group1 willing to supply a montmorillonite modified with a phosphonium salt instead of the usual ammonium surfactant. The study focused on two questions, on the comparison of the two types of surfactants, i.e. ammonium vs. phosphonium, and on the effect of structure on deformation mechanism. The effect of the two types of surfactants on exfoliation, structure and properties is compared in Chapter 5. The results proved the beneficial effect of the phosphonium salt on exfoliation, but called also the attention to the many factors influencing structure and properties in polymer/layered silicate nanocomposites. Besides the type of the surfactant, surface coverage also plays an important role in exfoliation, but also in interfacial adhesion. The structure developed and the strength of interfacial adhesion were quite different in the PA composites containing the two types of silicates. The detailed study of their micromechanical deformation processes reported in Chapter 6 revealed that several such processes take place in the composites. Surface modification changes considerably both the extent and sometimes even the direction of the composition dependence of properties. The results showed that

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although micromechanical deformations are influenced by the presence of heterogeneities, the behavior of the matrix is crucial in the studied case.

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 the major thesis points of the work. 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 of polymer/layered silicate nanocomposites, but also for other nanocomposites. As usual, quite a number of questions remained open in the various parts of the study, their explanation needs further experiments. Research continues in this project at the Laboratory and we hope to proceed successfully further along the way indicated by this and by the previous Theses.

### 1.9. References

91, 600-605.


120. Dharaiya, D., Jana, S. C., Polymer 2005, 46, 10139-10147.
Chapter 2

Kinetics of structure formation in PP/layered silicate nanocomposites

2.1. Introduction

Although the principles for the preparation of layered silicate nanocomposites are clear, complete exfoliation and the expected improvement in properties are rarely achieved. Quite a few controversial results are reported about the structure and properties of these materials as well as about the effect of various factors on them. The extent of exfoliation in a polymer/layered silicate nanocomposite is determined by thermodynamic and kinetic factors as discussed among others by Vaia et al. [1,2]. The competitive interactions acting among the various groups of the components are very difficult to estimate and control, which results in a wide range of structures often with inferior properties. Similarly to the uncertainties related to the role and effect of interactions on the structure and properties of nanocomposites, the effect of kinetics, i.e. processing conditions, on structure development is also quite unclear. Some groups claim that processing conditions, or even preparation conditions do not influence the structure of the composites [3,4], while others found a strong effect of processing [5,6] as described in Section 1.3.3.

In view of the controversies cited in the introductory part and above, the goal of our work was to study the effect of various factors on structure development in PP/layered silicate composites. The study focused mainly on kinetic factors, but interactions were also modified by the addition of a compatibilizer. The experiments were carried out in two series. In the first series several polypropylene homopolymers with different melt flow indices were used as matrix to modify shear stresses, and both the time and the rate of mixing were also changed. In the second series the same polymer was used in all experiments, but maleated PP was also added to assist exfoliation. The rate and time of mixing were changed also in this series at several levels. The structure of the composites was characterized by various methods and several properties were measured in order to identify the processes taking place during mixing and the most important factors influencing them.

2.2. Experimental

Five PP homopolymers produced by TVK, Hungary were used in the first series of experiments, the Tipplen H377 (PP90), H483 (PP65), H543 (PP40), H605

(PP30) and the H890 (PP03) grades. All polymers, their abbreviation and melt flow index (MFI) are compiled in Table 2.1 together with the composition of the nanocomposites studied. The abbreviation is based on the MFI of the polymers. All polymers contained a commercial additive package except the H605 grade. The Nanofil 848 (N 848) product of Süd-Chemie AG was used as silicate. This clay is coated with stearyl amine, its density is 1.8 g/cm$^3$, moisture content 2 wt%, organic content 25 wt% and particle size 3 µm. Composition was the same in all experiments, 2 vol% clay was added to the polymer. The Tipplen H 649 (PP25) grade was used as matrix polymer in the second series, the Nanofil SE 3000 (NSE 3000) silicate as reinforcement. The silicate was organophilized with 55 wt% distearyl dimethyl ammonium chloride, its density was 1.8 g/cm$^3$ and the average particle size was less than 10 µm. A small molar mass maleated PP, Licomont AR 504 (AR 504, Clariant AG) was used as coupling agent to promote exfoliation. Its maleic anhydride content was 3.5 wt% and it had very low viscosity (0.8 Pas at 170 °C). The composites contained 1 vol% clay and 20 vol% MAPP in this series.

Table 2.1  Characteristics of the polymers and composition of the nanocomposites studied.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbrev.</th>
<th>MFI$^a$ (g/10 min)</th>
<th>MAPP Type</th>
<th>vol%</th>
<th>Silicate Type</th>
<th>vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tipplen H 377</td>
<td>PP90</td>
<td>9.0</td>
<td>–</td>
<td>0</td>
<td>N 848</td>
<td>2</td>
</tr>
<tr>
<td>Tipplen H 483</td>
<td>PP65</td>
<td>6.5</td>
<td>–</td>
<td>0</td>
<td>N 848</td>
<td>2</td>
</tr>
<tr>
<td>Tipplen H 543</td>
<td>PP40</td>
<td>4.0</td>
<td>–</td>
<td>0</td>
<td>N 848</td>
<td>2</td>
</tr>
<tr>
<td>Tipplen H 605</td>
<td>PP30</td>
<td>3.0</td>
<td>–</td>
<td>0</td>
<td>N 848</td>
<td>2</td>
</tr>
<tr>
<td>Tipplen H 890</td>
<td>PP03</td>
<td>0.3</td>
<td>–</td>
<td>0</td>
<td>N 848</td>
<td>2</td>
</tr>
<tr>
<td>Tipplen H 649</td>
<td>PP25</td>
<td>2.5</td>
<td>AR 504</td>
<td>20</td>
<td>NSE 3000</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ determined at 230 °C and 21.6 N

Composites were prepared in a Brabender W 50 EH internal mixer attached to a Haake Rheocord EU 10 V driving unit at 190 °C. Charge volume was 42 cm$^3$ in both series. Samples were prepared at the combinations of 2, 5, 8, 10, 12, 15, 20 min mixing time and 50 rpm, as well as at 10, 30, 70, 100 rpm and 8 min in the first series. Time changed in six (5, 10, 15, 30, 45 and 60 min), while the rate of mixing in four (20, 50, 80 and 120 rpm) steps and samples were prepared at all combinations of the parameters in the second series. The homogenized samples were compression molded into 1 mm thick plates using a Fontijne SRA 100 machine at 190 °C and 3 min preheating and 3 min compression time.
The gallery structure of the silicate was characterized by X-ray diffraction (WAXS) using a Phillips PW 1830/PW 1050 equipment with CuK\(_\alpha\) radiation at 40 kV and 35 mA. The morphology of the samples was examined by transmission electron microscopy. 50-100 nm thick slices were cut at –80 °C with a Leica Ultracut UCT microtome. TEM images were created with a Philips CM30 Twin STEM electron microscope. Thin films of approximately 100 \(\mu\)m thickness were compression molded from the composites for Fourier transform infrared spectroscopy (FTIR). The spectra were recorded using a Mattson Galaxy 3020 spectrometer (Unicam) in the 4000-400 cm\(^{-1}\) wavelength range with 4 cm\(^{-1}\) resolution in 16 scans. The color of the samples was measured using a Hunterlab Colourquest 45/0 apparatus and it was characterized by the yellowness index according to the ASTM D 1925 standard. Rheological measurements were carried out using a Paar Physica UDS 200 apparatus at 200 °C in oscillatory mode in the frequency range of 0.1-600 1/sec on discs with 25 mm diameter and 0.5 mm thickness. The amplitude of the deformation was 5 %, which was in the linear elastic region checked by an amplitude sweep. The tensile properties of the samples were measured using an Instron 5566 apparatus. Young’s modulus was determined at 0.5 mm/min crosshead speed. 50 mm/min was used in the first and 5 mm/min in the second series for the determination of tensile strength and elongation-at-break. All characteristics were derived from three parallel measurements.

2.3. Results

The results are presented in three sections. The two series are discussed separately first, then they are compared in a subsequent section to draw general conclusions from the study. Mostly the time dependence of properties will be shown to simplify discussion, practically the same conclusions can be drawn from the effect of the rate of processing on structure and properties.

2.3.1. PP/OMMT composites

The torque developing in the mixer was recorded during the preparation of the samples. Torque is proportional to shear stress, and since average shear rate is constant, it is proportional also to the viscosity of the melt. The torque recorded at the end of the homogenization is plotted against mixing time in Fig. 2.1 for two composites with different matrices. The viscosity of the remaining three polymers was very similar to that of PP65, which was quite surprising since their MFI changed between 3 and 6.5 g/10 min. This similarity was observed in most properties, therefore we usually present only two correlations for the sake of clarity. However, the similarity of the behavior of the four polymers needs further study and explanation.

Torque decreases with time in both cases indicating changes in the structure of the composites. A definite explanation obviously cannot be given based on these correlations; one can only speculate on the possible reasons. Torque usually decreases in the first stage of the mixing until the material reaches constant temperature. In our case the decrease is continuous, thus it must be related to structural changes. Both the dispersed structure of the
composite and the molecular structure of PP may change during mixing. The relatively large micron sized particles are evenly distributed in the matrix, but possible intercalation and/or exfoliation may also lead to changes in viscosity. One would expect an increase in viscosity with exfoliation, since exfoliation creates new surfaces, and strong interaction should lead to the formation of an interphase with decreased mobility. On the other hand, we know that the surface free energy of organophilic MMT is small [7], thus weak interaction with the clay may result in the disruption of entanglements and weaker interaction among the chains, like in PVC nanocomposites [8]. Naturally this latter explanation is rather improbable considering the very small surface tension of PP and the resulting weak interactions in this polymer.

![Figure 2.1](image-url)

**Figure 2.1** Effect of processing time and the molecular weight of the matrix polymer on the viscosity (torque) of layered silicate composite melts containing 2 vol% OMMT.

Both of the polymers contain a commercial additive package, i.e. they are sufficiently stabilized for normal processing and application purposes. However, we know that PP is rather sensitive to degradation which proceeds through β-scission in this polymer resulting in the decrease of molecular weight. If the organoclay catalyses the chemical reactions occurring during the processing of the polymer and promotes degradation, chain scission may occur and molecular weigh decreases as a result. Only the analysis of further results may answer these questions.

Although extensive exfoliation is not expected in the absence of a compatibilizer in these PP/OMMT composites, structural changes may occur, which can influence their properties, including viscosity. The WAXS patterns of the composites prepared from PP03
with 2 vol% OMMT are presented in Fig. 2.2. Although not very dramatic, but a clear change can be observed in the traces. The characteristic peak of the silicate broadens and shifts towards smaller 2θ angles. This latter change is usually explained by the intercalation of the polymer into the galleries of the silicate, while the broadening indicates less regular stacking of the layers. Accordingly, the WAXS study indicates changes in the gallery structure of the polymer and/or limited exfoliation. In order to check the dispersed structure of the composites TEM micrographs were taken from selected samples. These also corroborate our conclusion that structure changes somewhat during the processing of the composites. A very large particle of at least 5 micron size is seen in the TEM micrograph taken from the PP65 composite after 5 min processing time (Fig. 2.3a). The particle is very compact, intercalation or exfoliation cannot be observed at all. On the other hand, structure changes considerably after 20 min homogenization as Fig. 2.3b shows. The size of this particle is much smaller, its structure looser and individual platelets as well as smaller fragments are also visible in the micrograph (see arrows). Longer mixing obviously resulted in the transformation of structure.

![Figure 2.2](image)

**Figure 2.2** WAXS patterns of PP03/OMMT composites processed under various conditions. See shift and broadening of the silicate reflection.
Figure 2.3  Changes in the gallery structure of the silicate with increasing processing time. PP65/2 vol% OMMT. a) 5 min, 50 rpm, b) 20 min, 50 rpm. Arrows indicate individual platelets or smaller particles.
However, these changes are not necessarily related to the decrease of viscosity during mixing. On the other hand, a very close correlation is obtained if we plot the intensity of the silicate reflection, characterized by the area under the peak, against the torque measured at the end of mixing (Fig. 2.4). The tendency is clear in spite of the small differences observed among the polymers with smaller molecular weights. The arrow in the figure indicates increasing processing time. Accordingly, gallery distance increases (not shown) and the intensity of the reflection decreases with decreasing viscosity. Obviously the magnitude of shear forces does not play a determining role in these structural changes, since it decreases continuously with increasing processing time. Larger mobility of the smaller molecules may facilitate diffusion into the galleries, but the degradation of the polymer might modify interactions as well.

![Figure 2.4](image)

**Figure 2.4** Correlation between the intensity of the silicate reflection and the torque (viscosity) measured at the end of the mixing.

The changes in the structure of the composites resulted in the modification of properties as well. The Young’s modulus of composites prepared with three matrices is plotted against mixing time in Fig. 2.5. The broken line in the figure indicates the stiffness of a PP/CaCO$_3$ composite containing 5 vol% filler. CaCO$_3$ does not exfoliate thus it is used as reference for non-exfoliated PP/OMMT composites. Stiffness is determined by the crystalline structure of the polymer and by the extent of exfoliation. The correlations are very difficult to explain. Modulus increases with increasing MFI of the matrix, which would indicate the effect of chain mobility. However, the decrease of stiffness cannot be explained at all, it must be related to changing crystalline structure or increased interaction hindering the crystallization of the polymer (see PP03). Both the position of the silicate reflection and its intensity decreased indicating increased intercalation and/or some exfoliation, confirmed
also by the TEM study. These changes should have resulted in an increase and not a decrease in stiffness.

Fig. 2.6 presents changes in the relative deformability of the samples with increasing processing time for composites prepared with three matrices. The elongation-at-break values of the neat polymers differ considerably due to their dissimilar molecular weight, thus relative values must be used for comparison. The results further complicate the situation and finding a plausible explanation for the changes. One would expect some correlation between molecular weight and changes in deformability here too, but the PP30 matrix maintains the largest deformability, while the PP03 polymer with the largest initial elongation-at-break has an intermediate value. At longer processing times the deformability of the PP65 polymer is close to zero. The relative order of the polymers is very difficult to understand, since the PP65 and PP03 polymers contained commercial stabilizer packages, while the PP30 polymer was not stabilized. Nevertheless, after considering all the results presented above, and those not shown, we may conclude that the degradation of the polymers and the resulting changes in their molecular structure may play a role in the determination of structure and properties.

In order to check this hypothesis, FTIR spectra were recorded on the neat polymers and on the composites. Evaluation was rather difficult in the latter case because of the intensive absorbance of the silicate. Nevertheless a peak was detected in the spectra at 1714 cm\(^{-1}\) in the range where usually carbonyl and carboxyl groups absorb. The intensity of this vibration is plotted against processing time in Fig. 2.7. The number of carbonyl groups seems to increase considerably during processing which supports our hypothesis about the degradation of the polymer.

![Figure 2.5](image-url)  
*Effect of matrix properties and processing time on the stiffness.*
Figure 2.6 Changes in the relative elongation-at-break values of PP/OMMT composites with the MFI of the matrix and with increasing processing time.

Figure 2.7 Increasing carbonyl content of PP03/OMMT composites with increasing time of homogenization.
In a further attempt to prove the role of degradation, we introduced additional amounts of stabilizer into the composite (0.1 wt% Irganox 1010). The change of torque with time is presented in Fig. 2.8 for composites prepared with the PP03 polymer with and without additional stabilization. The difference is clear, viscosity decreases somewhat at the shorter processing times, most probably because of increasing temperature, and remains more or less constant afterwards for the stabilized sample. We must mention here that the elongation-at-break values change similarly with stabilization indicating the clear effect of molecular weight and degradation in the determination of this property. We can conclude that PP degrades in smaller or larger extent during the production of these layered silicate composites. The extent of degradation must depend on the efficiency of stabilization. The clay seems to accelerate degradation. Thermal degradation modifies chain structure, which influences interactions and mobility, but also the structure of the composites. The degree of exfoliation is very limited but some intercalation definitely occurs in the studied PP/OMMT composites. The role of the clay in degradation processes needs further investigation.

![Figure 2.8](image-url)  
**Figure 2.8**  
*Effect of additional stabilization on the viscosity (torque) of PP03/PP composites. (●) without additional stabilization, (○) with 0.1 wt% Irganox 1010 stabilizer.*

### 2.3.2. PP/OMMT/MAPP composites

PP nanocomposites are prepared with a compatibilizer practically always in order to facilitate exfoliation. Exfoliation was very limited in the absence of MAPP indeed, as shown in the previous section. In the next series of experiments we added a small molecu-
lar weight MAPP compatibilizer with large functionality [9,10] to the composites. The effect of the compatibilizer on the gallery structure of the composites is shown in Fig. 2.9. The silicate peak completely disappears already after 5 min mixing time even under very moderate shear conditions (20 rpm). Further changes cannot be observed in the pattern with increasing processing load (60 min, 120 rpm). Some authors claim complete exfoliation based on the disappearance of the silicate reflection [11,12], but several studies proved that this is not true [13,14]. Nevertheless, the gallery structure of the composite changed considerably in the presence of the compatibilizer. This change is confirmed by the TEM micrograph taken from the sample processed at 50 rpm for 10 min (Fig. 2.10). A relatively large particle, but with a very loose structure can be observed in the figure. The density of platelets increases towards the center, gallery distance is larger at the edges and at the lower end of the particle. A few individual layers can also be seen in the upper left corner. The micrograph proves that the disappearance of the silicate does not indicate complete exfoliation, but the compatibilizer loosens up the structure and helps intercalation as well as exfoliation.

![Figure 2.9](image)

**Figure 2.9** Influence of MAPP compatibilizer on the gallery structure of the silicate in PP/OMMT nanocomposites. See the disappearance of the silicate reflection. a) PP/OMMT, 10 min, 50 rpm, b) PP/OMMT/MAPP, 10 min, 50 rpm.

Unfortunately, the proper evaluation of properties is very difficult when this small molecular weigh compound is used as compatibilizer. Especially the rheological properties change drastically in its presence. However, the time dependence of viscosity as well as the comparison of the viscosity of PP/MAPP blends to that of PP/OMMT/MAPP composites indicates that molecular weight decreases with increasing processing time (Fig. 2.11), but also with increasing shear rate (not shown). This result confirms and strongly supports our
previous observation about the possible degradation of the polymer during the processing of these layered silicate composites. A further proof for degradation is supplied by the changes in the color of the composites with processing conditions. The yellowness index of the composite processed at 50 rpm is plotted as a function of mixing time in Fig. 2.12. The drastic increase in color is a clear proof of chemical reactions occurring in the composite during processing. The results of two independent series of measurements unambiguously prove that degradation of the polymer occurs and influences properties.

Figure 2.10  TEM micrograph taken from a silicate particle in a PP/OMMT/MAPP nanocomposite. See the loose structure, changing platelet density and individual platelets.

2.3.3. Comparison, discussion

The stability of polymer/layered silicate nanocomposites is an often discussed topic in the literature, but not in the context encountered here. Layered silicates are claimed to improve thermal stability and the claim is usually supported by thermal gravimetric (TGA) measurements [15,16]. Degradation temperature is supposed to increase due to the formation of a silicate layer, which hinders the diffusion of flammable gases out of and that of the oxygen into the composite. This phenomenon might be important in the burning of plastic products and flame retardancy, but not during the processing and use of such composites. Although the deteriorating effect of the components (OMMT, MAPP) was shown
Figure 2.11 Effect of the compatibilizer, the clay and processing time on the complex viscosity of PP/OMMT/MAPP nanocomposites determined at 1 s⁻¹ frequency. See the detrimental effect of the components.

Figure 2.12 Increasing color of PP/OMMT/MAPP nanocomposites with increasing processing time at 50 rpm proving the occurrence of chemical reactions and degradation.
on the light stability of PP/layered silicate composites [17,18], very few papers were published on thermo-oxidative stability. However, degradation is obviously accelerated by the organoclay and probably also by the functionalized polymer shown by both series of measurements of this study. Changing molecular structure of PP influences properties and complicates the evaluation of structure-property correlations.

The apparently contradictory results reported in the previous two sections are the results of complex processes including degradation, which modifies interactions and the kinetics of intercalation. The degradation of the polymer leads to the formation carbonyl and carboxyl groups even in the presence of stabilizers. Only a few carboxyl groups were shown to change interactions drastically in PP/CaCO$_3$ composites [19-21]. The increasing number of carbonyl groups changes the interaction of the polymer with the organophilic silicate and decreasing chain length leads to increased mobility and faster diffusion. These result in increased intercalation in PP/OMMT composites (Figs. 2.2 and 2.3). However, stronger interaction modifies also crystallization and crystalline structure leading to a diverse response of modulus to changing processing conditions (Fig. 2.5). Deformability is determined mainly by molecular weight (Fig. 2.6).

In spite of the increasing number of carbonyl groups, intercalation and exfoliation is limited in PP/OMMT composites. The inclusion of MAPP assists intercalation, but complete exfoliation is not achieved even in this case. Degradation processes seem to be significant also in the presence of the functionalized polymer. The small molecular weight of MAPP and degradation further complicates the identification of the main factors determining structure and properties in these PP/OMMT/MAPP nanocomposites. Targeted experiments with proper experimental design are needed to separate the effects discussed here and resolve the complexity of the processes and factors playing a role in the preparation of PP nanocomposites.

### 2.4. Conclusions

The gallery structure of the organophilic silicate changed in spite of the fact that no compatibilizer was added to PP/OMMT nanocomposites. Silicate reflection shifted towards smaller 2$\theta$ angles, broadened and its intensity decreased indicating intercalation. TEM micrographs even showed individual platelets at long mixing times. However, the extent and direction of changes in the gallery structure of the silicate did not justify those observed in properties. The analysis of the results and additional experiments proved that the degradation of the polymer also takes place during processing leading to the formation of carbonyl and/or carboxyl groups, as well as to the decrease of molecular weight. The modification of chain structure influences interfacial interactions and the intercalation process. Some properties are directly determined by molecular weight (rheological properties, elongation). Both the clay and the functionalized polymer seem to accelerate degradation. Thermo-oxidative degradation must have disadvantageous effect during the application of PP nanocomposites and needs further study.
2.5. References

Chapter 3

Thermo-oxidative stability of PP/layered silicate nanocomposites

3.1. Introduction

One of the major advantages of adding a silicate to a polymer is claimed to be the improvement of thermal stability. Very often decomposition temperature is meant under the term of stability which is determined by thermogravimetric analysis (TGA) [1-6]. Decomposition temperature is claimed to increase in the presence of the silicate in the majority of the papers using this approach and the increase is explained with the formation of a silicate barrier layer during decomposition which hinders the diffusion of oxygen into and that of the volatile decomposition products out of the composite. In spite of the general belief, the picture is not that simple. Occasionally decomposition temperature increases, indeed, but the rate of decomposition increases at the same time [5]. In other cases decomposition temperature is higher than that of the neat polymer at small silicate content, but continuously decreases with increasing filler loading and becomes lower than that of the matrix polymer [1]. Such phenomena are either ignored or explained with the catalytic action of the heavy metal content, usually ferric ions, of the silicate. Contradictory information is published also about the effect of the components, i.e. silicate and functionalized polymer. Sometimes the catalytic effect of the silicate, but in other cases the presence of MAPP is blamed for the inferior stability. Even if we disregard these contradictions, the determination of decomposition temperature has very little practical relevance in our opinion. PP composites are rarely processed or used above 300 °C and the increase of this temperature by about 20 °C is really irrelevant for practice.

On the other hand, very little or almost negligible attention is paid to thermo-oxidative stability under the conditions of processing or application. Only a few papers discuss the effect of the components on the photo-oxidative stability of PP/layered silicate composites [7-9]. All studies done indicated that layered silicates accelerate the photo-degradation of PP, but do not change its mechanism. Gardette et al. [9] offered three possible explanations: the adsorption of stabilizers on the silicate, the catalytic effect of ferric ions, and the decomposition of the surfactant used for the modification of the silicate. Basically no papers are available which are dealing with the effect of OMMT and MAPP on the thermo-oxidative stability of PP, although this question is much more important for practice than any change in decomposition temperature.

The results reported in the previous chapter indicated that the thermal stability of PP/layered silicate composites decreases in the presence of both the silicate and the
functionalized polymer used for compatibilization [10]. The viscosity of the polymer and mechanical properties may deteriorate in an extent which makes processing impossible and/or the product useless. As a result we started several series of experiments to determine the effect of a commercial layered silicate and a functionalized PP on the thermo-oxidative stability of PP nanocomposites. We also wanted to answer the question often raised both in decomposition and stability studies, whether the components interact with each other and have synergistic or antagonistic effect on the stability of PP.

3.2. Experimental

A commercial grade polypropylene (Tipplen H 649) supplied by TVK, Hungary was used for the experiments. The polymer had a number average molecular mass of 97 kg/mol and a polydispersity of 5.0. Its melt flow index was 2.5 g/10 min (230 °C/2.16 kg) and it contained an additive package consisting of 500 ppm Irganox 1010 phenolic antioxidant, 1000 ppm Irgafos 168 phosphite stabilizer, both from Ciba Specialy Chemicals, and 400 ppm DHT-4A acid scavenger. The organophilic silicate was the Nanofil 5 grade of Rockwood Clay Additives surface modified with 35 wt% distearyl dimethyl ammonium chloride resulting in a surface coverage of 83 % related to the ion exchange capacity of the clay. Its average particle size was 8 µm and its density 1.8 g/cm³. The Polybond 3200 (Mn = 120 kg/mol, maleate content = 1 wt%) maleated PP coupling agent was obtained from Uniroyal Chemical Co.

A series of preliminary experiments were carried out with the commercially stabilized polymer to explore the effect of the components on stability. 1 vol% OMMT and 20 vol% MAPP was used in these experiments. The stability of the composite samples proved to be so low that 1000 ppm Irganox 1010 and 1000 ppm Irgaphos 168 were used additionally in further studies. An extended orthogonal experimental design was used at first with 1 and 6 vol% as the two levels for OMMT and 10 and 50 vol% for MAPP. Three parallel measurements were done at the center point of 3.5 vol% OMMT and 30 vol% MAPP in order to estimate the variance of random error independently of the model used. Additional measurements were carried out to check the prediction of the model and to increase the reliability of our conclusions. These brought the number of experiments to 26 in the stability study and covered the composition range of OMMT content 0 and 6 vol% and MAPP content of 0 and 50 vol%.

Composites were prepared in a Brabender W 50 EH internal mixer attached to a Haake Rheocord EU 10 V driving unit at 190 °C. Charge volume was 42 cm³. In the preliminary experiments mixing was done at 50 and 80 rpm, for 10, 15, 20 and 30 min to check the effect of shear rate and mixing time on stability. All other samples were prepared at 80 rpm and 10 min. The homogenized samples were compression molded into 1 mm thick plates using a Fontijne SRA 100 machine at 190 °C and 3 min preheating and 3 min compression time.

The residual thermo-oxidative stability of the samples was characterized by the oxygen induction time (OIT) determined at 180 °C using a Perkin Elmer DSC 2 appara-
Thermo-oxidative stability

Three to five parallel measurements were done on each sample. We determined also the onset temperature of oxidation (OOT). The measurements were carried out in the DSC 30 cell of a Mettler TA 4000 apparatus at 10 °C/min heating rate and 100 ml/min oxygen flow. The color of the samples was measured using a Hunterlab Colourquest 45/0 apparatus and it was characterized by the yellowness index according to the ASTM D 1925 standard. The gallery structure of the silicate was characterized by X-ray diffraction (WAXS) using a Phillips PW 1830/PW 1050 equipment with CuKα radiation at 40 kV and 35 mA. The morphology of the samples was examined by scanning electron microscopy (SEM) using a Jeol JSM 6380 apparatus. Samples were etched in an oxidative solution to increase contrast and visualize larger structural units. Rheological measurements were carried out using a Paar Physica UDS 200 apparatus at 200 °C 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. The oxygen permeation of the composites was determined on 1 mm thick plates with a measurement area of 5.72 cm² at ambient temperature and 0 % relative humidity using a Systec 8000 type apparatus (Thame, Oxfordshire, England). The tensile properties of the samples were measured using an Instron 5566 apparatus. Young’s modulus was determined at 0.5 mm/min while yield and ultimate properties at a cross-head speed of 5 mm/min. All characteristics were derived from five parallel measurements.

3.3. Results

The results are discussed in several sections. Because of their importance structure and properties will be presented first, and the effect of components on stability is shown in a subsequent section. This is followed by the analysis of possible interaction, synergism or antagonism. The effect of processing parameters will be briefly discussed next and finally we speculate about the possible reasons for the observations made and the mechanisms of degradation.

3.3.1. Structure and properties

Although the analysis and exact determination of structure is not the main goal of this communication, its thorough characterization is important for several reasons. First of all structure is usually more complicated than the intercalated/exfoliated morphology frequently claimed in papers dealing with these materials [11-14]. Polymer/layered silicate composites may contain four structural entities: individual layers, intercalated stacks or tactoids, larger particles, and a silicate network forming at large extent of exfoliation [15-17]. These latter two entities are usually not looked for and often completely neglected. Because of the complex structure quantitative characterization and the determination of the extent of exfoliation is difficult, although it has considerable importance also in our case. The degree of delamination determines the contact surface between the polymer and the silicate, and if the adsorption of additives or the catalytic effect of the silicate plays a role in degradation, it should increase with exfoliation.
Structure is usually characterized by two techniques, X-ray diffraction (WAXS) and transmission electron microscopy (TEM). The former offers information about non-exfoliated stacks and the gallery structure of the silicate, while the latter about the presence of individual platelets. The WAXS traces of selected composites are shown in Fig. 3.1. The trace of the neat OMMT indicates large gallery distance (2.8 nm), while relatively large degree of regularity in stacking can be deduced from the presence of interference peaks. The peaks of the silicate reflection can be detected also in the composites containing the silicate. The intensity of the peak changes with the amount of silicate present, and decreases with increasing MAPP content as shown by Fig. 3.1. The presence of the peak shows incomplete exfoliation, but decreasing intensity with increasing MAPP content indicates at least partial delamination of the silicate. SEM analysis confirms the change of morphology with MAPP content (not shown), but also the presence of larger, micron sized particles.

![Figure 3.1](image)

Figure 3.1  WAXS trace of the organophilic montmorillonite used (Nanofil 5) and that of selected composites. a) neat OMMT, b) 5 vol% OMMT, c) 5 vol% OMMT and 40 vol% MAPP.

Another proof for exfoliation is supplied by rheology. Cole-Cole plots created by plotting the two components of complex viscosity against each other are shown in Fig. 3.2 for selected composites. The composites contain 40 vol% MAPP and increasing amounts of silicate. Such plots are semi-arcs or distorted semi-arcs when only a single relaxation process characterizes the deformation of the melt and deviate strongly from an arc, when a second process appears due to structural changes, phase separation, aggregation or network formation [10,18]. Such a distortion was shown to be related to the formation of a silicate network in polymer/clay composites [10]. We can see two effects in Fig. 3.2. At small silicate content viscosity decreases (see smaller area of the arc) possibly as a result of deg-
Thermo-oxidative stability

Radation. Viscosity increases considerably and the arc distorts at 5 vol% silicate content due to exfoliation and the formation of the network. Exfoliation and changing structure is also proved by the results of oxygen permeation measurements, which are presented in Fig. 3.3. MAPP alone increases permeation due to decreased crystallinity, but increasing exfoliation decreases it quite considerably as predicted by theories and shown by several papers [19-23]. Finally, changes in mechanical properties (not shown to save place) also indicate the occurrence of two processes: degradation and structural changes. Modulus increases with silicate content, while yield stress remains more or less constant. Elongation-at-break and tensile strength strongly decreases indicating the degradation of the polymer both at large silicate and MAPP content. The study of the structure and properties of the polymer prove that incomplete exfoliation occurs in our composites, but also indicates that both components added to PP accelerate degradation, and the stability of the composites is worse than that of the neat polymer.

![Figure 3.2](image_url)  
**Figure 3.2** Effect of composition on viscosity, and silicate network formation in PP/OMMT composites at 40 vol% MAPP content. Symbols: (□) 0, (○) 1, (△) 2, (▽) 5 vol% OMMT.
3.3.2. Stability

The stability of the composites is characterized by the measurement of oxygen induction time (OIT) and the onset temperature of degradation (OOT). The effect of the components on OIT is shown in Fig. 3.4. Stability decreases very steeply with increasing silicate content and MAPP has a similar effect on OIT. Obviously both components decrease the residual stability of the polymer quite significantly either by consuming the stabilizers through adsorption or chemical reactions, or by catalyzing degradation reactions as suggested by some sources [7-9]. OOT changes in a similar way as OIT as a function of composition except that its decrease is not as steep as shown in Fig. 3.4. A very close, nonlinear correlation was found between OIT and OOT for the composites studied (not shown). OIT changed less at large silicate and MAPP contents, i.e. at smaller stability, than OOT.

Another parameter often used for the characterization of degradation is color. Phenolic antioxidants yield chinoidal compounds during stabilization, which generates slightly yellow color in the polymer. Unfortunately clays are grayish or yellowish themselves thus the separation of the discoloring effect of degradation and that of the silicate is quite difficult. Nevertheless, we determined the color of our composites since considerable changes were observed as a function of composition. Color is characterized by yellowness index which is plotted against silicate content at various levels of MAPP in Fig. 3.5. The linear increase of color with increasing silicate content is the direct effect of the filler, its
Figure 3.4  Residual thermo-oxidative stability (OIT) plotted against the silicate content of the composites. Symbols: (□) 0, (○) 10, (△) 20, (▽) 40 vol% MAPP.

Figure 3.5 Effect of composition on the color of the composites. Symbols: (□) 0, (○) 10, (△) 20, (▽) 40 vol% MAPP.
grayish-yellowish color results in the increase of yellowness. The presence of MAPP increases discoloration at smaller silicate content, but levels off at large filler contents. This could indicate degradation and/or the interaction of the components. Since the simultaneous effect of two variables is difficult to estimate form Fig. 3.5, we plot color also as a function of MAPP content (Fig. 3.6). MAPP itself does not discolor the polymer much. Yellowness increases in the presence of the silicate, but in a much lesser extent than without MAPP (see points on the vertical axis). The probable reason is the exfoliation, break down of the particles, since large silicate particles increase color proportionally to their amount (see Fig. 3.5). MAPP decreases both the number and the size of the particles thus color decreases or more exactly increases much less than without MAPP. The stronger effect of MAPP on color in the presence of the silicate than without it might be a further proof of degradation and indication for the interaction of the components.

![Figure 3.6](image)

**Figure 3.6** Yellowness index of the composites plotted against their MAPP content. Symbols: (□) 0, (○) 1, (△) 2, (▽) 5 vol% OMMT.

### 3.3.3. Interaction, synergism, antagonism

In order to estimate the effect of the components on the stability quantitatively, linear regression analysis was carried out using the Statistica for Windows (data analysis software system) 9.0 version of StatSoft Inc. (www.statsoft.com). The model used considered the linear and quadratic effects of the components on OIT and color in the following way:

\[ y = a_1x_1 + a_2x_2 + a_3x_1^2 + a_4x_2^2 + a_5x_1x_2 + A \]  \hspace{1cm} (3.1)
where $y$ is the studied independent variable, i.e. yellowness index or OIT, $x_1$ and $x_2$ are the concentration of OMMT and MAPP, respectively, and $A$ is the intersection of the multidimensional parameter field. The quadratic terms account for non-linear effects, while the $x_1x_2$ term offers information about the interaction of the components. The orthogonal experimental design makes possible the independent estimation of the effect of the variables.

We carried out the analysis with the orthogonal design and also with the full set of data. Variables in Eq. 3.1 which were not significant at the 90% level were omitted and the calculations were repeated. Final conclusions were drawn from the evaluation of significance levels, the magnitude of the sum of squares, as well as from the value and sign of the $a_n$ parameters in Eq. 3.1. We refrain from presenting all details of the analysis, but demonstrate the most important conclusions with two figures and a few representative numbers. Color calculated from the model is presented in Fig. 3.7 as a function of the two variables.

![Figure 3.7](image)

**Figure 3.7** Contour plot showing the color (yellowness index) of the composites as derived from statistical calculations according to Eq. 3.1. Effect of composition; contour lines represent different levels of discoloration.

Yellowness index increases with increasing amount of both components as expected. Their different effect is clearly seen if we follow the two axes; OMMT discoloring the polymer much stronger than MAPP. The stronger effect of OMMT is shown also in the level of significance ($p = 0.00045$ and 0.0011 versus 0.0033 and 0.014 for the linear and quadratic terms of OMMT and MAPP, respectively; the smaller the $p$ value the largest the significance and the effect) and in the values of the $a_n$ parameters (27.3 and -3.21 versus 1.13 and -0.01). A maximum is predicted in color at around the combination of 4.5 vol% OMMT and 50 vol% MAPP. Rather surprisingly the interaction term, $x_1x_2$ was not signifi-
significant at the 90% level; according to the statistical analysis the effect of the two variables is independent of each other.

The results of similar calculations are presented in Fig. 3.8 for OIT. The very strong degradation effect of both components is clearly seen in the figure. All components including the interaction term are significant at very high levels. The model predicts a minimum of stability with a value of about -10 min at around 3 vol% OMMT and 40 vol% MAPP which indicates clearly the limitations of statistical calculations. We can hardly expect stability to increase at large silicate and MAPP contents either as indicated in the upper right corner of the graph. The disagreement with experience and experimental facts results from the selection of the model. The linear regression model with the quadratic terms obviously does not express properly the very strong non-linear effect of the components on residual stability.

![Figure 3.8](image)

**Figure 3.8**  *Contour plot presenting the effect of the two components on the stability (OIT) of the composites.*

As a consequence, we tried to check the possible interaction of the components with another approach independently of the statistical analysis. A simple exponential decay function of the form

\[
y = A \exp\left(\frac{-x}{a}\right) + y_0
\]

where \(y\) is the independent variable, i.e. OIT, \(x\) is composition, i.e. OMMT or MAPP, respectively, and \(y_0\) is a constant that is practically zero was fitted to the two component materials first. Fig. 3.9 shows the fit for MAPP. The determination coefficient, i.e. the goodness of the fit is 0.9934, which is extremely good. A similar correlation with the de-
Figure 3.9  Exponential decay of stability with increasing MAPP content. (□) measured values, ——fitted with Eq. 3.2.

Figure 3.10  Comparison of measured and calculated stability. Calculation was done by assuming additivity of the effect of the two components.
termination coefficient of 0.9839 was obtained for the effect of OMMT. OIT was calculated from the combination of the two functions assuming additivity. The correlation of calculated and measured OIT values is plotted against each other in Fig. 3.10. The correlation is very close indicating the independent effect of the two components on stability.

3.3.4. Effect of processing

Since extensive exfoliation is a primary condition of producing polymer nanocomposites with appropriate properties, often high shear and long time are applied during their processing to assist the delamination process. Although we did not carry out a detailed study of processing conditions, we checked the effect of mixing speed and processing time on stability and properties in our preliminary study. We could show very little effect of mixing speed on the OIT of the commercial grade polymer with no additional stabilizer, because of its very limited residual stability. OIT was in the range of 1 min for samples produced at 50 and 80 rpm and 10 min mixing time. The practically zero OIT did not make possible any differentiation.

The situation was the same for the effect of mixing time, i.e. the samples had almost zero residual stability. However, we could check the effect of mixing time by rheology. The frequency dependence of complex viscosity is shown in Fig. 3.11 for samples containing 1 vol% OMMT and 20 vol% MAPP. Mixing was carried out at 80 rpm for the times indicated in the figure. The drastic decrease of viscosity is obvious, considerable

![Figure 3.11](image)

**Figure 3.11** Effect of processing time on the viscosity of PP/OMMT/MAPP composites at 1 vol% silicate and 20 vol% MAPP content. Symbols: (□) 10, (○) 15, (△) 20, (▽) 30 min mixing time.
Thermo-oxidative stability

Degradation is accompanied by a significant decrease of molecular weight. Although we could not measure OIT values having any practical meaning on the polymer containing only the commercial additive package, the effect of processing time could be shown at elevated stabilizer levels. OIT decreased from 57 to 14 min at an additional level of 1000 ppm Irganox 1010 and 1000 ppm Irgaphos 168 as processing time increased from 10 to 30 min, while it changed from 145 to 68 min when 2000 ppm of each stabilizer was introduced additionally. The very low level of residual stability and the drastic decrease of the viscosity of the commercial grade PP warrant the utmost caution during the preparation of such nanocomposites.

3.4. Discussion

The results presented above clearly prove that the components used in the preparation of PP/layered silicate nanocomposites decrease stability and deteriorate properties. This fact is rarely mentioned in the literature, but in the few cases when such results are presented usually the catalytic effect of the silicate is mentioned as the main reason. The most comprehensive explanation and list of possibilities were offered by Gardette et al. [9]. They proposed three possible reasons for the increased photo-oxidation of PP nanocomposites. The catalytic effect of heavy metal ions in the silicate is one of the items on their list as well, but they also mention the possible adsorption of the stabilizers on the surface of the silicate and the degradation of the surfactant used for surface modification.

The surface energy of the silicate is very high, the dispersion component of its surface tension is around 260 mJ/m² compared to 60 mJ/m² for CaCO₃ [24]. On the other hand, surface modification decreases surface energy significantly to values around 30 mJ/m². Although about 30 % of the silicate surface remains free after modification, it is still questionable if significant amounts of stabilizer can adsorb onto the surface. This explanation is questioned also by the fact that residual stabilizers could be removed quite easily from the composite in the experiments of Gardette et al. [9]. We have some doubts about the significance of surfactant degradation as well, although quite a few papers indicate that its decomposition starts at around 200 °C or even below it [7,25,26]. However, such conclusions are based almost exclusively on results obtained by TGA measurements carried out on the neat OMMT and not on the study of composites. Our samples were processed at 190 °C and we do not believe that considerable degradation of the surfactant took place under these conditions. Finally the effect of heavy metal ions is difficult to judge. However, the ions are located inside the silicate platelets, and only the surplus negative surface charge as well as the compensating ions of the surfactant come into contact with the polymer. Naturally, diffusion is possible, but not very probable.

On the other hand, the quite reactive MAPP was shown to react chemically with the surfactant under the conditions of processing [27]. Similarly, MAPP, but also the surfactant might interact or even react with the stabilizers, both with the phosphate, but especially with the phenolic antioxidant. Such reactions may consume the stabilizer and decrease stability drastically as shown for both components. The reactions do not yield the usual chinoidal compounds since discoloration does not increase significantly in the pres-
ence of MAPP (see Fig. 3.6) and yellowing is caused by the inherent color of the filler when OMMT is added (see Fig. 3.5). It is known in organic chemistry that maleic anhydride can acylate aromatic compounds including phenols. Acylation may occur either on the aromatic ring (C-acylation, Friedel-Crafts reaction) or on the phenolic –OH group (O-acylation). Both acids and bases catalyze nucleophilic substitution, i.e., O-acylation, but the reaction is faster in the presence of bases. Acylation of the aromatic ring may take place both on the phosphorus and the phenolic antioxidant, but O-acylation would result in a significant decrease in the efficiency of the primary antioxidant only. The resulting aromatic ester is not yellow, but it does not stabilize the polymer either. Besides acylation reactions, also the alkylation of the ring, the phenolic –OH group and the phosphor cannot be excluded as possible reactions either. According to literature sources quaternary ammonium salts may decompose at high temperatures resulting in the formation of alkenes [28]. Under appropriate conditions such compounds may enter both into C- and O-alkylation reactions with aromatic compounds which would also decrease the efficiency of the stabilizers. Although we expressed the opinion above that considerable degradation of the surfactant does not occur under the conditions of composite preparation, even limited degradation of the surfactant could consume some of the active stabilizer. According to literature sources silicates with acidic surfaces catalyze alkylation reactions [29]. Although according to an inverse gas chromatographic (IGC) study the surface of our silicate is more basic ($K_a = 0.40$) than acidic in character, a small number of electron acceptor groups can be also found on the surface ($K_a = 0.09$). Acidic groups on the surface of montmorillonite or the hydrolysis of the anhydride may also catalyze the transformation of the phosphate to phosphinic acid ester. Accordingly, both stabilizers are hindered in their stabilizing action or may be even consumed by reacting with the components. Naturally further study and experiments must be carried out to prove this tentative explanation.

3.5. Conclusions

Contrary to numerous claims published in the literature, which indicates the positive effect of layered silicates on the stability of polymer nanocomposites, our results clearly prove that both OMMT and MAPP accelerate degradation during processing and deteriorate the properties of PP composites. Residual stability decreases drastically with increasing amounts of both components, chain scission leads to the decrease of viscosity and to inferior strength and deformability. In spite of expectations, the effect of the components is independent of each other. Discoloration is caused mainly by the inherent color of the filler and it decreases with increasing exfoliation. The most probable reason for the decrease in stability is the reaction of the components with the stabilizers, but this explanation needs further verification. Processing conditions influence degradation considerably, increasing shear rate and longer residence times lead to more pronounced degradation. The basic stabilization of commercial grade polypropylenes is insufficient to protect the polymer against degradation and without additional stabilization processing under normal conditions results in products with inferior quality.
3.6. References

Chapter 4

Estimation of interphase thickness and properties in PP/layered silicate nanocomposites

4.1. Introduction

An interphase was shown to form in all heterogeneous polymers with properties different both from those of the matrix and the heterogeneity [1-4]. We do not have any reason to assume that such an interphase is absent in polymer/layered silicate nanocomposites. For uncoated fillers the thickness of the interphase depends on the strength of interaction between the phases [5,6]. The surface energy of NaMMT is large, its dispersion component is around 260 mJ/m$^2$, which decreases to the level of other coated fillers, to 30 mJ/m$^2$ upon organophilization [7]. Thus we can expect the development of a thick interphase in polymer/NaMMT composites and a strong change in thickness when surface modified clay is used. However, very little is known about interphase formation, and the thickness as well as properties of the interphase in polymer/layered silicate nanocomposites in spite of the crucial importance of this question.

As a consequence, the goal of this work was to study interphase formation and make an attempt to estimate the properties of the interphase in PP/layered silicate composites. PP composites were prepared with several montmorillonites with and without surface modification. The thickness and properties of the interphase were estimated with the help of a model from the mechanical properties of the composites. The benefits and the drawbacks of the approach are also discussed at the end of the chapter.

4.2. Background, the model

By assuming the spontaneous formation of an interphase in particulate filled polymers, the composition dependence of tensile yield stress was described with the following correlation [8-10]:

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

(4.1)

where $\sigma_y$ and $\sigma_{y0}$ are the yield stress of the composite and the matrix respectively, $\varphi$ is the volume fraction of the filler or reinforcement in the composite and $B$ is a parameter expressing the load-bearing capacity of the filler. $B$ is determined by the contact surface between the polymer and the filler expressed by the specific surface area of the filler ($A_f$) and by the properties of the interphase in the following way:

---

where $A_f$ and $\rho_f$ are the specific surface area and density of the filler, while $\ell$ and $\sigma_{yi}$ are the thickness and yield stress of the interphase.

If we prepare composites from fillers with different sizes and thus different specific surface areas, we can determine interphase properties with the help of Eq. 4.2. By assuming constant properties for the interphase we can write Eq. 4.2 in the following, simplified form:

$$B = (1 + A_f \rho_f \ell) \ln \frac{\sigma_{yi}}{\sigma_{y0}}$$

According to Eq. 4.3, if we plot parameter $B$ against the specific surface area of the filler we should obtain a straight line and we can calculate interphase properties from its slope and intersection, i.e.

$$a = \ln \frac{\sigma_{yi}}{\sigma_{y0}} \quad \text{and} \quad b = a \ell \rho_f$$

The model was successfully used for the determination of reinforcement in a large number of polymer/layered silicate nanocomposites [11,12]. To use the model for the determination of interphase properties we must assume that the surface characteristics of the original OMMT particles and individual, exfoliated silicate layers are identical. We must also know the particle size or the specific surface area of the filler accurately, which is one of the most difficult parts of the exercise. Moreover, particle characteristics cannot change during the preparation of the composites. Accordingly, we dedicate considerable attention to particle characteristics and composite structure in subsequent sections.

### 4.3. Experimental

A commercial grade polypropylene supplied by TVK, Hungary was used for the experiments. The polymer had a number average molecular mass of 97 kg/mol and a polydispersity of 5.0. Its melt flow index was 2.5 g/10 min (230 °C/2.16 kg) and it contained an additive package consisting of 500 ppm Irganox 1010 phenolic antioxidant, 1000 ppm Irgafos 168 phosphate stabilizer, both from Ciba Specialty Chemicals, and 400 ppm DHT-4A acid scavenger. Earlier experiments showed that the basic stabilization of commercial polymer grades is insufficient to protect the polymer against degradation during processing and the subsequent rheological study [13,14]. As a consequence, 2000 ppm Irganox 1010 and 2000 ppm Irgaphos 168 antioxidant were added to the composites during sample preparation. Two sodium silicates were supplied by Süd-Chemie AG and both were sieved to supply four fillers with different sizes and surface areas. The four organophilic silicates were acquired from Rockwood Clay Additives. The most important characteristics of the silicates are listed in Table 1. The surface of the organophilic clays was modified with the same surfactant, distearyl dimethyl ammonium chloride. The Polybond 3200 maleated PP coupling agent ($M_w = 120$ kg/mol, maleate content: 1 wt%) used in some experiments was obtained from Uniroyal Chemi-
The silicate content of the PP/NaMMT and the PP/OMMT composites changed between 0 and 30 vol% in 5 vol% steps. This filler content is much larger than the usual 5-10 wt% used in such experiments, but we did not expect any exfoliation in NaMMT and even in PP/OMMT composites not containing a coupling agent. The clay content of PP/OMMT/MAPP composites changed between 0 and 7 vol% at 5 vol% MAPP content. We must emphasize again that we did not want to achieve large extent of exfoliation, but intended only to modify interfacial interactions by the use of MAPP. Composites were prepared in a Brabender W 50 EH internal mixer attached to a Haake Rheocord EU 10 V driving unit at 190 °C and 80 rpm. Charge volume was 42 cm$^3$. The homogenized samples were compression molded into 1 mm thick plates using a Fontijne SRA 100 machine at 190 °C and 3 min preheating and 3 min compression time.

The gallery structure of the silicate was characterized by X-ray diffraction (WAXS) using a Phillips PW 1830/PW 1050 equipment with CuK$\alpha$ radiation at 40 kV and 35 mA. The morphology of the samples was examined by scanning electron microscopy (SEM) using a Jeol JSM 6380 apparatus. Samples were etched in an oxidative solution to increase contrast and visualize larger structural units. TEM was not done, since we did not focus on exfoliation, but on interfacial interactions and interphase formation. Rheological measurements were carried out using a Paar Physica UDS 200 apparatus at 200 °C 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. The tensile properties of the samples were measured using an Instron 5566 apparatus. Young’s modulus was determined at 0.5 mm/min while yield and ultimate properties at a cross-head speed of 50 mm/min. All characteristics were derived from five parallel measurements.

4.4. Results and discussion

The results are discussed in several sections. Because of their importance particle characteristics and composite structure will be presented first, followed by the estimation of reinforcement in the next section. We calculate interphase properties and present the limitation of the approach in the final section.

4.4.1. Particle characteristics

As Eq. 4.3 shows, the approach assumes the knowledge of the contact surface between the silicate and the polymer. If particle structure does not change during processing, this is proportional to the specific surface area of the filler appearing in the equation ($A_f$). Since we do not expect any or at least not much exfoliation in PP/NaMMT and PP/OMMT composites, the determination of the BET surface area of the silicates seemed to be sufficient for the calculations. The BET area measured by nitrogen adsorption is included into Table 4.1 ($A_{BET}$). We can see that very contradictory results were obtained both for NaMMT and OMMT. The very large surface areas measured for NaMMT result from the large surface energy of the silicate and possibly also from the
intrusion of nitrogen into the space inside the galleries. The large surface area measured would correspond to approximately 0.02 µm particle size which obviously contradicts reality as the second column of the table shows.

We also determined particle size with the intention to calculate specific surface area from it. We used two methods, the usual laser light scattering (Malvern Master Sizer 2000, dry mode, 2 bar, 50 % feed rate), but we also derived particle size and particle size distribution by SEM analysis. The particle size distribution of one of the silicates obtained by the two methods is presented in Fig. 4.1. We can see that much broader distribution and consequently larger average sizes were obtained by the scattering method than by SEM analysis. The possible reason for the discrepancy is aggregation, i.e. the adherence of smaller particles to larger ones which cannot be distinguished by scattering. As a result of the analysis we concluded that the most reliable method is the determination of particle size distribution by SEM, thus we derived specific surface area from this size by assuming spherical shape of the particles and we used these numbers in the calculations.

Table 4.1  Particle characteristics of the silicates used in the experiments.

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Particle size&lt;sup&gt;a&lt;/sup&gt; (µm)</th>
<th>D[4,3]&lt;sup&gt;b&lt;/sup&gt; (µm)</th>
<th>( A_{\text{BET}} ) (m²/g)</th>
<th>( A_{\text{F}} ) &lt;sup&gt;c&lt;/sup&gt; (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaMMT1</td>
<td>3.8</td>
<td>6.1</td>
<td>98.0</td>
<td>0.56</td>
</tr>
<tr>
<td>NaMMT2</td>
<td>4.5</td>
<td>5.9</td>
<td>84.0</td>
<td>0.48</td>
</tr>
<tr>
<td>NaMMT3</td>
<td>10.5</td>
<td>59.1</td>
<td>84.0</td>
<td>0.20</td>
</tr>
<tr>
<td>NaMMT4</td>
<td>19.3</td>
<td>84.5</td>
<td>95.0</td>
<td>0.17</td>
</tr>
<tr>
<td>Nanofil 8</td>
<td>2.1</td>
<td>4.5</td>
<td>9.2</td>
<td>1.59</td>
</tr>
<tr>
<td>Nanofil 5</td>
<td>4.4</td>
<td>6.3</td>
<td>11.6</td>
<td>0.76</td>
</tr>
<tr>
<td>Nanofil 15</td>
<td>16.5</td>
<td>85.8</td>
<td>5.1</td>
<td>0.20</td>
</tr>
<tr>
<td>Nanofil 948</td>
<td>19.9</td>
<td>39.4</td>
<td>3.8</td>
<td>0.17</td>
</tr>
</tbody>
</table>

<sup>a</sup> determined from the analysis of SEM micrographs  
<sup>b</sup> determined by laser light scattering  
<sup>c</sup> calculated from particle size (column 2) assuming spherical shape  

4.4.2. Structure

Considerable exfoliation usually is not observed in PP/silicate composites not containing a functionalized PP coupling agent [15-19]. In order to be able to use specific surface areas determined for the neat fillers in our calculations, the fillers must remain intact during compounding; apart from homogenization structure should not change. We checked structure and the change in silicate structure by various methods.
Figure 4.1  Particle size distribution determined by two methods for the Nanofil 5 organophilic silicate; (○) laser light scattering, (□) SEM analysis.

XRD patterns of the components and selected composites are presented in Fig. 4.2. In the case of complete or significant exfoliation the silicate reflection must disappear or change considerably in the patterns. We do not see such changes; the silicate reflection is quite pronounced both in the PP/NaMMT and PP/OMMT composites. We extended the XRD study to all composites and the results unambiguously indicate that a large part of the silicate remains intact during processing. This result was further confirmed by the analysis of SEM micrographs taken from the fracture surface of composites containing NaMMT.

Another method to check structure and extensive exfoliation is rheology. Frequency sweeps are often used to detect the formation of a silicate network. At large extent of exfoliation so many individual platelets are distributed in the polymer matrix that they interact with each other, and edge-to-plate interactions lead to the formation of a house of card structure [17,20-22]. Although aggregation or the formation of the network can be detected also by changes in storage modulus or complex viscosity in the low frequency range, Cole-Cole plots show them much more sensitively. The components of complex viscosity are plotted against each other in such plots and the deviation from a semi-arc or a distorted semi-arc is a clear indication of structural effects [23,24]. The Cole-Cole plots of the composites containing NaMMT in different amounts are presented in Fig. 4.3. The corresponding trace of the neat PP is also included as reference. We can see that the Cole-Cole plot of the matrix forms a part of a semi-arc in the range of the measurement. Similar plots were obtained for composites containing the silicate up to 20 vol% indicating the absence of structural effects. On the other hand, the
shape of the traces changes drastically above 20 vol%, the amount of silicate is large and the particles clearly aggregate above this filler content. Accordingly, calculations are valid only below this loading level. We may also consider the fact that the viscosity of the composites is smaller than that of the polymer itself. We must take into consideration several factors here. One is definitely the possible degradation of the polymer in the presence of the silicate, as shown by several papers [13,14]. However, we added considerable amount of stabilizers to the commercial grade PP to avoid degradation, thus this effect can be excluded as possible reason for decreased viscosity. Two factors acting simultaneously remain and their combined effect leads to the changes in viscosity observed in Fig. 4.3. Fillers are known to increase viscosity due to the adsorption of molecules onto their surface and this effect must be considered also here. The surface energy of NaMMT is very high thus adsorption is significant. The other effect is the selective adsorption of large molecules on the surface of the particles [25]. This leads to the decrease of the average molecular weight of the remaining, non-adsorbed molecules forming the matrix, which results in a decrease of viscosity. With increasing silicate content the first effect becomes dominating and the formation of aggregates further increases viscosity.

Figure 4.2 XRD traces of two of the silicates (Nanofil 5, NaMMT3) and that of selected composites. Composition: 5 vol% silicate, 5 vol% MAPP.
Interphase thickness and properties

Figure 4.3  Cole-Cole plots showing the change of structure (aggregation) above 20 vol% silicate content in PP/NaMMT1 composites. (•) PP, (Δ) 5, (▽) 10, (○) 15, (■) 20, (◇) 25, (▲) 30 vol% silicate.

The Cole-Cole plot of the viscosity of composites containing OMMT without a coupling agent is presented in Fig. 4.4. Unfortunately the traces deviate very much from the semi-arc of homogeneous composites already above 10-15 vol% silicate content, thus we cannot claim that the particles remain intact. Quite surprisingly considerable exfoliation must take place even in the absence of a compatibilizer. The change of particle structure is further corroborated by Fig. 4.5 showing the original particles (Fig. 4.5a) and the dispersed structure of a composite (Fig. 4.5b). Although large particles are present also in the composite, their size changed considerably compared to that of the neat filler. Accordingly, we cannot use the particle size and the surface area of the original filler in our calculations, but must derive a surface area from the analysis of the composites.

Since we observed considerable changes in particle structure already in composites not containing MAPP, we may expect even more in those prepared with the compatibilizer even if we used only 5 vol%. We must remind the reader that we did not intend to achieve complete exfoliation, but change the strength of interactions and model PP nanocomposites as prepared in practice. Although WAXS indicated unchanged silicate structure, the Cole-Cole plot presented in Fig. 4.6 indicates differently. We plotted only three traces in the figure, that of the neat PP, the one for the PP/OMMT composite containing 5 vol% silicate, and the trace obtained for the composite containing both the clay and MAPP in 5 vol%. We can see that the latter deviates from the semi-arc considerably already at this low clay content indicating considerable change in structure, probably exfoliation.
Figure 4.4  Complex viscosity of PP/OMMT composites plotted in the Cole-Cole representation.  

(✧) PP, (Δ) 5, (▽) 10, (○) 15, (□) 20, (◇) 25, (◇) 30 vol% Nanofil 8 silicate.
Figure 4.5  SEM micrographs showing the particle structure of neat Nanofil 8 silicate and the size, shape and distribution of the particles in a PP composite; a) Nanofil 8, b) PP/5 vol% silicate.

Figure 4.6  Comparison of the Cole-Cole plot of PP/OMMT and PP/OMMT/MAPP composites at 5 vol% Nanofil 5 content. MAPP content: 5 vol%.
Chapter 4

The SEM micrographs taken from the same composites further confirm these observations (Fig. 4.7), a much finer distribution of smaller particles is observed in the composite containing the compatibilizer than without it. These results clearly prove that only surface areas derived from the analysis of composite structure can be used for the calculation of interphase thickness and properties for PP/OMMT and PP/OMMT/MAPP composites, since the original structure (size, distribution) of particles changes considerably during processing.

4.4.3. Reinforcement

Our estimate about the thickness and properties of the interphase is based on the composition dependence of mechanical properties. Changes in mechanical properties offer information about the extent of reinforcement which is related to structure (exfoliation) and interactions. The composition dependence of yield stress is the easiest to evaluate, since the effect of strain hardening can be neglected at the relative small deformations involved. The tensile yield stress of three sets of composites is plotted against silicate content in Fig. 4.8. We can see that yield stress is the smallest for the PP/NaMMT and the largest for the PP/OMMT/MAPP composites reflecting very much the structural changes discussed in the previous section.

We can express these differences quantitatively if we apply the model expressed in Eqs. 4.1 and 4.2 to the results and plot yield stress against composition in a linear form. The correlation of the natural logarithm of reduced yield stress, which is composite yield stress divided by the second term in Eq. 4.1, is plotted against silicate content in Fig. 4.9. We can see that in spite of the considerable scatter in some cases, the correlations are straight lines and the increasing slope indicates the change in the extent of reinforcement. In accordance with the observed changes in structure, this is the largest for the PP/OMMT/MAPP composite. The slopes of the straight lines, i.e. parameter $B$, can be used for the estimation of interphase thickness and property, if we can come up with reasonable values for contact surface, that is for $A_f$ in Eq. 4.3.

4.4.4. Interphase properties

We calculated the thickness of the interphase using specific surface areas derived in various ways. The procedure is demonstrated by Fig. 4.10 showing the correlation between parameter $B$ and the specific surface area calculated from particle sizes determined by SEM ($A_{fc}$) for PP/NaMMT composites. The resulting interphase thickness is 0.57 $\mu$m. The importance of the specific surface area used is shown by the fact that we obtained negative interphase thickness when we calculated it from actually measured surface areas ($A_{BET}$, see Table 4.2). Naturally, negative interphase thickness does not make any sense. More data points, i.e. more silicates used, would have increased the reliability of the determination considerably, but unfortunately we were not able to acquire more samples with the same chemical and crystallographic characteristics, but different particle sizes. The thickness determined in this composite is approximately three times as large as thicknesses derived for PP/CaCO$_3$ composites with the
Figure 4.7  Change in composite structure as an effect of MAPP addition. Silicate: Nanofil 5, silicate content: 5 vol%, MAPP content: 5 vol%. a) PP/OMMT, b) PP/OMMT/MAPP.
Figure 4.8  Composition dependence of tensile yield stress of the three different types of composites; (O) PP/NaMMT3, (□) PP/Nanofil 5, (●) PP/Nanofil 5/MAPP(5 vol%).

Figure 4.9  Tensile yield stress of the composites of Fig. 4.8 plotted against silicate content in the linear representation of the model (see Eq. 4.1); (O) PP/NaMMT3, (□) PP/Nanofil 5, (●) PP/Nanofil 5/MAPP(5 vol%).
same approach (see Table 4.2). However, we can explain the formation of the thicker interphase easily with the much larger surface energy of NaMMT compared to CaCO$_3$. Interphase thickness was found to correlate very closely with surface energy in composites containing uncoated fillers [5,6].

![Figure 4.10](image)

**Figure 4.10**  Linear correlation between parameter $B$ and specific surface area ($A_{fc}$) for PP/NaMMT composites. Determination of interphase thickness (0.57 µm).

We carried out similar calculations for the other two sets of composites with all the surface areas which we could derive in different ways. Unfortunately most of the results were unacceptable or very unreliable. The best values were obtained using specific surface areas determined by the quantitative analysis of SEM micrographs ($A_{fc}$) taken from the etched surface of composites. The results are compiled in Table 4.2 and values determined in various polymer/CaCO$_3$ composites are also included as reference [6,26]. We can see that a very wide range of interphase thicknesses and yield stresses were obtained for the various composites. The most reliable of these are those obtained for NaMMT from calculated surface areas ($A_{fc}$, $A_{fcc}$) since the change in filler characteristics is the smallest here. The values calculated from surfaces obtained by BET are completely misleading and make no sense. Very thin interlayers are estimated for OMMT composites both with and without MAPP if we use $A_{fcc}$ values, i.e. surface area derived from SEM micrographs. Unfortunately, these are also doubtful both because of difficulties in the determination of particle size distribution, but also because of the large change in structure during processing as shown in Section 4.4.2. Finally, we must mention also the yield stress values predicted for the interphase developing in the various composites. Very large values are obtained for some of the composites, which are
probably not reliable or true, since, for example, the weaker interaction developing in PP/OMMT composites must lead to the formation of a softer, weaker interphase. We may conclude that the numbers in Table 4.2 must be treated with the greatest caution, because of the small number of fillers tested, the difficulties in the determination of contact surface, and especially because of the considerable change in the particle characteristics of the filler during processing.

### Table 4.2  
Interphase characteristics of PP/layered silicate composites; similar properties of polymer/CaCO$_3$ composites are shown for comparison.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>$A_f^a$ (m$^2$/g)</th>
<th>Thickness (µm)</th>
<th>Yield stress (MPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>un-coated</td>
<td>coated</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>coated</td>
<td>un-coated</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>CaCO$_3$</td>
<td>$A_{IBET}$</td>
<td>0.17</td>
<td>0.33</td>
<td>58.6</td>
</tr>
<tr>
<td>PMMA</td>
<td>CaCO$_3$</td>
<td>$A_{IBET}$</td>
<td>0.18</td>
<td>0.39</td>
<td>132.4</td>
</tr>
<tr>
<td>PVC</td>
<td>CaCO$_3$</td>
<td>$A_{IBET}$</td>
<td>0.23</td>
<td>0.40</td>
<td>106.8</td>
</tr>
<tr>
<td>PP</td>
<td>NaMMT</td>
<td>$A_{IBET}^b$</td>
<td>&lt;0</td>
<td>–</td>
<td>117.5</td>
</tr>
<tr>
<td>PP</td>
<td>NaMMT</td>
<td>$A_{fc}^c$</td>
<td>0.57</td>
<td>–</td>
<td>63.8</td>
</tr>
<tr>
<td>PP</td>
<td>NaMMT</td>
<td>$A_{fc}^c$</td>
<td>0.34</td>
<td>–</td>
<td>46.3</td>
</tr>
<tr>
<td>PP</td>
<td>OMMT</td>
<td>$A_{IBET}$</td>
<td>–</td>
<td>0.04</td>
<td>–</td>
</tr>
<tr>
<td>PP</td>
<td>OMMT</td>
<td>$A_{fc}^b$</td>
<td>–</td>
<td>0.20</td>
<td>–</td>
</tr>
<tr>
<td>PP</td>
<td>OMMT</td>
<td>$A_{fc}^c$</td>
<td>–</td>
<td>0.04</td>
<td>–</td>
</tr>
<tr>
<td>PP</td>
<td>OMMT/MAPP</td>
<td>$A_{fc}^c$</td>
<td>–</td>
<td>0.06</td>
<td>–</td>
</tr>
<tr>
<td>PP</td>
<td>silicate$^d$</td>
<td>$A_{fc}^c$</td>
<td>0.23</td>
<td>51.2</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ the method of the determination of specific surface area  
$^b$ calculated from particle size assuming spherical shape  
$^c$ calculated from particle size determined in composites by SEM  
$^d$ average values calculated from all available data for all three series of composites

However, we may obtain a more reliable picture about interphase properties from the overall correlation between parameter $B$ and $A_{fc}$ (Fig. 4.11). As we see the correlation is reasonable, in spite of the large deviation of some of the points from the general tendency. The analysis of individual series shows the difficulty of deriving reliable values for slope and intersection which would allow the calculation of interphase properties. Fig. 4.11 also indicates that the effect of structural changes is more important in the present case than differences in interactions. We must always keep in
mind that two factors must be considered always in these calculations: changing surface area and the strength of interaction. NaMMT has the highest surface energy, i.e. it should form the strongest interaction with the polymer, but contact surface is the smallest in this case. The surface energy of OMMT is much smaller [7], but the change of particle size and limited exfoliation increased contact surface. Finally, both the size of the interface and the strength of interaction are larger in composites containing also MAPP. The separation of the two effects is impossible in our case. If we use the straight line in Fig. 4.11 to calculate the overall properties of the interphase, we obtain 0.23 µm as thickness and 51.2 MPa as interphase yield stress, values which are very close to those determined for other polymer/filler composites. Naturally this assumes the same interaction between NaMMT and the coated silicates, which is not true. However, the calculation of overall characteristics of the interphase gives at least some idea about interphase formation and properties in PP/layered silicate composites.

![Figure 4.11](image-url)

**Figure 4.11** Parameter B plotted against the specific surface area ($A_{fcc}$) derived from SEM analysis for all composites studied. (○) PP/NaMMT, (□) PP/OMMT, (●) PP/OMMT/MAPP (5 vol%). See overall interphase properties in the last line of Table 4.2.

### 4.5. Conclusions

The experiments carried out with NaMMT and OMMT with different particle sizes and model calculations proved the formation of an interphase in the PP composites studied. The determination of interphase properties, however, was hampered by several factors. First of all, the particle size of the filler changed quite considerably in
PP/OMMT composites in spite of earlier observations and expectations. Particle characteristics changed even further when a relatively small amount of functionalized polymer (MAPP) was added to the composite. As a consequence, the estimation of the contact surface between the silicate and the polymer became extremely difficult. In spite the uncertainties some overall values of interphase properties were obtained using the results of all composites prepared. The prediction for the average thickness of the interphase is 0.23 \( \mu m \) and we obtained 51.2 MPa for interphase yield stress, but this estimate neglects the different interactions developing in composites containing the uncoated and the modified silicate, respectively.

4.6. References


Chapter 5

Effect of clay modification on the structure and properties of PA6 nanocomposites

5.1. Introduction

According to the vast number of papers published on layered silicate nanocomposites, the extent of exfoliation depends on several factors including the type and amount of the surfactant used for organophilization [1,2], the polymer [3], the presence of coupling agents and other dispersion aids [4-15], processing conditions [16-23], etc. Unfortunately the role and relative weight of these factors changes from system to system, thus unambiguous relationship could not be established among them. Probably this is the main reason for the contradictory conclusions published about the role of surfactant structure on the extent of intercalation and exfoliation. We referred to the contradictory conclusions of Fornes et al. [1] and Vaia [2] on this question already in Section 1.2.2. The structure of the surfactant obviously influences intercalation and exfoliation, but because of the effect of other factors, its role is not completely clear.

Since the type and amount of surfactant seem to play a crucial role in structure development, the goal of our study was to compare the effect of two different types of organophilization on the structure and properties of PA nanocomposites. Commercial organophilic clays are modified with ammonium salts as surfactants. In a paper our Belgian partners proved that phosphonium salts are more stable, thus more suitable for the preparation of PA composites than ammonium based surfactants [24-26]. In this chapter we compare a clay modified with a phosphonium salt to a commercial product organophilized with an ammonium surfactant of similar structure. Sodium montmorillonite is used as reference filler showing no or little exfoliation. PA was selected as matrix, since the largest extent of exfoliation and the best properties were achieved in this polymer [1,27-31]. Unlike in most papers, the clays were characterized extensively, the complex structure discussed previously (particles, tactoids, platelets, network) was assumed, and reinforcement as well as the extent of exfoliation was estimated quantitatively.

5.2. Experimental

Cloisite 20A modified with bis(hydrogenated tallowalkyl) dimethyl ammonium chloride (Scheme 5.1) (NoMMT) and sodium montmorillonite (NaMMT) were obtained from Rockwood Additives Ltd. Phosphonium organoclay (PoMMT) was prepared as

follows: 3 kg of as-received NaMMT were modified with 1.1 kg of trihexyl tetradecl phosphonium salt (Scheme 5.2) in supercritical carbon dioxide medium at 200 bar, 40 °C, upon constant stirring for 24 hours in a high pressure pilot reactor of a 50 litre capacity. After depressurisation, a dry and homogeneous powder is obtained and used without further purification. The process is described elsewhere in detail [32]. The polyamide-6 (density: 1.14 g/cm³, MFI measured at 230 °C and 2.16 kg: 4 g/10 min) used as matrix was obtained from Domo Chemicals (Domamid 27).

![Scheme 5.1 Ammonium salt present in Cloisite 20A (n, m = 1 to 3).](image)

![Scheme 5.2 Trihexyl tetradecl phosphonium chloride.](image)

The gallery structure of the fillers and the composites was characterized by X-ray diffraction (WAXS) using a Philips PW 1830/PW 1050 equipment with CuKα radiation at 40 kV and 35 mA anode excitation. The surfactant content of the silicates was determined by thermogravimetric analysis (TGA) using a Perkin-Elmer TGA6 apparatus. 20 mg of the various clays was heated from 35 to 750 °C with 10 °C/min rate in nitrogen atmosphere and the total weight loss minus the loss measured up to 150 °C was identified as the amount of surfactant used for the organophilization of the silicate. Weight loss below 150 °C was assigned to the evaporation of water. Surface coverage was calculated from the theoretical surface area of the completely exfoliated clay and also from the ion exchange capacity of the clay (92.6 meq/100 g) [33-35]. The specific surface area of the fillers was determined by nitrogen adsorption (BET method) using an Autosorb 1 (Quantachrome, USA) apparatus. Inverse Gas Chromatography (IGC) measurements were carried out using a Perkin Elmer Autosystem XL apparatus with columns of 50 cm length and 6 mm internal diameter to determine the surface energy of the clays. Vapor samples of 5-20 µl were injected into the column and retention peaks were recorded by flame ionization (FID) detector. High purity nitrogen was used as carrier gas and its flow rate changed between 5 and 20 ml/min depending on measurement temperature and on the type of adsorbent. Each reported value is the result of three parallel runs. Measurements were done both on samples stored under ambient conditions and after preconditioning in the column at 140 °C for 16 hours. The particle size
and size distribution of the silicates were determined by SEM analysis using a Jeol JSM 6380 LA apparatus. The characteristics of the clays used in the study are summarized in Table 5.1.

Table 5.1  The most important characteristics of the clays used in the study.

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Amount of surfactant (wt%)</th>
<th>Surface coverage (%)</th>
<th>Gallery structure</th>
<th>Surface energy $\gamma_s$ (mJ/m$^2$)</th>
<th>Particle size$^d$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nominal</td>
<td>Measured</td>
<td>$A_f^a$</td>
<td>CEC$^b$</td>
<td>$2\theta$ (°)</td>
</tr>
<tr>
<td></td>
<td>NoMMMT</td>
<td>38</td>
<td>106</td>
<td>120</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>PoMMMT</td>
<td>27</td>
<td>67</td>
<td>74</td>
<td>3.8</td>
</tr>
</tbody>
</table>

$^a$ calculated from the theoretical surface area of completely exfoliated clay [33-35]  
$^b$ calculated from the ion exchange capacity of the clay  
$^c$ measured at different temperatures and extrapolated to 100 °C  
$^d$ most frequent particle size determined from SEM micrographs

Composites containing 0.5, 1, 2, 3, 5 and 7 vol% clay were homogenized using a Berstorff ZE 34 Basic twin-screw extruder with the temperature program of 60-210-225-230-230-230-230 °C and 50 rpm screw speed. Tensile bars were injection molded using a Demag IntElect 50/330-100 injection molding machine at 40-235-240-250-260 °C temperatures, 50 mm/s injection rate, 350 bar holding pressure and 20 s holding time. The temperature of the mold was set to 60 °C and cooling time to 45 s.

XRD traces were recorded on the composites as described above. Morphology was characterized by electron microscopy. Transmission electron micrographs were taken from ultrathin sections prepared with a Leica EM FC6 apparatus (50-80 nm) by a Tecnai G2 Twin microscope (LaB6, 200 kV). SEM micrographs were taken by a Jeol JSM 6380 LA apparatus on fracture surfaces created by cryogenic fracture of neat and deformed samples. 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. The specimens were conditioned in an atmosphere of 50 % RH and 23 °C for 3 days before testing.

5.3. Results and discussion

The results are presented in several sections. First we discuss clay characteristics which are relevant for exfoliation and structure development. The complex structure
of the composites is demonstrated next, while mechanical properties, reinforcement and an estimation of the extent of exfoliation are presented in the last section.

5.3.1. Clay characteristics

As described previously, the type and amount of the surfactant used are crucial for exfoliation and structure development. These parameters determine the arrangement of the surfactant among the galleries of the clay, thus also gallery distance. The nominal amount of surfactant used for organophilization is listed in Table 5.1, together with the quantity determined by TGA. Since the molecular mass, size and shape of the compounds are different, amount alone does not determine surface coverage. Surface coverage was calculated from the theoretical specific surface area of completely exfoliated clay (750 m$^2$/g [33-35]), but also from the ion exchange capacity of the clays. The calculated values agree quite well. We can conclude from these results that the surface coverage of the commercial clay is larger than its ion exchange capacity, while the surface of the clay modified with the phosphonium salt is not covered completely.

Surface coverage is one of the most important characteristics of modified clays. However, gallery distance and the ease of exfoliation depend also on the arrangement of the surfactant molecules inside the galleries. Gallery structure is reflected well by WAXS traces recorded on clays in the lower 2$\theta$ range of the spectrum. The shape and position of the silicate reflection indicates gallery distance and the regularity of stacking. The XRD traces of the three clays used in the study are presented in Fig. 5.1. Peak positions and layer distances determined from the traces are included in Table 5.1. The position of the silicate reflection of NaMMT indicates the presence of water confirmed also by TGA measurements (6.6 wt%). The characteristic silicate reflection of the commercial NoMMT is located at smaller 2$\theta$ value than that of the clay modified with the phosphonium salt indicating larger gallery distance ($d_{001} = 2.7$ vs. 2.3 nm) [36]. It is interesting to note that different XRD pattern and larger gallery distance (3.5 nm) was determined earlier for commercial clays modified with a similar surfactant (distearyldimethyl ammonium chloride). The difference probably results from the amount of surfactant used. Cloisite 20A was treated with 38 wt% surfactant, while 44 wt% was used in the other case. The larger amount resulted in more regular arrangement of the platelets and larger layer distance, which would be expected to facilitate exfoliation during processing. Earlier we speculated that surfactants with a single long aliphatic chain added in amounts to achieve approximately 100 % surface coverage lay parallel with the surface of the platelets [36]. One chain covers each surface, thus two aliphatic chains are located between each gallery. In the case of surfactants with two long aliphatic chains and large coverage, one chain was predicted to orientate vertically to the surface resulting in a layer distance corresponding to the thickness of 6 aliphatic chains. The gallery distances determined here indicate 3 and 4 aliphatic chains lying parallel with each other for the clays modified with the phosphonium and the ammonium salt, respectively. Such an arrangement is improbable thus we may assume that one chain of the surfactant is tilted in Cloisite 20A. It is more difficult to predict the arrangement of the phosphonium salt, but the relatively sharp peak in the XRD spectrum indicates considerable regularity in the stacking of the platelets, and we may assume that one of the shorter chains is positioned at a certain angle to the platelet.
Another important characteristic is the surface energy of the silicate. The dispersion component of the surface energy of the clays measured by IGC is also listed in Table 5.1. The surface energy of the uncoated clay is very high. Coverage with the surfactant decreases surface tension considerably. This leads to weaker forces among the platelets and easier exfoliation, but also to weaker interaction with the polymer matrix. Decreased interaction may result in less reinforcement in the end, and not to improved “compatibility” as claimed in many papers [33,37,38]. Another characteristic which can influence structure development and the final morphology of the composite is particle size that is rarely considered in publications. If we accept the model of Paul [16] for the mechanism of exfoliation, larger particles need more time to exfoliate completely. The particle size of the fillers was determined by laser light scattering and by the analysis of SEM micrographs. The most frequent particle size determined from SEM micrographs is around 10 µm and very similar for the three silicates (see Table 5.1), but we must mention that all three fillers contain also large particles with sizes up to 60-80 µm in detectable amounts. The particle analysis done by scattering confirmed these results. It yielded an average particle size of about 20 µm for all three fillers and a size distribution range between 0.3 and 80 µm. Realistically we cannot expect the complete exfoliation of these particles and they might influence properties considerably.

5.3.2. Structure

The standard methods for the characterization of layered silicate polymer
nanocomposites are XRD and TEM. The latter technique is used to prove the presence and dispersion of individual silicate layers, while the disappearance of the silicate reflection from the XRD trace recorded on composites is frequently claimed to indicate complete exfoliation [4,7,39,40]. Although this latter claim was proved to be incorrect on several occasions [41,42], XRD may offer information about the gallery structure of the silicate in the composite and the amount of non-exfoliated, ordered stacks of clay platelets. The XRD traces of three composites containing the clay in 7 vol% are compared to each other in Fig. 5.2. Several changes can be observed in the shape of the traces and the position of the silicate peak, if we compare them to those presented in Fig. 5.1. The intensity of the reflection of NaMMT is small as usual, but its position moved towards smaller angles. The only change expected is the evaporation of water, but this would decrease and not increase gallery distance. The only explanation for the shift is the limited intercalation of the polymer into the galleries leading to the change of interlayer distance from 1.2 to about 1.7 nm. The small intensity of the wide peak indicates limited order in the stacking of the layers.

![Figure 5.2](image)

**Figure 5.2**  Gallery structure of the studied clays in PA composites containing 7 vol% silicate; a) NaMMT, b) NoMMT, c) PoMMT.

The reflection of the clay organophilized with the ammonium salt also shifted towards smaller angles indicating increasing gallery distance. The increased distance is around 3.35 nm compared to the 2.7 nm of the neat clay independently of composition. Rather surprisingly the reflection of the silicate became sharper at least at 7 vol% clay content than that of the neat clay. These changes indicate intercalation and increased order for larger tactoids and particles, and incomplete exfoliation. However, the strong intensity of the silicate reflection shows the presence of considerable amounts of non-
exfoliated silicate. On the other hand, the XRD trace of the clay modified with the phosphonium salt changed completely differently. The intensity of the reflection decreased considerably, it broadened and moved towards larger angles, i.e. to smaller gallery distances (to 2.0 from 2.3 nm). These changes are quite difficult to explain. We may speculate that one part of the silicate may exfoliate, but some particles remain intact or even loose small molecular weight components (water) resulting in smaller gallery distance. We must call the attention here to the fact that the surface coverage of this filler is only around 70%, which, in the case of uneven distribution of the surfactant, may explain the changes observed.

We determined the intensity of the silicate reflection by subtracting the baseline and integrating the area under the peak. The result is presented in Fig. 5.3. The differences in intensity are clear. The small intensity is usual and normal for NaMMT because of the irregular stacking of the layers. On the other hand, the difference between the two organophilic clays is rather surprising especially if we consider that the intensity of the silicate reflection was approximately the same in the neat clays (see Fig. 5.1). Although it is extremely dangerous to draw farfetched conclusion from this analysis, since intensity depends on a number of factors including regularity of stacking, orientation and amount, we may tentatively assume that the composites prepared with Cloisite 20A contain more non-exfoliated clay particles and/or tactoids than those containing the phosphonium modified silicate.

![Figure 5.3](image)

**Figure 5.3** Composition dependence of the intensity of the silicate reflection in PA/clay nanocomposites; amount of non-exfoliated silicate; (Δ) NaMMT, (□) NoMMT, (○) PoMMT.
In spite of the uncertainty of the analysis, TEM micrographs offer some support for this conclusion (Fig. 5.4). Large compact particles can be seen in the micrographs taken from the composite containing NaMMT as expected (see Fig. 5.4a). We must call, however, the attention to several facts. The size of the particle or tactoid in Fig. 5.4a is much smaller than the original particle size of the silicate (around 10 µm). This indicates some break down of the filler in spite of the lack of surface modification. The change agrees well with the increasing gallery distance observed and it is also supported by the presence of small platelets and tactoids in Fig. 5.4a. We must emphasize though that large particles must be present, but cannot be seen in the micrograph because of its small scale.

Figure 5.4  *Exfoliation and dispersion of clay in PA composites at 3 vol% silicate content; TEM micrographs; a) NaMMT, b) NoMMT, c) PoMMT.*
The micrographs taken from the composites prepared with the two organophi-lized clays confirm even more our conclusions presented above. More compact structural entities can be seen in the composite containing Cloisite 20A (Fig. 5.4b), while a more homogeneous distribution of platelets and tactoids is shown by Fig. 5.4c. We must emphasize again the danger of drawing conclusions about the overall structure of the composites from the TEM micrographs because of the limited area scanned and because of the dependence of the view obtained on sampling.

The possible presence of larger structural units or even particles is usually ignored, only one paper out of 100 mentions this possibility [43-45]. The possible reason is that everyone hopes for complete exfoliation, on the one hand, and in most cases TEM does not reveal the presence of such particles (see Fig. 5.4a, but compare alsoFig. 5.4b and 5.4c to Fig. 5.5). The fact that the expected properties are rarely achieved indicates the presence of large particles, but several studies also prove explicitly this fact. Fig. 5.5 presenting SEM micrographs taken from composites prepared with the three silicates confirms further these observations. The size of the particles is approximately the same and corresponds to the most frequent size of the particle size distribution. The micrographs were taken from surfaces created by cutting with an ultramicrotom and the particles were broken during the operation. The NaMMT particle is very well defined, the interface is clear, while the exact size and also the interface of the other two particles are much more uncertain. The diffusion of the polymer into the galleries of the clay and partial intercalation must have occurred on the surface resulting in the more diffuse interphases. Unfortunately the etching technique used in PP [46] did not work in these PA composites thus we could not carry out a more detailed analysis of the particles and could not determine their size distribution either. Nevertheless, we can
Figure 5.5  Non-exfoliated large particles in PA/clay composites containing 3 vol% silicate. SEM micrographs taken from microtomed slices; a) NaMMT, b) NoMMT, c) PoMMT.
conclude that large particles are also present in our composites, but we do not know their size distribution and amount, although both may influence properties considerably.

The other structural formation which receives relatively limited attention is the silicate network, which forms under certain conditions (sufficient exfoliation) although several groups proved its existence. The best method for the detection of the formation and existence of the network is rheology, rotational viscometry \cite{19,46,47}. The appearance of a yield stress during flow, or changes in storage modulus at low frequencies clearly indicate network formation \cite{19}. The complex viscosity of the PA polymer and the composites containing the silicates in 3 vol\% is plotted against frequency in Fig. 5.6. Increasing viscosity at low frequencies clearly indicates the existence of a yield stress and the formation of the network in the composites containing the organophilic montmorillonites. Viscosity is considerably larger for the composite containing the silicate modified with the phosphonium salt, which indicates larger extent of exfoliation and denser network. The differences in exfoliation are confirmed by the composition dependence of complex viscosity as well (Fig. 5.7). Viscosity measured at 0.1 s\(^{-1}\) increases only slightly with increasing silicate content for composites containing NaMMT, but considerably larger values are measured in the two series prepared with the modified clays. The difference between the clays treated with the phosphonium and the ammonium salts, respectively, seems to support rather strongly our earlier conclusions drawn from the XRD and TEM studies, i.e. the phosphonium salt modified clay exfoliates more than the one treated with the traditional ammonium surfactant.

![Complex viscosity vs. Frequency](image)

**Figure 5.6** Frequency dependence of the complex viscosity of the PA6 matrix polymer and the composites containing 3 vol\% silicate; formation of a silicate network; (●) PA, (△) NaMMT, (□) NoMMT, (○) PoMMT.
A final question concerning structure in PA nanocomposites that must always be considered is the crystal modification of polyamide. Clays were shown to promote the formation of the $\gamma$ modification of PA instead of the usual $\alpha$ form irrespectively of surface modification [48,49]. Changes in crystal modification usually modify properties as well. The effect is also observed in our composites although not in the same extent as before when a different type of PA was used. DSC study (details not shown) proved that the neat PA crystallized in the $\alpha$ form as usual, while about 60 $\%$ $\gamma$ modification forms in the presence of the clays irrespectively of amount or type of surface modification.

**5.3.3. Mechanical properties, reinforcement**

Reinforcement at small filler content was one of the initiatives of the research on nanocomposites. Considerable increase in modulus and heat deflection temperature was shown by several groups [27,50-52]. Yield stress and/or tensile strength values are reported much less frequently and the published data usually do not support the original assumption of large reinforcement at small silicate content. Although modulus depends on the aspect ratio of the filler, a quantity used for the characterization of the extent of exfoliation [52], the measured effect also depends on orientation, which is rarely known. Moreover, stiffness does not indicate very sensitively changes in interfacial interaction, but properties measured at larger deformations do.

**Figure 5.7** *Effect of silicate content on the complex viscosity of PA/clay nanocomposites at 240 °C and 0.1 s$^{-1}$ shear rate; (Δ) NaMMT, (□) NoMMT, (○) PoMMT.*
The Young’s modulus of the three series of composites is plotted against composition in Fig. 5.8. At small silicate content the correlations run very close to each other supporting our statement that stiffness is not very sensitive to structure and interaction, but it is determined mainly by the volume fraction of the silicate. In fact at small silicate content the modulus of the composites containing NaMMT is larger than that of the materials prepared with the organophilized clays. Strong deviation is observed at larger silicate content for the series containing NaMMT. We can only speculate about the reason, easy debonding of large particles, their aggregation and the failure of the aggregates, or the fracture of the particles might be the main reason for the phenomenon. We do not think that debonding occurs here, because of the large surface energy of the neat sodium montmorillonite on the one hand, and also because the phenomenon does not appear at small filler content on the other hand. The fracture of particles cannot be excluded the same way, since the number of very large particles breaking easily increases with increasing filler content.

Contrary to stiffness, the yield stress of the composites differs considerably (Fig. 5.9); the reinforcing effect of the clay modified with the phosphonium salt is much stronger than that of the other two silicates. Moreover, quite surprisingly, the composites containing NaMMT have larger yield stress than those prepared with the clay organophilized with the ammonium salt. The effects and correlations are difficult to explain at first. TEM micrographs and rheology clearly proved a partial exfoliation of Cloisite 20A thus the exfoliated clay platelets should reinforce PA much better than the
large silicate particles of NaMMT. However, we must consider the effect of two factors here, that of increased specific surface area resulting from exfoliation, on the one hand and decreased interaction due to the coverage of silicate surface with a surfactant (see Table 5.1, surface energy), on the other. Sodium montmorillonite has large surface energy thus it forms strong interaction with PA and carries considerable load, while the larger surface area of the exfoliated clay is counteracted by its smaller surface energy. The main question is the strong reinforcing effect of the clay modified with the phosphonium salt compared to Cloisite 20A. We must call attention here to results presented in previous sections which indicated larger extent of exfoliation for this clay. Moreover, the smaller surface coverage of the clay (see Table 5.1) might allow stronger interaction with the polymer, although its small surface energy contradicts this argument. Finally, the increase in yield stress with silicate content also confirms that debonding is limited in these composites.

![Figure 5.9](image)

**Figure 5.9** Dependence of the tensile yield stress of PA nanocomposites on silicate content; (●) PA, (△) NaMMT, (□) NoMMT, (○) PoMMT.

The relationships are shown much better and reinforcement can be expressed quantitatively with the help of a simple model developed earlier for particulate filled composites. As described earlier the composition dependence of tensile yield stress can be described by Eqs. 4.1 and 4.2. Parameter $B$ is related to the load carried by the dispersed component; at zero interaction all the load is carried by the polymer. 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 ($A_f$) (Eq. 4.2). Since $A_f$ represents the contact surface between the polymer and the clay, which increases with increasing extent of exfoliation, thus the value of parameter $B$ should also
increase proportionally and indicate reinforcement. If the model is valid, we should obtain linear correlation when the natural logarithm of reduced yield stress is plotted against filler content. The plot is shown in Fig. 5.10 for the three series of composites. We obtain straight lines as expected, but intersection does not correspond to the value of the matrix. We must remind the reader here to the fact that the structure and properties of the matrix changed upon the addition of the silicate, about 60 % of the polymer crystallizes in the γ form. Published literature references show this effect also in other PA composites [53,54]. Deviation from linearity can be observed only for NaMMT. Such deviations usually indicate structural effects or a change in deformation mechanism. Aggregation of large NaMMT particles or their fracture can be possible reasons for the deviation. Reduced yield stress is plotted only up to 0.03 volume fraction for composites containing PoMMT. Samples failed without yield above this silicate content probably because of the larger extent of exfoliation and stronger interaction compared to composites prepared with NoMMT. The difference in the reinforcing effect of the two organophilic clays is clear and striking. The stronger reinforcing effect of NaMMT, as well as the smaller slope of the correlation obtained with Cloisite 20A are also clearly seen in the figure. Parameter B expressing reinforcement is around 3.5 for the latter, 5.0 for NaMMT, while as large as 7.6 for the clay modified with the phosphonium salt. The analysis of data published in the literature for 22 composite series showed B values between 1.7 and 13.0 in spite of the fact that in most cases similar, intercalated/exfoliated structure was claimed.

![Figure 5.10](image)

**Figure 5.10** Reduced tensile yield stress plotted against silicate content; reinforcement is proportional to the slope of the straight lines. See the effect of changing crystal modification of the matrix PA: (●) PA, (Δ) NaMMT, (□) NoMMT, (○) PoMMT.
The determination of parameter $B$ allows us the estimation of the extent of exfoliation as well. In this case we assume that sodium montmorillonite does not exfoliate, on the one hand, and that the surface area of completely exfoliated clay is $750 \text{ m}^2/\text{g}$. We must also assume that the strength of interaction and thus the thickness and properties of the interphase formed are the same in all cases. If exfoliation were complete, $B$ should assume the value of 195, thus actual $B$ values obtained for the composites allow us the calculation of a contact surface ($A_f$) and from that we can predict the extent of exfoliation by comparing this number to the theoretical value ($750 \text{ m}^2/\text{g}$) [3,55]. The results of the calculations are summarized in Table 5.2. Average value from 22 composites published in the literature [see Ref. 3] and the representative value of Fornes and Paul [1] are also included. We can see that exfoliation is rather small in our case, less then 2% of the theoretical value for Cloisite 20A and about 4% for the clay modified with the phosphonium salt, but completely corresponds to values published in the literature. We must emphasize here that we did not optimize either surface coverage or processing conditions, both of which influence the extent of exfoliation, structure and properties, but only compared the two clays.

### Table 5.2

*Estimation of reinforcement and the extent of exfoliation using the model described by Eqs. 4.1 and 4.2. Comparison to results published in the literature.*

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Parameter $B$</th>
<th>Specific surface area ($\text{m}^2/\text{g}$)</th>
<th>Extent of exfoliation (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>oMMT</td>
<td>195&lt;sup&gt;a&lt;/sup&gt;</td>
<td>750</td>
<td>100</td>
<td>33-35</td>
</tr>
<tr>
<td>NaMMT</td>
<td>5.0</td>
<td>19.6</td>
<td>0</td>
<td>this paper</td>
</tr>
<tr>
<td>NoMMT</td>
<td>3.7</td>
<td>14.5</td>
<td>1.9</td>
<td>this paper</td>
</tr>
<tr>
<td>PoMMT</td>
<td>7.6</td>
<td>29.3</td>
<td>3.9</td>
<td>this paper</td>
</tr>
<tr>
<td>oMMT&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.9</td>
<td>26.5</td>
<td>3.5</td>
<td>3</td>
</tr>
<tr>
<td>NoMMT&lt;sup&gt;c&lt;/sup&gt;</td>
<td>11.5</td>
<td>44.4</td>
<td>5.9</td>
<td>1</td>
</tr>
</tbody>
</table>

<sup>a</sup> calculated from published specific surface area assuming complete exfoliation  
<sup>b</sup> average value published in the literature  
<sup>c</sup> taken from the frequently cited paper of Fornes and Paul [1]

### 5.4. Conclusions

The detailed characterization of clays organophilized with a phosphonium and an ammonium salt, respectively, showed differences in their surface coverage and gallery structure. The particle size of the fillers was similar and their surface energy differed only slightly. Different gallery structure led to dissimilar extent of exfoliation. Rather surprisingly the clay modified with the phosphonium salt exfoliated better in PA
PA6 nanocomposites; effect of surface modification

than the silicate treated with the ammonium salt in spite of its smaller surface coverage. The nanocomposites showed the usual complex structure: besides individual platelets and intercalated stacks, also large particles were present and the development of a silicate network could be also shown at larger clay contents. The reinforcing effect of the clays was determined quantitatively and the results showed that two factors determine the extent of reinforcement: contact surface and the strength of interaction. The first increases with exfoliation, but the latter decreases as an effect of organophilization. The extent of exfoliation was also estimated quantitatively, and the calculation confirmed the results of qualitative evaluation showing larger extent of exfoliation for the clay modified with the phosphonium salt.

5.5. References

23. Garcia-Lopez, D., Lopez-Quintada, S., Gobernado-Mitre, J. C., Pastor, J. M.,
Chapter 6

Effect of clay modification on the mechanism of local deformations in PA6 nanocomposites

6.1. Introduction

The deformation and failure of polymer/layered silicate nanocomposites is not studied in the extent as structure and certain properties. Even less attention is paid to local micromechanical deformation processes occurring around clay entities, although they may determine the macroscopic properties of the composites [1-3]. Deformation may be dominated either by that of the matrix or by processes related to the silicate reinforcement. The polymer may deform by shear yielding, but its cavitation, cracking or fracture can also take place. Voiding was shown to occur during the deformation of neat polyamide [4]. Somewhat larger is the number of possible deformation processes related to the silicate. According to Kim et al. [2] fracture or peeling off the silicate layers and the slipping of individual layers or stacks may occur during deformation. If we allow also the presence of larger entities, and this is definitely the case when sodium montmorillonite (NaMMT) is used as filler, the debonding of the silicate from the matrix must be also considered as a possible deformation mechanism [5]. Basically all silicate related processes depend on interaction, both on the forces acting among the layers and on matrix/filler adhesion. As a consequence, the quality of organophilization, i.e. the type and amount of the surfactant used, is expected to influence the mechanism of deformation and the properties of the composites considerably.

The advantages of phosphonium modification of clay were shown earlier indicating better stability for composites prepared with such a clay compared to the silicate modified with the usual ammonium salt [6]. In the previous chapter we compared composites prepared with clays organophilized with a phosphonium and an ammonium salt, respectively. The two modifications led to different structures and to dissimilar extent of exfoliation. Reinforcement was much stronger in the composite containing the clay modified with the phosphonium salt because of a better combination of exfoliation and surface coverage. In the next stage of the research we studied local deformations in the nanocomposites mentioned above. Micromechanical deformations were analyzed by following the volume increase of specimens during deformation and by the detection of acoustic signals emitted by local processes. Characteristic stresses derived from the measurements were compared to macroscopic properties, and the main factors determining properties as well as the dominating deformation mechanism were identified.

6.2. Experimental

The components used in the study, composite preparation and characterization were described in the previous chapter. Only the details of micromechanical measurements are given here. Acoustic emission (AE) signals were recorded with a Sensophone AED 40/4 apparatus. 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 measurements were carried out at 5 mm/min crosshead speed. We assumed that dimensional changes are the same in both lateral directions. Five parallel specimens were measured in all mechanical and micromechanical experiments.

6.3. Results and discussion

In this chapter we focus our attention on the mechanism of deformation and do not discuss structure and properties in detail; we refer to the previous chapter where necessary [7]. The results are discussed in separate sections; first we present those obtained by volume strain and then those of acoustic emission measurements. Deformation mechanisms and their relation to macroscopic properties are discussed in a separate section.

6.3.1. Volume strain

As mentioned in the introductory part several micromechanical deformation processes may take place during the tensile testing of specimens prepared from PA6 nanocomposites. Some of these are accompanied by volume increase, while others are not. Shear yielding, plastic flow, or the slipping of platelets [2] do not result in the increase of specimen volume, while many others like crazing, cavitation or debonding lead to detectable volume strain. Volume increase is plotted against longitudinal elongation in Fig. 6.1 for the matrix PA and for the composite containing 7 vol% OMMT modified with the ammonium salt (NoMMT). The corresponding stress vs. strain traces are also presented for reference. The volume of the matrix polymer increases with a smaller slope first, then with a larger rate after a certain, relatively small deformation. Although the difference in slope is small, it could be detected on all traces. Volume increase in the first section is the result of the Poisson’s ratio of the polymer being different from 0.5. The Poisson’s ratio calculated from the slope of this section is 0.39 which is a reasonable value for PA [8]. The increase of volume beyond the critical deformation must be caused by a micromechanical deformation process, probably by cavitation, which was shown to occur during the deformation of PA [1,4]. At larger deformations, above 4 % elongation, the volume of the specimen seems to decrease. This apparent decrease results from plastic deformation and necking; values beyond the maximum loose their meaning and the measurement was stopped close to that point. Unfortunately, the mechanical strain gauge used in these experiments initiated the necking of the sample.
The presence of the silicate results in further volume increase as shown by the full line in Fig. 6.1. The maximum volume increase is in the range of 2% which agrees well with values observed by others in PA nanocomposites prepared from different components under dissimilar conditions [1,3]. We must call attention here to the fact that the shape of the traces is the same in all materials independently of the presence or absence of silicate or the type of surface modification, including also the uncoated NaMMT. We might conclude from this similarity that deformation proceeds with the same mechanism and the silicate does not initiate a new process. However, this tentative conclusion needs further proof.

Figure 6.1  Stress vs. strain and volume strain vs. strain traces of the neat PA (-----) and those of the composite containing 7 vol% OMMT modified with the ammonium salt (-----).

A characteristic or initiation deformation ($\varepsilon_{\text{VOLS}}$) as well as stress ($\sigma_{\text{VOLS}}$) can be determined from the change of slope in the way indicated in Fig. 6.1. These characteristic values were derived for all materials and $\sigma_{\text{VOLS}}$ is plotted against silicate content in Fig. 6.2. Although the standard deviation of the determination is rather large, which is not very surprising considering the traces in Fig. 6.1, the effect of the silicates is clear. Sodium montmorillonite hinders, while organophilic silicates promote the process leading to volume increase. The difference in the effect of the two modified clays must be caused by their dissimilar surface coverage and the resulting different extent of exfoliation.

The correlations presented in Fig. 6.2 clearly indicate that the presence of the silicate influences the process, probably cavitation, resulting in volume increase. In
order to check the role of the silicate, initiation stress was plotted against the intensity of
the silicate reflection determined by WAXS (Fig. 6.3). Such a reflection is detected if
ordered, non-exfoliated tactoids or particles are present in the composite. We assume
that the intensity of the reflection is proportional to the amount of these structural units.
We must keep in mind, though, that the intensity of the reflection depends on several
factors [9] and the direct comparison of composites containing different silicates might
be misleading. However, the correlations presented in Fig. 6.3 are clear showing that
volume increase depends on structure, on the degree of exfoliation and on the presence
of non-exfoliated particles. Assuming that the mechanism of deformation is similar or
even the same in all cases we may explain the different effect of the silicates by their
dissimilar surface free energy. Cavitation is caused by negative hydrostatic pressure and
results in the formation of voids. Large surface energy [7] and good adhesion to the
surface of NaMMT hinders this process, while weak interaction with the organophilic
clays facilitates it. Deviation of the intersections of the correlations from the matrix
value indicate that the size and amount of these structural units also play a role, and the
explanation might be even more complicated than presented here. One may assume that
two factors determine the extent of volume increase, the fracture and/or debonding of
particles and interaction, both acting in different extent in composites containing the
two types of silicates (NaMMT, OMMT). We may also consider that the presence of the
silicate changes the crystalline structure of PA, a considerable part crystallizes in the γ
form in the composites instead of the usual α modification. Nevertheless, we may con-
clude that cavitation occurs in all composites and it is initiated at a relatively small
stress (10-15 MPa) compared to the yield stress of the polymer (61.5 MPa).

![Figure 6.2](image)

Figure 6.2  Effect of silicate content and surface modification on the initiation stress
of volume increase; (Δ) NaMMT, (◊) PoMMT, (□) NoMMT, (●) PA.
Figure 6.3 Correlation between the intensity of the silicate reflection (WAXS) and the initiation stress of volume increase; (Δ) NaMMT, (○) PoMMT, (□) NoMMT.

6.3.2 Acoustic emission

Some of the local deformation processes occurring around heterogeneities are accompanied by the release of energy. Energy is released in the form of sound waves, which can be detected by appropriate microphones. Although the technique has limitations, it is very useful for the study of micromechanical deformation processes and the number, energy, amplitude and other characteristics of the signal as well as further characteristics derived from the measurements offer valuable information. The result of a typical measurement done on the composite containing 0.5 vol% of the NaMMT clay is presented in Fig. 6.4. The stress vs. strain trace is also plotted as reference; it helps to locate the position of the acoustic events during deformation. Each small circle corresponds at least to one acoustic event (signal, hit). We see that considerable number of signals is detected during deformation and most of them occur at relatively small elongations. The amplitude of these events covers a relatively wide range.

Unfortunately the observation of individual events allows the drawing of only limited conclusions thus primary results are transformed for analysis. The cumulative number of signals is plotted in Fig. 6.5 for the neat PA and for the composite of Fig. 6.4. The corresponding stress vs. strain traces are presented again for reference. We can see that these latter are rather similar for the two materials, but the number of events differ significantly for them. The number of signals is about one order of magnitude larger in the composite containing only a small amount of clay and acoustic activity increases
further with increasing clay content. Considering the results presented in the previous section, we must conclude that the process resulting in the acoustic events do not initiate significant volume increase otherwise much larger volume strains initiated at larger stresses must have been measured in the presence of the clays, but the magnitude of volume increase was the same in all polymers including the neat PA. Characteristic values are derived also from the acoustic emission measurements as indicated in Fig. 6.5; the results will be discussed later.

![Graph](image)

**Figure 6.4** Acoustic emission signals detected during the deformation of the PA composite containing 0.5 vol% NaMMT. Symbols: (o) individual acoustic signals, (—) stress vs. strain trace.

The acoustic behavior of composites containing the organophilic clays and NaMMT, respectively, also differ from each other. A typical trace obtained on the composite containing 1.5 vol% of the clay modified with the phosphonium salt is presented in Fig. 6.6; the behavior of neat PA is shown for comparison. The acoustic activity of the composite is only slightly larger than that of the matrix polymer. Moreover, instead of a well defined step like in the case of NaMMT (see Fig. 6.5), the acoustic activity is spread along the entire range of elongation, the cumulative number of hits increases continuously with a small step at around 3-5% deformation. This difference indicates a deformation mechanism dissimilar from that occurring in the composite containing NaMMT. Since the matrix also gives a limited number of signals, the silicate might promote the same process, but the events might be created also by another process related solely to the particles. The determination of characteristic deformation ($\varepsilon_{AE}$) and stress values ($\sigma_{AE}$) is much more difficult in this case and the values are also much less reliable. The method of determination is also indicated in Fig. 6.6.
Figure 6.5 Acoustic activity of the matrix PA (-----) and the composite containing 0.5 vol% NaMMT (——). The corresponding stress vs. strain traces are also included for reference.

Figure 6.6 Comparison of the acoustic activity of the neat PA polymer (-----) and the composite containing 1.5 vol% OMMT modified with the phosphonium salt (——).
The number of signals detected up to yield strain is plotted against the intensity of the silicate reflection in Fig. 6.7 in order to check the relation between non-exfoliated structural units and acoustic activity. The results obtained on composites containing NaMMT and the OMMTs, respectively, had to be plotted on different scales. The silicate reflection of NaMMT is weak because of disordered stacking, but the number of signals is large, while the opposite is valid for composites prepared with OMMT. In spite of the considerable standard deviation, the correlations are clear as well as the different influence of the two types of clay on the acoustic activity of the composites. We may conclude from these results that acoustic events are also related to the silicate and that NaMMT and modified clays have different effect on composite behavior, might even deform according to a dissimilar mechanisms.

Characteristic deformations and stresses were determined also from the acoustic emission measurements as shown in Figs. 6.5 and 6.6. Initiation stresses determined by the two techniques, i.e. VOLS and AE, are plotted against each other in Fig. 6.8. We can draw several conclusions from the complete or almost complete lack of correlation. In other composites acoustic events usually precede volume increase and the two processes are closely related, in fact the process detected by acoustic emission initiate volume increase [1]. Considering the characteristic deformations and stresses we can see that the initiation stress for volume increase is much smaller than that determined by acoustic emission; volume increase precedes the emission of sound. Moreover, as the figure shows, the two processes are independent of each other, i.e. the process resulting in volume increase does not initiate the one emitting sound.

Figure 6.7 Correlation between the number of signals detected up to the yield stress of the composites and the intensity of the silicate reflection (WAXS). Symbols: (Δ) NaMMT, (○) PoMMT, (◻) NoMMT.
6.3.3. Micromechanics and properties

The detailed analysis of structure and properties indicated better exfoliation for the clay modified with the phosphonium salt than that achieved with the traditional ammonium surfactant (see previous chapter). The result was considerably stronger reinforcement for the former silicate demonstrated by Fig. 5.9 presenting the composition dependence of tensile yield stress for the three sets of composites. The figure also proves that besides exfoliation, the strength of interfacial adhesion determined by surface coverage also influences properties. The strong reinforcing effect of PoMMT is clear. However, NaMMT reinforces our PA more than the clay modified with the ammonium salt, which might be slightly surprising. We explained this lack of reinforcement of NoMMT with the smaller extent of exfoliation and the more than 100 % surface coverage of this clay compared to the clay modified with phosphonium salt (120 vs. 74 % for NoMMT and PoMMT, respectively). The different interception of the correlations from the value determined for the matrix polymer can be explained with the change in crystal modification as a result of silicate reinforcement. A considerable amount of $\gamma$ form of PA was found in the composites, while the $\alpha$ modification dominated in the neat PA.

However, the magnitude of yield stress is more important for us in this moment than differences in the extent of reinforcement. In spite of the apparently large changes,

Figure 6.8 Lack of correlation between characteristics stresses derived from volume strain and acoustic emission measurements. Symbols: (Δ) NaMMT, (○) PoMMT, (□) NoMMT.
composite yield stresses vary between 60 and 69 MPa. These values are much larger than the characteristic stresses determined by micromechanical testing. The relationship of the three characteristic stresses is demonstrated well by Fig. 6.9 presenting their composition dependence. Values determined by the different techniques (VOLS, AE, tensile testing) clearly separate into well defined groups indicating different processes which are practically independent of each other. Silicates influence the initiation stress of volume increase and yield stress only slightly at this scale, and the amount and type of silicate has more significant effect only on the characteristics stress determined by acoustic emission. The independence of processes was demonstrated by Fig. 6.8 and similar correlations could be presented for the other combination of characteristic stresses as well. Fig. 6.9 indicates also that the process resulting in the emission of sound is different for composites containing NaMMT and the two OMMTs, or at least it occurs at larger stresses.

Figure 6.9  Dependence of characteristic stresses derived from various measurements on the silicate content of the composites. The shape of the symbols is the same as in previous figures. The origin of the characteristic stress is indicated in the figure.

Mechanical and micromechanical testing can and do indicate that several independent local processes occur during the deformation of PA nanocomposites, but cannot reveal their nature. We carried out SEM studies on deformed samples to obtain more information about these processes. Specimens were deformed to twice the yield strain \( (2\varepsilon_y) \), the deformed samples were cut along their axis with a razor blade, cooled in liquid nitrogen and then broken. SEM micrographs were taken from these fracture surfaces. The micrograph recorded on the fracture surface of the composite containing
3 vol% NaMMT is presented in Fig. 6.10. Since NaMMT does not exfoliate practically at all, a large number of particles are seen in the micrograph revealing considerable plastic flow, but also particle related processes. In the middle of the micrograph the fracture of a particle or large aggregate is seen, but we might find indication of debonding, separation of the matrix and the silicate particles as well. Apparently larger particles and aggregates fracture during deformation, while debonding occurs on medium size clay particles. A closer scrutiny reveals smaller holes without particles, which may indicate matrix cavitation. However, particles might have fallen out during fracture or might be too small to be detected at this magnification, thus based on these micrograph we cannot prove the occurrence of this mechanism.

![SEM micrograph taken from the surface of a specimen deformed to 2σ and then freeze fractured; 3 vol% NaMMT.](image)

At the first glance the fracture surface of deformed composites containing the modified clays resembles very much the one shown in Fig. 6.10, and clays with different modifications result in similar fracture surfaces. As a consequence, only two micrographs are presented here for the composite containing 5 vol% of the clay modified with the ammonium salt. However, experience during the study as well as a closer analysis of the micrographs revealed some differences. The number of particles was much smaller in the composites containing the modified clays, and this number is even smaller for PoMMT than for the clay modified with the ammonium surfactant. Only three or four larger particles can be seen in the micrograph presented in Fig. 6.11a compared to the much larger number and wider size distribution observed in Fig. 6.10 (consider also the different magnifications and silicate contents). A closer scrutiny reveals a larger number of submicron particles adhering strongly to the matrix, but their identification is difficult.
and questionable. Obviously larger particles and aggregates break in these composites as well and debonding may also occur. On the other hand, the number of cavities not related to particles is much larger in composites containing organophilic clays as shown by Fig. 6.11b. In fact apart from the top of the large hole seen also in the middle of Fig. 6.11a, the entire matrix seems to consist of a maze of elongated cavities. These cavities might be related to particles, but might form simply by the cavitation of the matrix shown to occur by the volume strain measurements.

Taking into account all the results and considerations presented in this and in previous sections we must conclude that several, three or four, micromechanical processes take place during the deformation of our PA composites. Obviously considerable cavitation occurs in the matrix polymer and the process is modified slightly by the presence of the clay. Interfacial adhesion, silicate content and particle size influences the process. NaMMT mainly hinders it due to its large surface free energy and strong adhesion with the matrix, while organophilic clays seem to facilitate its initiation. Cavitation is initiated at surprisingly low stresses, around 10 MPa. Cavitation does not seem to emit sound. Acoustic emission signals can be assigned mostly to the fracture of large clay particles and aggregates. This process occurs at medium stresses between 20 and 40 MPa. The effect of surface modification on this process is significant and the stress necessary to initiate it seems to be related to the surface energy of the clay. NaMMT with high surface energy fractures at 40-45 MPa, while OMMTs at smaller stresses, at around 20-30 MPa. Larger surface coverage of NoMMT results in smaller fracture energies. The much smaller number of large particles, and thus fractures, is shown also by the drastically smaller number of acoustic events in composites containing the modified clays (see Fig. 6.7). According to SEM micrographs debonding may also occur, but it cannot be identified and/or separated from the fracture of the particles. Surprisingly, yield stress is not influenced much by these processes and it is dominated by the plastic deformation of the matrix. Tensile yield stress is larger than 60 MPa for all composites.

The independence of the tensile yield stress of PA nanocomposites of micromechanical processes is rather surprising, since in most other composites a very close correlation was found between yield stress and/or tensile strength and the initiation stress for local deformations [10,11]. This statement is demonstrated by Fig. 6.12 showing the correlation between the characteristic stress derived from acoustic emission experiments and the tensile strength of polymer/wood composites. The correlation is universal and independent of the characteristics of the matrix or the reinforcement. Empty symbols indicate PP, while full circles PLA composites in the figure. Several matrix polymers were used to prepare the PP composites and the type of wood reinforcement varied in a wide range for both matrices. Considering all these facts, the deviation from the general tendency is surprisingly small. No correlation was found between local processes and macroscopic properties in our nanocomposites proving that composite properties are determined mainly by matrix characteristics, and the influence of the type and amount of the silicate is limited.
Figure 6.11  SEM micrographs recorded on composites containing 5 vol\% NoMMT; magnification a) 2500x, b) 10000x.
6.4. Conclusions

Micromechanical testing, SEM study and the analysis of mechanical and micromechanical characteristics revealed that several micromechanical deformation processes take place in the PA/MMT composites investigated. The results showed that cavitation occurs in the matrix at relatively small stress. Processes related to non-exfoliated clay structural units, particles or tactoids, are initiated at larger stresses. Sound is emitted mainly by the fracture of particles, but debonding may also occur with the emission of sound. Plastic deformation of the matrix dominates at larger stresses and deformations. The various local processes are independent of each other and composite properties are not determined by silicate related processes, but by the deformation of the matrix. The modification of clay influences all processes in smaller or larger extent, the key factors are exfoliation and interfacial adhesion, a proper combination of which leads to considerable reinforcement.

6.5. References

Chapter 7

Summary

The interest in polymer/layered silicate nanocomposites is still considerable, but progress slowed down in recent years and these materials have not achieved the expected position in the market yet. The lack of success is caused by several factors including insufficient extent of exfoliation, the overly complicated structure and our limited knowledge about structure-property correlations. Research continues all over the world to answer these challenges. Recently the work done in our laboratory focused on unfinished projects, unsolved problems and new ideas. Some of the smaller or larger projects addressed practical issues like the stability of polypropylene nanocomposites, others focused on questions completely neglected up to now, like interphase formation and properties while some dealt with a completely new problem at least for us, the use of a different surface modification to achieve the desired goal of large extent of exfoliation. This Thesis reports the progress achieved in the last few years. Although we summarized the most important results of the research at the end of each chapter, we briefly repeat them here to give a concise overview of our results. At the end of this chapter we compile the most important new findings of this work in a few thesis points.

First we studied the kinetics of structure development in PP/silicate composites with and without a functionalized PP compatibilizer. The gallery structure of organophilic silicate changed even in the absence of compatibilizer. Silicate reflection shifted towards smaller \( \theta \) angles, broadened and its intensity decreased indicating intercalation. TEM micrographs even showed individual platelets at long mixing times. However, the extent and direction of changes in the gallery structure of the silicate did not justify those observed in properties. The analysis of the results and additional experiments proved that the degradation of the polymer also takes place during processing leading to the formation of carbonyl and/or carboxyl groups, as well as to the decrease of molecular weight. The modification of chain structure influences interfacial interactions and the intercalation process. Some properties are directly determined by molecular weight (rheological properties, elongation). Both the clay and the functionalized polymer seem to accelerate degradation. Thermo-oxidative degradation must have disadvantageous effect during the application of PP nanocomposites and needs further study.

Following the observation made in the previous stage of the research we studied the thermo-oxidative stability of PP nanocomposites. Contrary to numerous claims published in the literature, which indicate the positive effect of layered silicates on the stability of polymer nanocomposites, our results clearly proved that both OMMT and MAPP accelerate degradation during processing and deteriorate the properties of PP composites. Residual stability decreases drastically with increasing amounts of both components, chain scission leads to the decrease of viscosity and to inferior strength and deformability. In spite of the expectations, the effect of the components is independent of each other. Discoloration is caused mainly by the inherent color of the filler
and it decreases with increasing exfoliation. The most probable reason for the decrease in stability is the reaction of the components with the stabilizers, but this explanation needs further verification. Processing conditions influence degradation considerably, increasing shear rate and longer residence times lead to more pronounced degradation. The basic stabilization of commercial grade polypropylenes is insufficient to protect the polymer against degradation and without additional stabilization processing under normal conditions results in products with inferior quality.

Experiments carried out with NaMMT and OMMT with different particle sizes and model calculations proved the formation of an interphase in the PP composites. Unfortunately, the determination of interphase properties was hampered by several factors. First of all, the particle size of the filler changed quite considerably in PP/OMMT composites in spite of earlier observations and expectations. Particle characteristics changed even further when a relatively small amount of functionalized polymer (MAPP) was added to the composite. As a consequence, the estimation of the contact surface between the silicate and the polymer became extremely difficult. In spite of the uncertainties some overall values of interphase properties were obtained using the results of all composites prepared. The prediction for the average thickness of the interphase is 0.23 \( \mu \)m and we obtained 51.2 MPa for interphase yield stress, but this estimate neglects the different interactions developing in composites containing the uncoated (NaMMT) and the modified (OMMT) silicate, respectively.

The detailed characterization of a commercial ammonium organoclay and a silicate modified with a phosphonium salt in supercritical CO\(_2\) showed differences in their surface coverage and gallery structure. The particle size of the fillers was similar and their surface energy differed only slightly. Different gallery structure led to dissimilar extent of exfoliation in polyamide 6. Rather surprisingly the phosphonium organoclay exfoliated better in PA than the ammonium organoclay in spite of its smaller surface coverage. The nanocomposites showed the usual complex structure: besides individual platelets and intercalated stacks, also large particles were present and the development of a silicate network could be also shown at larger clay contents. The reinforcing effect of the clays was determined quantitatively and the results showed that two factors determine the extent of reinforcement: contact surface and the strength of interaction. The first increases with exfoliation, but the latter decreases as an effect of organophilization. The extent of exfoliation was also estimated quantitatively, and the calculation confirmed the results of qualitative evaluation showing larger extent of exfoliation for the clay modified with the phosphonium salt.

Micromechanical testing, SEM study and the analysis of mechanical and micromechanical properties revealed that several micromechanical deformation processes take place in PA/MMT composites. The results showed that cavitation occurs in the matrix at relatively small stress. Processes related to non-exfoliated clay structural units, particles or tactoids, are initiated at larger stresses. Sound is emitted mainly by the fracture of particles, but debonding may also emit sound. Plastic deformation of the matrix dominates at larger stresses and deformations. The various local processes are independent of each other and composite properties are not determined by silicate related processes, but by the deformation of the matrix. The modification of clay influences all
processes in smaller or larger extent, the key factors are exfoliation and interfacial adhesion, a proper combination of which leads to considerable reinforcement.

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

1. In spite of the general belief that exfoliation does not take place in PP containing only an organophilic silicate without compatibilizer we proved in more than one series of experiments that structure changes and a small extent of exfoliation occurs even in such cases. The extent of exfoliation depends on component properties, processing conditions and on the stabilization of the polymer.

2. Contrary to numerous claims published in the literature, which indicate the positive effect of layered silicate on the stability of polymer nanocomposites, we proved unambiguously that both OMMT and MAPP accelerate degradation during processing and deteriorate the properties of PP composites. Residual stability decreases drastically with increasing amounts of both components, chain scission leads to the decrease of viscosity and to inferior strength and deformability. We also showed that in spite of the expectations, the effect of the components is independent of each other.

3. Using commercial PP grades and surplus stabilization we pointed out that the basic stabilization of commercial grade polypropylenes is insufficient to protect the polymer against degradation and without additional stabilization processing under normal conditions results in products with inferior quality.

4. We proved with the help of well designed experiments and model calculations that an interphase forms spontaneously also in polymer/layered silicate nanocomposites. In spite of the theoretical and technical difficulties we estimated overall values for the thickness and properties of the interphase in PP/silicate composites for the first time.

5. In PA6/layered silicate composites we estimated quantitatively the reinforcing effect of the clays used and proved that two factors determine the extent of reinforcement: contact surface and the strength of interaction. The first increases with exfoliation, but the latter decreases as an effect of organophilization.

6. With the help of micromechanical testing, SEM study and the detailed analysis of various mechanical and micromechanical properties we proved that several micromechanical deformation processes take place in PA/layered silicate composites. Rather surprisingly the processes are independent of each other.

7. We also proved that in PA6/layered silicate nanocomposites composite properties are not determined by silicate related processes, but by the deformation of the matrix. This result contradicts previous experience obtained on PP and PLA composites in which particle related processes dominate.
List of symbols and abbreviations

Symbols

\( \varepsilon_{AE} \)  
initiation deformation derived from acoustic emission measurement (%)  
\( \varepsilon_y \)  
tensile yield strain (%)  
\( \varepsilon_{VOLS} \)  
initiation deformation derived from volume strain measurement (%)  
\( \gamma_s \)  
dispersion component of the surface tension of the silicate (mJ/m\(^2\))  
\( \phi \)  
volume fraction of the filler in the composite  
\( \eta^* \)  
complex viscosity (Pas)  
\( \eta' \)  
real part of complex viscosity (Pas)  
\( \eta'' \)  
imaginary part of complex viscosity (Pas)  
\( \rho_f \)  
density of the filler (g/cm\(^3\))  
\( \sigma_{AE} \)  
initiation stress derived from acoustic emission measurement (MPa)  
\( \sigma_y \)  
composite yield stress (MPa)  
\( \sigma_{yo} \)  
matrix yield stress (MPa)  
\( \sigma_{yi} \)  
yield stress of the interphase (MPa)  
\( \sigma_{yred} \)  
reduced yield stress of the composite (MPa)  
\( \sigma_{VOLS} \)  
characteristic stress derived from volume strain measurement (MPa)  
\( \omega \)  
frequency (s\(^{-1}\))  
\( A_f \)  
specific surface area of the filler (m\(^2\)/g)  
\( A_{fBET} \)  
specific surface area measured by the BET method (m\(^2\)/g)  
\( A_{fc} \)  
specific surface area calculated from the particle size assuming spherical shape (m\(^2\)/g)  
\( A_{fcc} \)  
specific surface area calculated from the particle size determined in composites by SEM analysis (m\(^2\)/g)  
\( B \)  
load bearing capacity of fillers  
\( K_d \)  
donor parameter  
\( K_a \)  
acceptor parameter  
\( \ell \)  
thickness of the interphase (µm)

Abbreviations

AE  
acoustic emission  
CaCO\(_3\)  
calcium carbonate  
CEC  
cation exchange capacity (meq/100 g)  
DSC  
differential scanning calorimetry  
FID  
flame ionization detector  
FTIR  
Fourier transformed infrared spectroscopy  
IGC  
inverse gas chromatography  
MAPP  
maleic anhydride modified polypropylene
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>MFI</td>
<td>melt flow index (g/10 min)</td>
</tr>
<tr>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>weight average molecular weight (kg/mol)</td>
</tr>
<tr>
<td>NaMMT</td>
<td>sodium montmorillonite</td>
</tr>
<tr>
<td>NoMMT</td>
<td>montmorillonite organophilized with ammonium salt</td>
</tr>
<tr>
<td>OIT</td>
<td>oxygen induction time</td>
</tr>
<tr>
<td>OMTMT</td>
<td>organophilized montmorillonite</td>
</tr>
<tr>
<td>OOT</td>
<td>onset temperature of oxidation</td>
</tr>
<tr>
<td>PA</td>
<td>polyamide</td>
</tr>
<tr>
<td>PA6</td>
<td>polyamide 6</td>
</tr>
<tr>
<td>PoMMT</td>
<td>montmorillonite organophilized with phosphonium salt</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermal gravimetric analysis</td>
</tr>
<tr>
<td>vol%</td>
<td>volume percent</td>
</tr>
<tr>
<td>VOLS</td>
<td>volume strain</td>
</tr>
<tr>
<td>WAXS</td>
<td>wide angle X-ray scattering</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
List of publications

Papers used for the preparation of the Thesis


Other publications


Conference presentations


11. Pukánszky, B., Dominkovics, Z.: Late night show or molecular dynamics vs. continuum mechanics for nanocomposites, *Late Night Show With Polymer Nanocomposites*, 4-5 September 2008, Brno, Czech Republic (lecture)


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 am deeply grateful for my colleague Erika Fekete for her continuous support and useful advice during my Ph.D work.

I should like to thank all of my friends and colleagues 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, Chemical Research Center, Hungarian Academy of Sciences for their help and for the pleasant atmosphere they created.

I would like to express my sincere gratitude to Balázs Imre, Éva Kapin, Piroska Pataki, Zoltán Link, Csaba Kenyó and Ede Tatay for their help in sample preparation and characterization of the composites. I am indebted to József Hári for his help in the preparation and evaluation of SEM micrographs. I am grateful for János Kovács for his help in the execution and evaluation of the rheological measurements. István Sajó is acknowledged for his assistance in the measurement and evaluation of XRD traces. I should like also thank to Károly Renner and János Móczó for their help in volume strain and acoustic emission measurements.

I am grateful for Elodie Naveau and Michaël Alexandre at the Center for Education and Research on Macromolecules (CERM), University of Liège for the fruitful and interesting collaboration.

I am also indebted to the National Research Fund of Hungary (OTKA Grant No. K 68748 and K 67936) for financial support.

And at last but not the least, I should like to thank my parents, my grandparents, my brothers and my friends for their continuous love, understanding and support in reaching my goals.