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

Ph. D. Thesis

by

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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. Layered silicate nanocomposites are one class of these materials containing finely dispersed silicate particles\(^1\), \(^2\), \(^3\). The results of the Toyota group called the attention to the potentials of these materials and intensive research has been going on in this field since then\(^4\). 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\(^5\). 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\(^6\). 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\(^1\), \(^2\), \(^3\). However, a more detailed study on a wider length scale proved that the structure of nanocomposites is more complicated than ex-

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pected, besides tactoids and individual layers also large particles and a silicate network may be present in the composite. 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 Ph.D. theses. 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. 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. 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.

2. Experimental

Polypropylene (PP)/organophilized montmorillonite (OMMT) and polypropylene/organophilized montmorillonite/maleic anhydride grafted polypropylene (MAPP) composites were prepared in an internal mixer under a wide range of processing conditions to study the kinetics of structure formation. Composite structure was characterized by various methods including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and rheology. Mechanical properties of the composites were characterized by tensile testing.

In the next part of the research an extended orthogonal experimental design was created exploring the effect of OMMT and MAPP and their possible interaction on the stability of PP/layered silicate nanocomposites. The composites were prepared in an internal mixer, mixing speed and time were changed to study the effect of processing conditions on stability. The structure of the samples was characterized by various methods, while stability by the induction time of oxidation (OIT), the onset temperature of degradation (OOT) and by color.

Nanocomposites were also prepared from sodium montmorillonite (NaMMT) and organoclays with different particle sizes as a function of silicate content. Structure and properties were characterized by a variety of techniques. Model calculations were carried out to estimate the thickness and yield stress of the interphase forming in the composites.

Polyamide-6 (PA6) nanocomposites were prepared from clays organophilized with a phosphonium and an ammonium salt, respectively. Sodium montmorillonite was used as reference. The composites were homogenized by twin-screw extrusion, the clay content of the composites was varied from 0 to 7 vol% in 7 steps. The clays were characterized in detail; X-ray diffraction, SEM, TEM and rheology were used for the characterization of composite structure. Micromechanical deformations were followed by volume strain (VOLS) and acoustic emission (AE) measurements and the mechanism of local deformation was studied by SEM.

3. Results

In the first part of the research we studied the kinetics of structure development in PP/silicate composites with and without a functionalized PP compatibi-
lizer. The gallery structure of organophilic silicate changed even in the absence of compatibilizer. Silicate reflection shifted towards smaller 2θ 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 the uncertainties some overall values of interphase properties were obtained using the results of all composites prepared (Figure 1). The prediction for the average thickness of the interphase is 0.23 µm 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.

**Figure 1** Parameter B plotted against the specific surface area ($A_{f/cc}$) derived from SEM analysis for all composites studied. (O) PP/NaMMT, (□) PP/OMMT, (●) PP/OMMT/MAPP.

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 clay modified with an 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.

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.

Figure 2  Independence of composite yield stress of the micromechanical deformation process resulting in acoustic emission signals. Symbols: (Δ) PA6/NaMMT, (○) PA6/PoMMT, (□) PA6/NoMMT. Results obtained on PP/wood (○) and PLA/wood (●) composites are included as reference.
4. New scientific results

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. [1]

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. [2]

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. [2]

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. [3]

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. [4]

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. [5]
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. [5]

5. Publications

The Thesis is based on the following papers


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)


