



BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS

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**Structure - property relationships in
polymer/layered silicate nanocomposites**

Ph.D. Thesis

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I. Introduction

Polymers are extensively used in all fields of economy; they form an essential part of our life these days. Considerable effort is spent on the development of new polymers and on the improvement of the price/performance ratio of these materials. One way to create new materials is modification with other polymers or fillers in order to create heterogeneous polymer systems. Although, the use of particulate filled polymers looks back to a long tradition, research on composites gained new impetus with the appearance of nanocomposites. The interest in layered silicate nanocomposites was generated by reports from the Toyota research group at the end of the eighties, which prepared polyamide/montmorillonite composites by in-situ polymerization. Incorporation of montmorillonite into polyamide resulted in considerable reinforcement. The interest as well as the number of papers dealing with preparation, structure, properties and possible applications of these materials increased exponentially in the last ten years. Although much information was collected as a result of these efforts and some composites even found new applications since then, the expected breakthrough has not been achieved yet; further research is needed in this field.

The Department of Plastics and Rubber Technology has longstanding experience in the research and development of heterogeneous polymer systems. Particulate filled polymers have been studied for more than 20 years at the Department, but experience was gained also on polymer blends and fiber reinforced composites. These studies were directed mainly to model the composition dependence of properties, to determine the effect of interfacial interactions, to find correlations between structure and properties, to reveal the mechanism and effect of micromechanical deformation processes in various heterogeneous polymer systems, etc. All of these questions play an important role also in nano-

composites. As a consequence, the decision was made a few years ago to use the compiled experience for the study of layered silicate nanocomposites. The first results of this program were summarized in the PhD Thesis of András Pozsgay. The experience and conclusions gained in that stage were used to determine the focus of further research and the goals of this thesis.

The idea of using layered silicates as reinforcement in polymers is based on several observations and a hypothesis. Colloid scientist observed quite some time ago that layered silicates exfoliate in water; the filler particles fall apart into individual layers of 1 nm thickness and about 200-500 nm diameter. In water suspension the solvated surplus cations of the silicate can be exchanged to long chain aliphatic amines, the silicates precipitate from the suspension and form particles with larger gallery distance. After treatment the layers are attached to each other by weaker forces, which are supposed to facilitate exfoliation also during processing, when the silicate is introduced into the polymer. Often complete exfoliation is assumed, which results in an extremely large interface in the composite. The large interface should lead to considerable reinforcement at small silicate content and unique properties generally. The most important advantages of these materials in addition to the expected significant increase in strength and stiffness is claimed to be the improved dimensional stability, decreased flammability, or the limited permeation of small molecular weight materials through them. These attractive features make the polymer/layered silicate nanocomposites extremely interesting in the field of design and creation of new construction as well as packaging materials.

Unfortunately, the properties of nanocomposites reported in the literature are rarely exceptional. In spite of the claims of the authors, published results indicate very small improvement in properties which often does not reach that achieved with fiber reinforcements, sometimes even with particulate fill-

ers. As a consequence, very few experimental results support the original hypothesis that the exfoliation of clay particles leads to the development of large interfaces and extreme reinforcement. In fact our previous experience indicated that exfoliation is seldom complete. On the other hand, very few methods are available for the estimation of exfoliation. Moreover, the structure of nanocomposites is usually characterized by wide angle X-ray diffraction (XRD) and transmission electron microscopy (TEM), attention is mainly focused on the dispersion of individual silicate layers. The formation and presence of other structural units is not even considered in most cases, in spite of the fact that some authors occasionally claim the formation of a silicate network. The formation of large interfaces emphasizes the significance of interfacial interactions. Nevertheless, very few attempts are made for the proper characterization of the surface properties of neat and organophilic clays or for the determination of interfacial interactions. These latter are assumed to be perfect in spite of the fact that numerous results and papers prove that the coverage of an inorganic surface with a surfactant leads to a significant decrease in interfacial adhesion. Indeed, some experimental results indicate that the interaction of the phases in nanocomposites is not always as good as claimed. Additionally, several other factors which might influence composite properties are neglected and important phenomena remain unexplained. As a consequence, this thesis focused on the issues listed above, i.e. on interfacial interactions, on the structure of the composites and on structure-property correlations.

II. Materials and methods

A sodium montmorillonite and six organophilic montmorillonites coated with different surfactants were characterized in various ways and used for composite preparation. Four maleic-anhydride modified polypropylenes

and two unmodified polypropylenes were chosen as the matrix of our composites. The surfactant content of the silicates and the temperature of decomposition of the samples were determined by thermogravimetric analysis (TGA). Particle and surface characteristics were determined by nitrogen adsorption and inverse gas chromatography (IGC), respectively. Model reactions of surfactants as well as the crystallization and melting characteristics of composites were studied by differential scanning calorimetry (DSC). The reaction products were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). The composites were homogenized using a Brabender internal mixer and then compression molded to plates. The plates themselves, or dog-bone type tensile specimens cut from them were used for the different measurements. The gallery structure of organophilic montmorillonite, the orientation of surfactants in the galleries and surface coverage was estimated by X-ray diffraction (XRD) measurements and model calculations. The morphology of the composites was examined by scanning (SEM) and transmission electron microscopy (TEM) combined with image analysis. The rheological properties of the composites were characterized by dynamic viscosimetry, while the mechanical properties were measured by tensile testing.

III. New scientific results

1. Similarly to others we found that in commercial silicates the long chain surfactants used for the coating of montmorillonite orientate more or less parallel to the surface and usually cover the platelets in a single layer. However, we pointed out additionally also that surplus surfactant is not located in the galleries, but among the particles and might influence the properties of composites negatively.

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2. We showed that the surface tension of clay decreases as an effect of surface coating and it is practically the same for all organophilic silicates irrespectively of the type of the surfactant used for treatment. Decreased surface tension may facilitate exfoliation and the effect can be further enhanced by the use of surfactants with two long aliphatic chains, one of which orientates vertically to the surface and results in larger gallery distance. However, polymer/silicate interaction decreases as an effect of organophilization.
 3. With the help of model reactions which were carried out with components frequently used for the preparation of intercalated or exfoliated polypropylene nanocomposites we proved that maleinated polypropylene can react chemically with the surfactant applied for the organophilization of the filler, if this latter contains active hydrogen groups. Chemical reactions remove the surfactant from the surface of montmorillonite and hydrogenated silicate sites are left behind. The high energy surface interacts either with the anhydride or the amide groups by dipole-dipole interactions. Even the unmodified polypropylene chains may be attached much stronger to the surface by London dispersion forces than to the silicate covered with aliphatic chains.
 4. Unlike others we characterized the structure of polypropylene/layered silicate composites over several length scales in detail and proved that these materials possess a very complex structural architecture. Original clay particles, intercalated stacks and individual silicate layers can be found simultaneously in the composites in relative amounts depending on composition and experimental conditions. We also showed that in the case of efficient exfoliation, i.e. in the presence of a large number of individual layers, a silicate network structure may form, which can be detected very sensitively by Cole-Cole plots of dynamic viscosity.

5. We analyzed the composition dependence of the tensile yield stress of a large number of composites with the help of a simple model and estimated the extent of reinforcement, as well as exfoliation quantitatively. The analysis of about 40 polypropylene composites indicated that the extent of exfoliation is very low in most of them; it reaches maximum 8 % of the theoretically possible value in the best case. This result strongly supports our previous thesis point claiming that complete exfoliation can be seldom reached in thermoplastic/clay composites; the structure is complex and hierarchical including large particles and individual silicate layers.
6. We extended the analysis also for nanocomposites with matrices other than PP and found that several processes may take place during the preparation of these materials and a considerable number of factors influence composite properties, quite a few of which are often neglected. The most important of such effects are changing matrix properties when a functionalized polymer is used to promote adhesion (PE, PP), modification of crystalline structure due to nucleation (PA, PP), plasticization or lubrication (PVC) or chemical reactions (PVC, PP, PET, rubbers). Some of these processes lead to composites with very poor properties compared either to the matrix polymer or to traditional microcomposites.

IV. The thesis is based on the following papers

1. **Százdi, L.**, Pukánszky Jr., B., Földes, E., Pukánszky, B.: Possible mechanism of interaction among the components in MAPP modified layered silicate PP nanocomposites, *Polymer* **46**, 8001-8010 (2005)
2. Gatos, K. G., **Százdi, L.**, Pukánszky, B., Karger-Kocsis, J.: Controlling the deintercalation in hydrogenated nitrile rubber (HNBR)/organo-

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- montmorillonite nanocomposites by curing with peroxide, *Macromol. Rapid Commun.* **26**, 915-919 (2005)
3. Choi, J. S., Lim, S. T., Choi, H. J., Pozsgay, A., **Százdi, L.**, Pukánszky, B.: Viscoelastic properties of exfoliated polyamide-6/layered silicate nanocomposite, *J. Mater. Sci. Lett.* **41**, 1843-1846 (2006)
 4. Choi, J. S., Lim, S. T., Choi, H. J., Pozsgay, A., **Százdi, L.**: Effect of interfacial interaction on structure and rheological property of Polyamide-6/Clay nanocomposites, *accepted to Comp. Interfaces*
 5. Kádár, F., **Százdi, L.**, Fekete, E., Pukánszky, B.: Surface characteristics of layered silicates; influence on the properties of clay/polymer nanocomposites, *submitted to Langmuir*
 6. **Százdi, L.**, Ábrányi, Á., Pukánszky Jr., B., Vancso, J. G., Pukánszky, B.: Morphology characterization of PP/clay nanocomposites across the length scales of the structural architecture, *submitted to Macromol. Mater. Eng.*
 7. **Százdi, L.**, Pukánszky Jr., B., Vancso, J. G., Pukánszky, B.: Quantitative estimation of the reinforcing effect of layered silicates in PP nanocomposites, *submitted to Polymer*
 8. Pukánszky Jr., B., Ábrányi, Á., **Százdi, L.**, Pukánszky, B.: A kölcsönhatás módosítása polipropilén/rétegszilikát nanokompozitokban, *Műanyag és Gumi* **40**, 417-422 (2003)

V. Other publications

9. **Százdi, L.**, Gulyás, J., Pukánszky, B.: Electrochemical oxidation of carbon fibres: adsorption of the electrolyte and its effect on interfacial adhesion, *Composites* **A33**, 1361-1365 (2002)

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10. **Százdi, L.**, Gulyás, J., Pukánszky, B.: Surface characterization of electrochemically oxidized carbon fibers: surface properties and interfacial adhesion, *Compos. Interfaces* **9**, 219-232 (2002)
 11. Pozsgay, A., Fráter, T., **Százdi, L.**, Müller, P., Sajó, I., Pukánszky, B.: Gallery structure and exfoliation of organophilized montmorillonite: effect on composite properties, *Eur. Polym. J.* **40**, 27-36 (2004)
 12. Pozsgay, A., Csapó, I., **Százdi, L.**, Pukánszky, B.: Preparation, structure, and properties of PVC/montmorillonite nanocomposites, *Mater. Res. Innov.* **8**, 138-139 (2004)
 13. Dányádi, L., **Százdi, L.**, Gulyás, J., Bertóti, I., Pukánszky, B.: Surface chemistry and adhesion in carbon fiber reinforced epoxy microcomposites, *Compos. Interfaces* **12**, 243-258 (2005)
 14. Ábrányi, Á., **Százdi, L.**, Pukánszky, B. Jr., Vancso, J. G., Pukánszky, B.: Formation and detection of clay network structure in polypropylene/layered silicate nanocomposites, *Macromol. Rapid Comm.* **27**, 132-135 (2006)
 15. **Százdi, L.**, Gulyás, J., Pukánszky, B.: Anódosan oxidált szénszálak felületi jellemzőinek vizsgálata, *Műanyag és Gumi* **38**, 405-410 (2001)
 16. Ábrányi, Á., **Százdi, L.**, Pukánszky, B.: Delamináció kinetikája polipropilén nanokompozitokban, *Műanyag és Gumi* **41**, 466-471 (2004)
 17. **Százdi, L.**, Pukánszky, B.: Nanokompozitok és alkalmazási területei, *Műanyag és Gumiipari Évkönyv* **2**, 87-90 (2004)

The subject of the thesis is formed by additional 20 international and 9 Hungarian presentations.