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Quantitative Characterization of the Structure of PP/Layered Silicate Nanocomposites at Various Length Scales

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Summary: The structure and rheological properties of a large number of layered silicate polypropylene nanocomposites were studied with widely varying compositions. Unlike general practice, morphology was characterized at different length scales covering several decades by SEM, TEM, and XRD. Rheological measurements supplied additional information about structure. The results showed that these materials possess a very complex structural architecture. The introduction of a functionalized polymer decreases the size of the original clay particles. However, relatively large silicate particles were found also in composite samples yielding XRD traces without silicate reflection. We found that not only two (individual layers, intercalated stacks), but four morphological entities, i.e. also particles and a silicate network, may be present simultaneously in the composites. An attempt was made to characterize morphology quantitatively, wherever possible. SEM and TEM micrographs were evaluated by image analysis, XRD traces by curve fitting, while a model was developed to determine relaxation time from rheological measurements, but only XRD and SEM results are reported here.

Keywords: layered silicates; PP; rheology; SEM; structure; TEM; WAXS

Introduction

Layered silicate polymer composites attracted much interest recently because of their potential advantages. They are claimed to have improved thermal and dimensional stability, better barrier properties, and flame resistance than the unfilled polymer matrix.[1] One of the main advantages of fillers dispersed on the nanoscale in polymers is claimed to be large reinforcement reached at very low filler content, which should lead to light composites with considerable stiffness and strength. However, to really utilize all the potential advantages of polymer/layered silicate nanocomposites, the silicate must be exfoliated to a large extent into individual layers. Unfortunately, exfoliation is practically never complete. The majority of the papers published on these materials indicate the formation of an intercalated/partially exfoliated structure.[2] The claim is based on the results of X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM), which are routinely used for the characterization of layered silicate polymer nanocomposites. However, a more detailed study on a wider length scale proved that the structure of nanocomposites is more complicated than expected[3], besides tactoids and individual layers also large particles and a silicate network may be present in the composite. To control the structure of layered silicate nanocomposites and fully

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utilize their potential advantages, their structure must be characterized as thoroughly as possible. The goal of this study was to describe the structure of PP/layered silicate nanocomposites quantitatively. Techniques were used which offer information about structure at different length scales. Because of the limited length of the paper, only results obtained by XRD and SEM are reported here. The results related to the formation of a silicate network is reported in a separate paper in the same issue.[4]

Experimental Part

The Tipplen H 649 grade PP homopolymer (MFR = 6.0 g/10 min at 230 °C, 21.6 N) produced by TVK, Hungary, was used as matrix, while Nanofil 848 (Süd-Chemie GmbH) was employed as clay. A small molar mass maleinated PP, Licomont AR 504 (Clariant GmbH), was used to promote exfoliation. Its maleic anhydride content was 3.5 wt% and it possessed very low viscosity (0.8 Pas at 170 °C). The silicate content of the composites changed from 0 to 3.0 vol%, while the amount of MAPP varied between 0 and 50 vol%. The components were homogenized in a Brabender W50 EH internal mixer at 190 °C, 50 rpm for 10 min and then compression molded to 1.0 mm thick plates. The gallery structure of the silicate was characterized by XRD using a Phillips PW 1830/PW 1050 equipment with CuK$_\alpha$ radiation at 40 kV and 35 mA in reflection mode. The morphology of the samples was examined by scanning (SEM) and transmission electron microscopy (TEM), respectively. TEM images were created with a Philips CM30 twin STEM electron microscope. SEM images were recorded on etched surfaces using a LEO Gemini 1550 FEG-SEM. 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.

Gallery Structure, XRD

The quantitative characterization of the extent of exfoliation would help the determination of structure-property correlations enormously. Several attempts were made to quantify structure from TEM micrographs, but XRD traces are rarely evaluated quantitatively for several reasons. The intensity of the silicate reflection depends on the regularity of the layers within the stacks, their distance and orientation. The deconvolution of XRD traces and the separation of various effects are extremely difficult.[5] However, if we assume that average orientation is the same and that the regularity within the stacks do not change, we may deduce useful information from the quantitative analysis of XRD traces.[3] PP nanocomposites cannot be prepared from the polymer and an organophilic silicate alone, a coupling agent, usually functionalized PP must be also added to help exfoliation. The effect of the amount of MAPP on the XRD traces of PP/OMMT nanocomposites is shown in Figure 1 for composites containing 2 vol% silicate. The characteristic silicate reflection shifts towards smaller 2θ angles and its

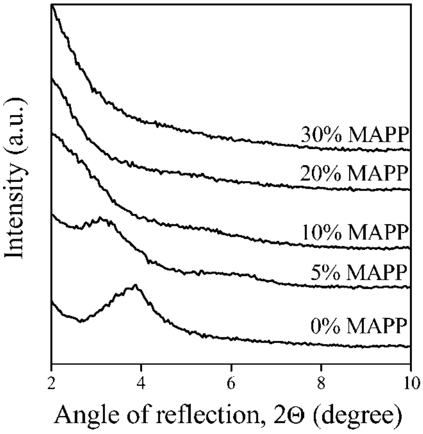

Figure 1.
Effect of the amount of MAPP on the position and intensity of the silicate reflection in PP/OMMT/MAPP composites. Silicate content 2 vol%.

intensity decreases with MAPP content, what is often interpreted as increasing extent of exfoliation. At 30 vol% MAPP content the silicate reflection is practically absent, which could indicate the complete exfoliation of the silicate particles (layers). This might not be completely true, but we may conclude that the introduction of MAPP changes structure significantly and the changes in the XRD traces correspond to the expectations.

The traces presented in Figure 1 can be evaluated quantitatively, although the approach is not straightforward. In an earlier study we subtracted the trace of the PP matrix from that of the composite, fitted a Lorenzian function to the silicate reflection and determined both the location and the area under the peak. The latter amount is plotted against MAPP content in Figure 2a. The intensity of the silicate reflection increases continuously, what seems to contradict the results of Figure 1. We may argue, however, that the peak shifts towards smaller 2θ angles with increasing MAPP content thus a large part of the peak falls outside the lower limit of the scale, on the one hand, while increasing layer distance and regularity leads to an increase of intensity, on the other.

Nevertheless, one has lingering doubt about the validity of the approach. Subtraction of the XRD trace of the matrix polymer is not necessarily correct, since changing composition modifies also background scattering. As a consequence, we decided on trying also another approach. Instead of using the trace of the neat polymer as reference, we fitted a separate baseline to the trace of each composite, and then followed the procedure described above, i.e. fitted a Lorentzian function to the silicate reflection and determined its characteristics. The results of the calculation are presented in Figure 2b and they reflect much better the qualitative conclusions drawn from Figure 1 than those derived by the previous approach (see Figure 2a), i.e. the second approach leads to more realistic results. We may conclude that the intensity of the silicate reflection decreases with increasing MAPP content probably due to exfoliation and/or because of changing regularity of intercalated stacks.

Particle Structure, SEM

Based on results similar to those presented above, several authors claimed complete exfoliation of the silicate in their composite.[6,7] However, structure is always

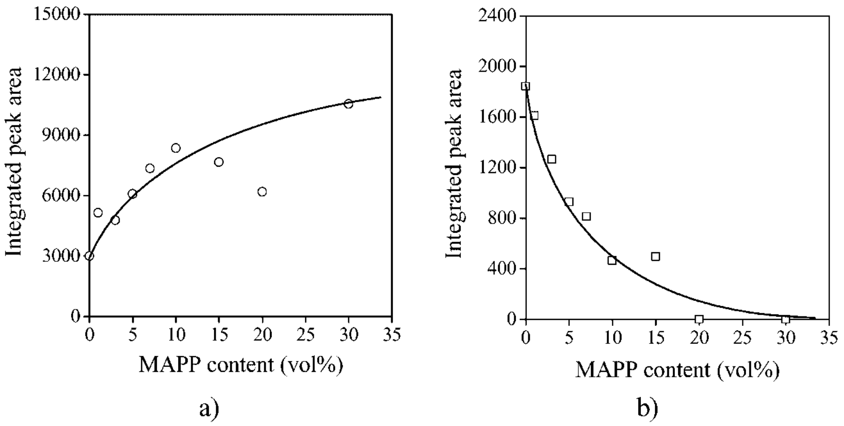

Figure 2.

Quantitative evaluation of the XRD traces of PP/OMMT/MAPP composites with two different approaches. a) using the neat polymer as reference, b) fitting separate baselines for each composite. Silicate content: 2 vol%.

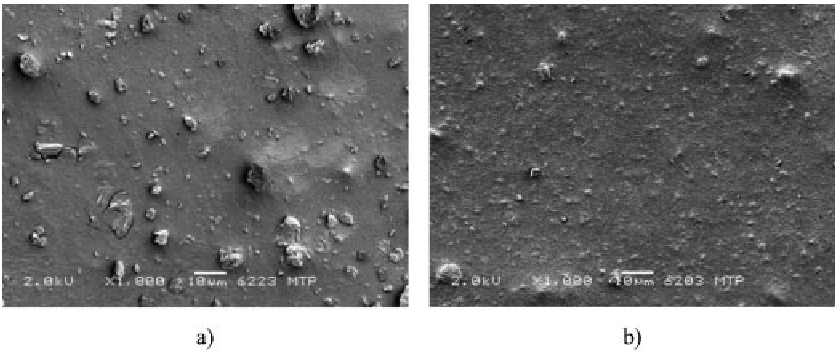

Figure 3.
Changes in the particle structure of PP/OMMT upon the introduction of MAPP. a) 0 vol% MAPP, b) 30 vol% MAPP. Silicate content: 2 vol%.

studied at the nanometer scale and rarely checked at smaller magnifications. The SEM micrograph in Figure 3a clearly shows the particulate structure of the PP/OMMT composites prepared. It also proves that nanocomposite cannot be prepared from a neat PP and an organophilic silicate; limited intercalation may take place in such composites at most. Based on the results of Figure 1 and 2b, one would expect a completely homogeneous surface on the micrometer scale in the presence of MAPP. However, relatively large particles are present in our composite containing as much as 30 vol% MAPP (see Figure 3b), which seems to contradict results presented above.

The apparent contradiction between Figure 3b and the XRD traces of Figure 1 might be resolved if we consider a few facts. MAPP was shown to intercalate OMMT by many papers and the shift of the silicate reflection towards smaller 2θ angles also proves that it enters the galleries of the clay. Intercalation probably decreases the regularity of the platelets in the stacks what leads to a decrease in the intensity of the silicate reflection. Finally, the reflection is relatively weak already in the PP/OMMT composite. The comparison of Figure 3a and 3b indicates the break-down of the particles to smaller units. We must assume that very small particles disappear completely, which must also decrease the intensity of the silicate reflection. This decrease in intensity and changes in the regularity of the stacks may lead to the complete loss of silicate reflection in Figure 1. The results prove again that the lack of silicate reflection in the XRD spectrum does not indicate complete exfoliation.

The extent of changes was estimated quantitatively; the micrographs were evaluated by image analysis. The process yielded several quantities, which characterize structure. The average area of the particles is presented in Figure 4 clearly proving that particle size decreases continuously and significantly with increasing MAPP content. Probably even further

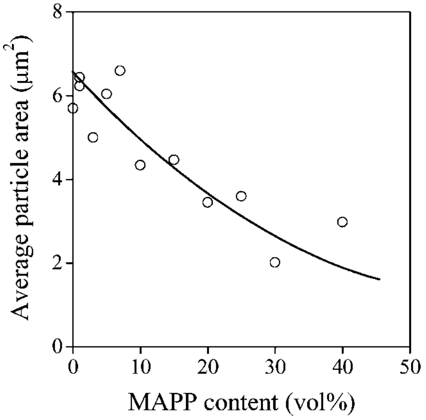

Figure 4.
Changes in the particle size of the silicate with MAPP content. Silicate content: 2 vol%.

decrease of size could be achieved by changing the conditions of processing, i.e. increasing the intensity of mixing or residence time.

Conclusions

The structure of layered silicate nanocomposites is more complicated than usually claimed; at least four structural entities (particles, tactoids, layers, network) are present in them. Currently used protocols do not characterize structure properly, quantitative characterization requires further work. XRD offers information about gallery structure, but does not supply unassailable proof about exfoliation. Particulate structure can be described by the image analysis of SEM micrographs. TEM and rheology offers information about exfoliated layers and the formation of a silicate network. Several methods must be used simultaneously to obtain a clear picture of nanocomposite structure.

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