

Polyolefin/Silicate Nanocomposites

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It is known that the addition of inorganic substances in polymeric materials leads to hybrids with lower permeability to gases, higher heat and flame resistance, increased mechanical properties and smaller cost than the parent polymers. Lately, there is a special interest in layered-silicate based polymer nanocomposites which represent an attractive set of organic-inorganic materials with great technological importance and at the same time convenient macroscopic systems for studying fundamental scientific problems. Mixing polymers with such silicated materials results in three different micro- or nano- structures, the *phase separated* composites where the polymer and inorganic material are immisible, the *intercalated* where the polymer chain is intercalated between the inorganic layers and the *exfoliated* where the silicate layers are dispersed in the polymer matrix [1]. Figure 1 shows these three resulting structures.

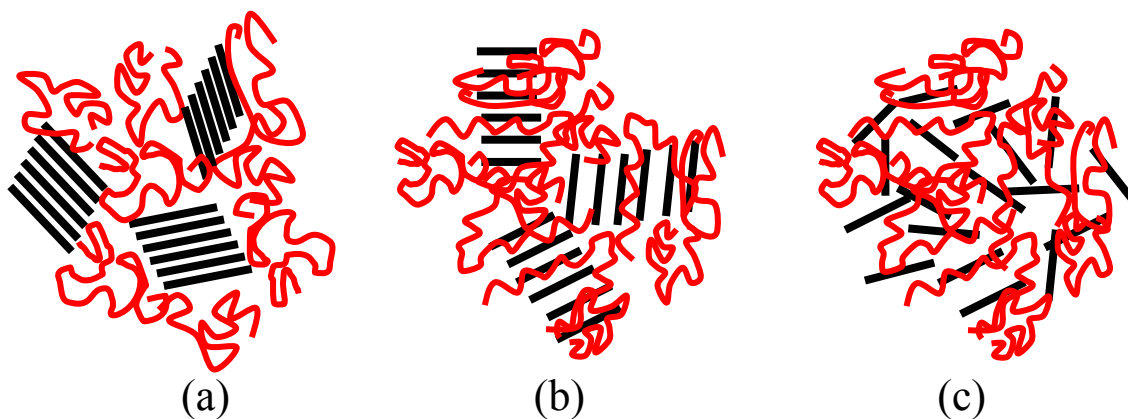


Figure 1: Structures resulting from the mixing of polymer chains with layered silicates. (a) phase separated, (b) intercalated and (c) exfoliated.

For hydrophilic polymers, intercalation or exfoliation can be achieved by directly mixing the clay with the polymer above its softening temperature. In the case of less or non polar polymer chains, the mixing is attempted with an organoclay produced via a cation exchange reaction to transform its initially organophobic surfaces to organophilic.

In this work we are mostly interesting in the preparation of polyolefin/silicate nanocomposites. For example, polyethylene, PE, or polypropylene, PP, are materials widely used in many applications, as food packaging, films or in the automotive and electronics industry, so the need of enhancing their properties with at the same time lowering their cost is of great importance. Unfortunately, the preparation of polyolefin based nanocomposites is

extremely difficult. We are using different additives like homopolymers with functional groups or suitable diblock or graft block copolymers aiming in achieving either the intercalation of the chains or the exfoliation of the silicate layers.

The composites are prepared in a DSM 5cm³ micro-mixer and micro-extruder. The final structure of the composite is characterized in every case using X-ray diffraction. In certain cases intercalation or exfoliation can occur depending on the percentage of the additive. Figure 2 shows the diffractograms of such a case where PE-graft-maleic anhydride has been also mixed with the PE and the silicate in different portions. The d_{001} spacing of the pure organoclay is found to be $d_{001} \sim 30 \text{ \AA}$ and it remains unchanged by the addition of PE. If a fraction of the PE chains in this composite are substituted by PE-graft-maleic anhydride chains, a small but finite increase of the d_{001} by 3-4 \AA is obtained whereas further increase of the amount of PE-graft-maleic anhydride can lead to an exfoliated structure. Rheological and thermal measurements are in progress in order to investigate whether this change in the structure is followed by a respective change in the properties of the materials.

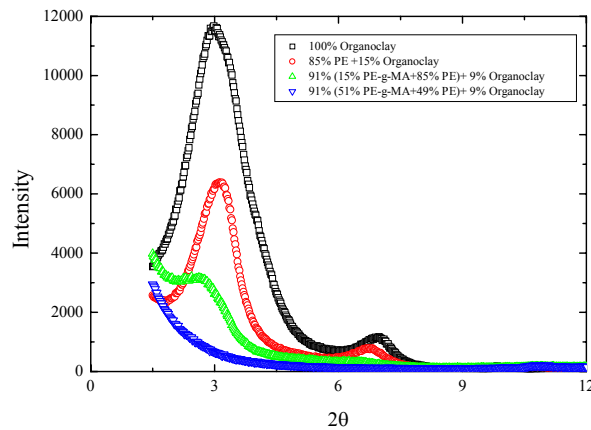


Figure 2: Diffractograms of PE/PE-graft-maleic anhydride/Silicate in different percentages. For comparison the spectra of pure organoclay and PE/organoclay composites are included.

In other cases irrespectively of the presence of the polymeric additive, intercalation or exfoliation cannot be achieved and the system remains phase separated. Even in these cases, however, there are indications that there is a change in the mechanical and thermal properties of the composite.

Furthermore, besides the change in the rheological and thermal properties of these materials, there is strong evidence that mixing the polymer chains with the silicates may lead to changes in their crystalline structure.

References:

[1] E. P. Giannelis, *Advanced Materials*, **8**, 29, (1996); R. K. Krisnamoorti, et. al., *Chem. Mat.* **8**, 1728 (1996); E. P. Giannelis, et. al., *Adv. Polym. Sci.* **138**, 107 (1998).

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