Kalmar ECO-TECH '05 and
The First Kalmar Nanotechnology Workshop
KALMAR, SWEDEN, November 28-30, 2005

NANO-CLAYS IN POLYMER COMPOSITES - TINY PARTICLES WITH HUGE POTENTIAL

Ignacy Jakubowicz
SP Swedish National Testing and Research Institute, Sweden

ABSTRACT

The definition of nano-composite material is broad and includes a large variety of systems such as one-dimensional (layered silicates), two-dimensional (cellulose whiskers and carbon nanotubes), three-dimensional (silica-titanium oxides) and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale (10^{-9} meter). Nanoplastics or polymeric nanocomposites (PNC) means polymeric composites filled with nanoscale superfine inorganic particles. They often have properties that are superior to conventional microscale composites and can be synthesized using surprisingly simple and inexpensive techniques. A nanoscale dispersion of sheet-like inorganic silicate particles in a polymer matrix, for example, is superior to either constituent in such properties as optical clarity, strength, stiffness, thermal stability, reduced permeability, and flame retardancy.

Depending on the chemical composition of the clay, the sheets bear a charge on the surface and edges. This charge is balanced by counter-ions, which are situated in part in the inter-layer spacing of the clay. The best properties are obtained if the clay is fully exfoliated into single clay layers. During exfoliation, the clay particles do not only become much smaller but simultaneously their shape changes from cubical blocks to flat platelets. The shape of clay platelets is usually expressed in its aspect ratio. This is the ratio between the diameter and the thickness of a platelet. The thickness of the layers (platelets) is of the order of 1 nm and aspect ratios are high, typically 100-1500. As a result of their small dimensions, the clay platelets have a large specific surface area of about 700-800 m^2/g. Their small size also results in small inter platelet distances in a polymer-clay nanocomposite. At a loading of 1 weight percent of clay these distances are about 200 nanometers while they are merely 10 nanometers at a loading of 10 weight percent. In the context of PNC's, it is important to note that the molecular weight of the platelets (ca. 10^8) is considerably greater than that of typical commercial polymers (ca. 10^5) a fact, which is often misrepresented in schematic diagrams of PNC's. In addition, platelets are not totally rigid, but have a degree of flexibility. The clays are also characterised by their ion exchange capacities (e.g. cation), which can vary widely. One important consequence of the charged nature of the clays is that they are generally highly hydrophilic and therefore normally incompatible with most of the polymer types.

A necessary prerequisite for successful formation of polymer-clay nanocomposites is therefore alteration of the clay polarity to make the clay “organophilic”. An organophilic clay can be produced from a normally hydrophilic clay by ion exchange with an organic cation such as an alkylammonium ion. For example, in Montmorillonite (MMT), the sodium ions in the clay can be exchanged for an amino acid such as 12-aminododecanoic acid (ADA). Other materials variables which can be controlled and which can have a profound influence on the nature and properties of the final nanocomposite include the type of clay, the choice of clay

pre-treatment, the selection of polymer component and the way in which the polymer is incorporated into the nanocomposite. Due to the nano-scale effects polymer-clay nanocomposites show dramatic improvements in plastic properties i.e. strength, modulus, fire resistance, and lower-weight gas permeability barrier properties with far less silicate content than what is used in conventional filled polymer composites. Thus during the processing of polymer nanocomposites (PNC), the nanoscale silicate layers can be dispersed in the polymer matrix and reinforcement phase forms in situ on the molecular level which is very different from conventional filled composites. Furthermore the nanoclay is environmentally friendly, naturally abundant and with a potential to be economically favourable. Nanocomposite can be prepared by conventional processing techniques for example extrusion and injection methods.

Current research frontier in nanocomposites includes developing an understanding of the characteristics of the interphase region, its dependence on nanoelement surface chemistry, the relative arrangement of constituents and, ultimately, its relationship to the PNC properties. Equally important is the development of a general understanding of the morphology-property relationships for mechanical, barrier, and thermal response of these systems. This necessitates also the use of advanced analysis methods. In nano-material formulation, the structural properties are conventionally monitored and characterised using imaging techniques such as SEM, TEM, surface spectroscopy and AFM.

Especially, the scanning electron microscope (SEM) has become a powerful tool for ultrastructural research with improvement of the instrument's resolution. Nanocomposite formation and the degree of dispersion of nanoparticles is frequently monitored using transmission electron microscopy (TEM). TEM allows the user to determine the internal structure of materials and the shape and size of particles. Materials for TEM must be specially prepared to thicknesses which allow electrons to transmit through the sample. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms. The energy of the electrons in the TEM determines the relative degree of penetration of electrons in a specific sample, or alternatively, influence the thickness of material from which useful information may be obtained. X-ray crystallography is one of the most useful methods for exploring the nature of matter. X-ray diffraction measurements (XRD) allows the user to determine the crystallisation behaviour of materials and the size of and the distance between clay particles.

Topics covered by the research program at SP – Polymer technology

1. evaluation of potential advantages and pitfalls of the current crop of PNC materials as compared to conventionally filled polymers
2. possible replacement of existing conventional materials with polymer nanocomposites
3. development of PNC materials for sufficiently rapid process of blending a molten thermoplastic with an organosilicate to take place in a commercial mixing extruder
4. selection or development of additives that must not excessively degrade the other performance properties of the polymer, and that must not create environmental problems in terms of recycling or disposal of the final product
5. evaluation of long-term performance and durability of PNCs
6. estimation of the potential risks for release of nanoparticles into environment and risks associated with nanotoxicity.