

## CLAY/POLYMER NANOCOMPOSITES A NEW FRONTIER

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In 1989 the first clay/nanocomposite was introduced by Toyota Central Research. This nanocomposite was made utilizing Nylon-6 and surface modified montmorillonite clay. This composite yielded very substantial increases in tensile strength, modulus, and heat distortion temperature without loss in impact strength at loadings of clay that were less than 5%. Traditional composites of talc or mica require 35 to 40% loadings to reach these levels modulus improvements but result in a loss of impact strength. Films of the Nylon-6 nanocomposite also exhibited substantial decreases in vapor transmission rates while maintaining clarity. This improved transmission rate has strong implications for the food packaging industry. In addition the Nylon-6 nanocomposite exhibited improved chemical resistance and flame retardancy. All of the above property enhancements stimulated a large amount of interest in the polymer industry and significant research efforts to expand the nanocomposite technology to other polymer types. These efforts are not bearing fruit as a number of new clay/polymer nanocomposites are being introduced into commercial applications. It appears that this new technology will become a platform technology in the polymer industry and will be a major market for the industrial minerals industry in the 21<sup>st</sup> century.

### Engineering Applications of Nanocomposites

The physical property enhancements characteristic of nanocomposites show promise for many applications. In the auto industry two areas of application involve the engineering properties of nanocomposites are of interest. The first is for external and interior body parts. The improved modulus and tensile increases without loss of impact of nanocomposites are very attractive as compared to metal. The possibility of obtaining in mold color with class A surface would be a major cost savings to auto manufacturers. This goal is not attainable with current composite technology. The current practice of glass filling polymers can exceed the physical properties of nanocomposite but at the cost of surface quality and the ability to have in mold color. Glass filled systems also sacrifice the weight advantage seen in nanocomposites since glass filler levels are in the range of 30 to 40% by weight as compared to nanocomposites at 2 to 5%.

The second area of interest to the auto industry is applications under the hood of a car where the heat load is substantial. It has been well documented that nanocomposites increase the heat distortion temperature of the polymer composite relative to the pure polymer substantially. In fact the very first application of a nanocomposite was as a timing belt cover on the Toyota Camry. This would allow intake manifolds, air plenums, valve covers, timing belt

covers, and other parts under the hood to be utilized at substantial weight savings.

In the United States a third area that nanocomposites could impact is in gas tanks. Current environmental regulations will require gas tanks in the United States to meet very stringent emissions standards. The only current technology that can meet these standards is a multi-layered laminate that is fairly expensive. Nanocomposites are well known to enhance the barrier properties of polymers. This may allow a single ply fuel tank that will meet the emissions standards and save money for the auto manufacturers.

### Barrier Applications

The majority of current applications of nanocomposites involve the ability to enhance barrier properties in various food packing applications. Currently a number of companies offer flexible nylon-6 film grade nanocomposites which give a two-fold decrease in oxygen transmission rate. Recently a nanocomposite beer bottle has been introduced that economically practical plastic beer container. This same technology will also extend plastic bottles to smaller carbonated beverage containers that in the past were not feasible because of shelf-life constraints. Early work in elucidating the mechanism of barrier improvement in nanocomposites utilized a tortuous path model where the aspect ratio of the smectite clay was the main variable. This model has proven to be inadequate in predicting the barrier characteristics of many nanocomposites. A more satisfactory model involves not only the aspect ratio of thermectite but also effects due to a region around the clay plates where the polymer is constrained in a way that is different from bulk polymer. This model will be discussed in some detail.

### Flame Retardancy

Nanocomposites have been shown to impact flame retardancy to polymers of various types. In tests where the peak heat release has been measured in cone calorimeters the value for the nanocomposite is consistently 60 to 80% lower than the pristine polymer. It appears that the clay acts as a char former thus passivating the surface and retarding flame propagation. The concern in recent years about halogen contain flame retardants could be addressed by the use of nanocomposite technology. Several specific examples will be given of this flame retardancy effect.

### Implications for Industrial Minerals

Nanocomposites in general require a highly purified smectite clay in order to reap maximum benefits. This

level of purity is only attainable by water washing bentonite clays. Currently world wide the total capacity for water washing clays is roughly 70,000 tons. The vast majority of the capacity is consumed in traditional manufacture of organoclay thixotropes for paint, grease, drilling muds, inks, and cosmetics. The total production of thermoplastic polymers in the world is in the range of 100 – 150 billion pounds per year. A typical nanocomposite will contain 5 wt. % of clay. Considering only a 5% penetration of the polymer market for nanocomposites would give a need for 150,000 tons of water washed clay. This would require a tripling of the current world capacity for water washed clay. These products also require surface modification and therefore will most likely retail in the range of \$4,000 to \$8,000 per ton. This would mean the potential size of the nanocomposite clay supplier industry could be in the range of one billion per year. This is the largest potential market every for value added industrial minerals.