

Reducing the Cation Exchange Capacity of Lithium Clay to Form Better Dispersed Polymer-Clay Nanocomposites

Maggie Liang

The Ohio State University

Major: Biochemistry

Undergraduate, Sophomore

Mentor: Sandi Campbell

Abstract

Polymer-clay nanocomposites have exhibited superior strength and thermo-oxidative properties as compared to pure polymers for use in air and space craft; however, there has often been difficulty completely dispersing the clay within the matrices of the polymer. In order to improve this process, the cation exchange capacity of lithium clay is first lowered using twenty-four hour heat treatments of no heat, 130°C, 150°C, or 170°C to fixate the lithium ions within the clay layers so that they are unexchangeable. Generally, higher temperatures have generated lower cation exchange capacities. An ion exchange involving dodecylamine, octadecylamine, or dimethyl benzidine (DMBZ) is then employed to actually expand the clay galleries. X-ray diffraction and transmission electron microscopy can be used to determine whether the clay has been successfully exfoliated. Finally, resins of DMBZ with clay are then pressed into disks for characterization using dynamic mechanical analyzer and oven-aging techniques in order to evaluate their glass transition, modulus strength, and thermal-oxidative stability in comparison to neat DMBZ. In the future, they may also be tested as composites for flexural and laminar shear strength.

Improving the lifetime and overall performance of its high-temperature polymer materials is of constant interest to the Polymers Branch at NASA Glenn Research Center. One technique that is currently being studied is the dispersal of clay within composites in order to reinforce various polymers. Researchers have noted improvements in strength, heat stability, and gas barrier properties of polymer-clay nanocomposites in comparison to neat polymers. Moreover, all of these improvements can be attained at a relatively low clay loading of two to ten weight percent and without alteration to the polymer's basic properties or loss of clarity in the polymer.

Not only is clay a naturally very stable substance, its structure lends itself well as an even more promising means of fortification. Natural clay is composed of impermeable clay layers stacked very closely together, approximately 1 nanometer apart. Upon dispersal, however, the layers are separated and become aligned in random directions. The result is that these exfoliated clay layers create a treacherous pathway for any permeant to penetrate through the nanocomposite. This proves to be a significant advantage since one of the major concerns when dealing with polymers is the threat of degradation, particularly due to oxidation.

X-ray diffraction and transmission electron microscopy (TEM) are typically used to analyze the extent of clay dispersal. X-ray diffraction techniques can quantitatively determine the distance of separation between the clay layers. Using the Bragg equation, $n\lambda = 2d\sin\theta$, the d-spacing of the clay gallery for both the unmodified and dispersed clay can be calculated and then compared. The TEM also confirms dispersal by providing a qualitative picture of the separated clay layers. Characteristics of a successful dispersal image include clearly defined, thin clay layers that are spaced far apart and lie in many different directions.

However, due to strong electrostatic forces between the layers, clay generally disperses poorly in the matrices of the polymer. In order to make the inorganic clay more compatible with the organic polymer, an ion exchange is used to displace the cations present in the clay, such as sodium or lithium, with protonated diamines and protonated alkyl amines. The diamines are added to react with the ester/acid monomers used in polymer synthesis, while the long carbon chains are inserted between the clay layers to expand the gallery; thus, the clay becomes somewhat organophilic. Also, as the clay layers are separated, the surface area of the clay layers increases and the polymer chains are better able to integrate with the clay sheets. A series of three ion exchanged clays were prepared for each heat treatment using dodecylamine, octadecylamine, or dimethyl benzidine (DMBZ) for a total of twelve samples.

This summer I am particularly interested in lowering the cation exchange capacity (CEC) of the clay so that it will disperse better within the polymer matrices. In order to accomplish this, the clay is heat treated at various temperatures. These include unheated, 130°C, 150°C, and 170°C treatments for 24 hours each. During heating the cations

migrate from exchange sites throughout the gallery space into the actual clay layers, thus becoming unexchangeable. With fewer cations present, the electrostatic forces in the clay are even further weakened. The clay initially arrives, though, containing interlayer sodium ions which are too large to facilitate this process. For that reason, the first step is to exchange the sodium ions in the clay with smaller lithium ions using lithium chloride, even before the clay is heat treated. Thus, it is the fixation of lithium after modification rather than the naturally occurring sodium cations that result in a decreased CEC.

Afterward, the CEC is determined by repeated saturation of the samples with 0.10N aqueous ammonium acetate, added drop-wise. After centrifuging the sample, the supernatant is analyzed for lithium using inductively coupled plasma (ICP). The sample is placed into a high-temperature plasma or gas. When the atoms relax, they give off light which can be separated into wavelengths by spectroscopy. This makes it possible to analyze the chemical makeup of a substance as well as quantify these values by comparing the sample to a known standard sample. Repeating this procedure a total of three times, the CEC is calculated as the total number of milliequivalents of lithium extracted in the three washings divided by the mass of the clay used. Increasing the heat treatment temperature has been observed to cause a reduction in CEC values.

All of the clay samples are dispersed in the polyimide DMBZ. The resins are then prepared for testing by pressing them into small disks. They are tested using the dynamic mechanical analyzer (DMA) for modulus strength and glass transition temperature. The glass transition generally indicates the upper limit usage temperature. Also, the thermo-oxidative stability of the samples is monitored through oven-aging at 550°F for 1000 hours. The samples may be tested as composites for other mechanical properties such as flexural and laminar shear strength. Results of these tests are in the process of being compiled, but it is the hope that certain properties will greatly improve without losing the integrity of other properties.

Already used in other industries such as automobile manufacture, polymer-clay nanocomposites show great promise for aerospace application. The polymers currently used by NASA for air and spacecraft have the potential to be reinforced with a relatively small amount of clay to enhance their performance and durability.