

Polymer Clay Nanocomposite Membrane Dynamics  
Characterization via combined NMR and Neutron  
Scattering Studies

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The use of flexible, long chain polymers is an approach that has been pursued in the development of ion transport membranes such as those for use in the replacement of liquid electrolytes in batteries. Poly(ethylene oxide) (PEO) is one potential replacement and has shown considerable conductivity at elevated temperatures near or above the melting point of the polymer. Since ionic transport is strongly dependent on the host polymer segmental motion, maintaining the polymer in an amorphous state is important for significant conduction to occur and thus requires operating high temperatures. Plasticizers are often used to increase the percentage of PEO that is amorphous and thus reduce the temperature at which significant conduction can occur. (1,2) However, many of these plasticizers can also reduce the beneficial mechanical properties that come with the use of flexible, long chain polymers such as PEO. An alternative nanocomposite material that is now being examined is a synthetic lithium hectorite (SLH) clay (3) with platelet sizes on the order of 10nm, which serves not simply as a filler material but also as an intercalation host for the PEO. Isolation of the polymer segments from the bulk can prevent crystallization of the PEO while confinement of the polymer may also affect its segmental motion thus lowering the temperature at which significant conductivity is achievable. A series of PEO/clay nanocomposites were studied with variable temperature nuclear magnetic resonance (NMR) and incoherent quasielastic neutron spectroscopy (QENS) order to understand the effect of the nanocomposite interface on the motion of the intercalated PEO and as a result its effect on the mobility of the lithium cation.

The variable temperature NMR studies of the PEO-SLH clay systems were conducted on a Bruker Avance DMX-360 spectrometer with an 8.5 T magnet.  $^7\text{Li}$  spectra were observed with a frequency of 139.95 MHz and  $^2\text{H}$  spectra was observed with a frequency of 55.45 MHz. A variable temperature wide-line static probe with flowing nitrogen gas was used for all samples. The clay samples were studied over a temperature range of 243 K to 363 K. Quasielastic neutron spectroscopy was conducted on the QENS instrument at the Intense Pulsed Neutron Source at Argonne National Laboratory. Samples were studied over a temperature of 353 K to 393 K.

The  $^2\text{H}$  spectra of the PEO could be separated into two components, one corresponding to the intercalated PEO and a second corresponding to the PEO external to the clay (Figure 1). Separate relaxation times were observed for the two components. The temperature dependence was determined using a spectral density function for deuterium motion based on autocorrelation

functions designed to describe the polymer motion in terms of a conformational jump model. Separate activation energies for PEO intercalated into the clay and external to the clay were observed. Wide-line  $^7\text{Li}$  NMR spectra of the PEO/SLH nanocomposite films reveal two types of lithium environments. With increasing temperature, the NMR spectra showed that the number of mobile, lithium gallery cations as well as their mobility increased. However, the lithium cation motion was independent of the PEO content of the film. Nevertheless, quasi-elastic neutron scattering (QENS) measurements of the films show that the PEO has increased dynamics with higher polymer content. Elastic scan measurements show an increase in the mean square displacement with higher PEO content at temperature above the melting point. (Figure 2). These results and the utility of the combination of NMR and QENS for the examination of lithium ion transport in the nanocomposite films will be discussed. This work is supported by the U.S. Department of Energy, BES-Materials Science, under contract W-31-109-Eng-38.

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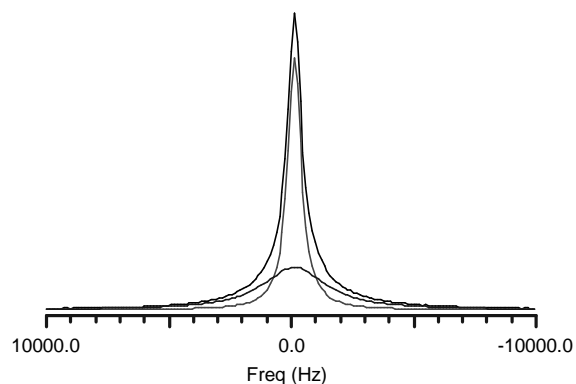


Figure 1.  $^2\text{H}$  spectrum of PEO:SLH = 1.2 at  $T = 90^\circ\text{C}$   
Internal PEO (broad), External PEO(narrow)

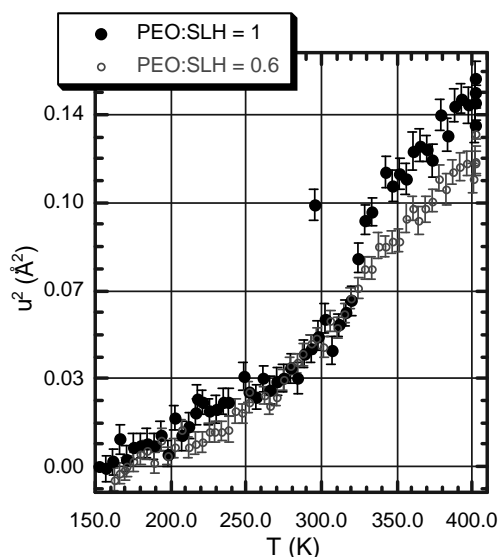


Figure 2. Elastic scans of PEO-SLH composites as a  
function of temperature.