VARIATION OF ELECTRICAL PROPERTIES WITH EXFOLIATION CONDITION IN NANOCOMPOSITES

Michael McBrearty; Chemical ElectroPhysics Corp., Hockessin DE 19707
Anthony J. Bur; National Institute of Standards and Technology, Gaithersburg MD 20899-8542
Steven C. Roth; National Institute of Standards and Technology, Gaithersburg MD 20899-8542

Abstract

Dielectric measurements were made on clay filled nylon and polyethylene-ethyl vinyl acetate (PE-EVA) copolymer nanocomposites during processing by extrusion. Nylon without clay had a small dielectric dispersion while PE-EVA did not. The addition of Na treated clay to the PE-EVA copolymer increased the dielectric constant (relative permittivity) above that of the PE-EVA copolymer but did not increase the conductivity or cause any dispersion. In both PE-EVA and nylon, addition of akyl ammonium chemically treated clays gave substantial increases in dielectric dispersion that are associated with the intercalated or exfoliated state. X-ray diffraction measurements were made on the composites.

Introduction

Mineral fillers are added to polymers to produce compounds with enhanced physical properties. Typical particle sizes are greater than 10^{-6} m and loadings are up to 30 % and higher. Recently introduced nanocomposite materials employ fillers with much smaller sizes, of order 10^{-9} m, that exfoliate under the correct, and often difficult to achieve, conditions to yield superior flame-retardant and physical properties at much lower loading levels (3 % – 5 % mass fraction). Producers of nanocomposite materials must control both the concentration of filler and the extent of exfoliation to maintain the quality of their products.

In-line dielectric sensors [1] have been successfully used to quantitatively measure in real time concentrations of fillers, additives, solvents and gases in polymers, compounds and other materials. Dielectric analyzers are among the few in-line instruments that can measure chemical concentrations in opaque as well as transparent liquids. This work suggests that in-line dielectric spectrometers might also monitor exfoliation and intercalation conditions in clay nanocomposites during processing.

Theory

When a material, for example a polymer melt, is subjected to an electrical field, bound charges are displaced and dipoles are oriented. The extent of this displacement is characterized by the relative permittivity ε of the material. In non-polar materials, displacement is due to electrons that polarize quickly and ε is substantially independent of frequency,

additive by molecular groups and capable via mixing rules of yielding quantitative concentration determinations. In polar or inhomogeneous materials, larger slower structures or interfaces can polarize in applied electric fields. They contribute to ε only if the frequency of the applied field is low enough. As the frequency of the applied field increases in these materials, fewer of the dipoles can orient (relax) quickly enough to keep up or less charge accumulates at the interfaces, and ε decreases. Conductivity σ can include a frequency independent component σ_{DC} associated with the drift of unbound charges and also a frequency dependent component σ_r related to dielectric relaxation [2].

$$\sigma = \sigma_{DC} + \sigma_r \qquad (1)$$

The relaxation part ε_r'' of the dielectric loss factor is defined as

$$\varepsilon_r'' = \frac{\sigma_r}{\omega \varepsilon_0} \qquad (2)$$

where $\omega = 2\pi$ x frequency and $\varepsilon_0 = 8.854$ x 10^{-12} F/m. In cases where dipolar motions have a single characteristic relaxation time, plots of ε'' vs ε' at different frequencies describe semicircular arcs. In materials with dipoles of different sizes, there is a distribution of relaxation times and the arcs are skewed. For composite materials, a distribution of permittivities and conductivities produces a distribution of relaxation times that is seen as a skewed arc on the ε'' vs ε' plot.

Equipment

To an 18 mm diameter Haake twin screw extruder was bolted a 25 mm thick adapter plate with a conical interior that tapered down to 12.7 mm inside diameter (ID).[a] Installed next in-line was a housing that contained a dielectric sensor, a 12.7 mm ID by 25 mm long ceramic ring. Resin flows inside the ring and experiences electric fields that fringe between interdigitated electrodes (0.33 mm spacing) on the sensor's inner surface. The electric field lines fringe about a millimeter into the processed

[a] Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

materials. Beyond the sensor housing was a 12.7 mm ID die piece 25 mm long. Assembly to the extruder was accomplished using bolts that were inserted through the die

plate and sensor housing and tightened into threaded holes in the adapter plate at the exit of the extruder. The dielectric sensor assembly was temperature controlled and included melt temperature and pressure transducers.

The sensor's capacitance C and resistance R are given by

$$C = \varepsilon_0 g\left(\varepsilon + \varepsilon_{cer}\right) \qquad (3)$$

$$\frac{1}{R} = g\left(\sigma + \sigma_{cer}\right) \qquad (4)$$

where g is a geometrical constant (units meters) characterizing the sensitivity of the sensor and ε_{cer} and σ_{cer} are the relative permittivity and conductivity of the ceramic material of which the sensor body is constructed. The calibration quantities ε_{cer} and σ_{cer} depend on temperature and frequency while g is a constant. Electronic instrumentation applies sinusoidal voltages (amplitude programmable, set at 1.0 V) to the sensor electrodes and measures the resulting current and phase angle to determine C and R. It then uses Equations (3) and (4) to determine the ε and σ of the process fluids at sixteen point frequencies between 500 Hz and 100,000 Hz in continually repeating sweeps that take about two minutes each. The present equipment can measure at lower frequencies (down to 10^{-3} Hz) but it takes more time. Data is automatically archived in a database with time stamps.

Standard uncertainties for the measurements were 1 °C for temperature and 70 kPa (10 psi) for pressure. Uncertainty in the electrical measurements is discussed below.

EVA copolymer was Equistar UE630-000 with 17 % vinyl acetate. Nylon 6 was from Honeywell. Clays were Southern Clay Products Cloisite Na, and Cloisite 15A and 30B nanoparticles of alkyl-quaternary ammonium montmorillonite.[3] Clay samples were dried at 100 °C under vacuum for at least an hour before use. Pax-purge was from Paxton Polymer Co.

Powder x-ray measurements were obtained on the composites after extrusion and on clays before extrusion.

Procedures

On a test stand at a temperature of 35 °C, g is determined by measuring capacitance when the sensor was empty, i.e. filled with air, and then measuring again when it was filled with a reference solvent of known permittivity. After this, with g entered in the software and the sensor empty, ε_{cer} and σ_{cer} were determined at each frequency at temperatures between 35 °C and 222 °C in 10 °C steps to establish the calibration. During subsequent operation ε_{cer} and σ_{cer} were determined at the measured operating temperature by linear interpolation between the nearest calibration temperatures.

At the beginning of the PE-EVA experiments, the system was heated to 150 °C and measurements were taken in air. Then unfilled PE-EVA copolymer was extruded at 40 revolution / min (see Figure 1). Small batches of 4.7 % mass fraction of Na clay in PE-EVA (5 g clay per 100 g polymer) were frequently mixed by manual weighing and added to the extruder when the hopper ran nearly empty. The weight fraction of clay was controlled to within 0.2 %. After the Na clay compound thoroughly pushed out the unfilled PE-EVA and stable measurements were obtained, the type of clay was changed to 30B. Again, extrusion was continued until the measured values stopped changing. Extruding unfilled PE-EVA, Pax-purge and then more PE-EVA cleaned the extruder. Subsequent experiments with PE-EVA and nylon were conducted similarly, but with nylon the mass fraction of clay was lower, 2.9 %, and the extrusion temperature was at 230 °C.

Results

Figures 1 and 2 show ε at all the measurement frequencies versus time for the first PE-EVA and nylon tests. ε of the unfilled EVA copolymer melt at 150 °C measured 2.33 at 500 Hz. This is consistent with the prediction of additive group calculations [4]. Na clay was added, and this caused ε to increase gradually with no dispersion (variation in ε with frequency) or increase in σ. The alkyl ammonium modified clay 30B was added and again ε increased, but this time ε showed a small amount of dispersion and σ increased. Next, the alkyl ammonium modified clay 15A was added and this time ε and σ increased dramatically and a large dispersion appeared.

Figure 2 shows ε at all the measurement frequencies versus time for the nylon tests. In this case, significant dispersion was observed in the resin alone, and much larger dispersions were observed for the clay/nylon composites.

Figures 3 and 4 show permittivity and conductivity versus frequency for PE-EVA and its clay composites. Figures 5 and 6 show loss factor versus permittivity for PE-EVA composites and for nylon and its composites.

X-ray diffraction data are shown in Figures 7 and 8.

Analysis

Uncertainties in the electrical measurements were negligible compared to the systematic errors that were readily quantified by comparing empty sensor readings at the start of tests to the known electrical properties of air ($\varepsilon_{air} = 1.00$ and $\sigma_{air} = 1.5 \times 10^{-12}$ S/m). The discrepancies represented the accumulated systematic errors and are shown in Figures 2, 3, and 4. They were worst at 10^5 Hz where they were 0.2 for ε and 4×10^{-7} S/m for σ. At 500 Hz they were 0.04 for ε and 2×10^{-9} S/m for σ. The combined uncertainties and systematic errors were small enough to clearly identify

differences between the materials. Two possible causes of the systematic errors were: a.) The tests were run at 150 °C but the nearest calibrations were at 97 °C and 177 °C; and b.) On a previous day nylon 6 was measured. The sensor was cleaned but some residual contamination may have remained. Systematic errors determined from empty sensor readings could be reliably removed by subtraction if they originated in the temperature calibration, but not if they originated from contamination. At 10^5 Hz, ε_{cer} was 9.82 at 97 °C and 9.93 at 177 °C. The difference, 0.11, represents the largest possible error contribution from the temperature dependence of calibration at that frequency. Since the empty sensor readings at 10^5 Hz showed approximately twice this amount of systematic error, some other cause, possibly contamination, must have contributed. Therefore, no subtractions were made. From past experience with this sensor, we have observed that, in the absence of systematic errors, the standard uncertainty in relative permittivity is 0.01 and for conductivity it is 1×10^{-10} S/m.

The dielectric data for both nylon and PE-EVA composites show distinct differences between the unfilled resin and the three clay fillers. These differences reflect the exfoliated, intercalated or aggregate structure of the clay composite. The dielectric and x-ray (Figures 7 and 8) data taken together provide a basis for interpretation.

The intercalated state of the 15A clay/PE-EVA composite is clearly seen in the x-ray diffraction pattern of Figure 7 by peaks at increasing orders corresponding to 4.08 nm spacing between silicate layers. The corresponding dielectric data of Figure 5 shows a large dispersion. It is the nature of the intercalated state to display a broad dielectric dispersion because its layered structure is the equivalent of capacitance/resistance in series that results in a broad distribution of electrical relaxation times.

By comparison, a much smaller dielectric dispersion was observed for 30B clay/PE-EVA composite, and, from the x-ray data it is clear that the 30B clay does not form the intercalated state with PE-EVA because no ordered x-ray pattern was observed. However, from these data alone, we can not distinguish between the exfoliated or aggregate state for the 30B clay/PE-EVA composite. If we interpret the x-ray peak at 1.52 nm as a higher order of diffraction that occurs at a very small angel (beyond our measurement capability), then some material is in an ordered structure of large spacing that gives rise to the observed dispersion.

Regarding the Na-clay/PE-EVA composite, it is known that this clay is in the aggregate state and does not form either intercalated or exfoliated composites with organic polymers. Na-clay is the least compatible of the three clays with organic polymers and forms particulate aggregates in the composite. For both unfilled PE-EVA copolymer and the Na-clay/PE-EVA composite, the dielectric dispersions are extremely small when compared to those of Figure 5 and if plotted on that scale would appear as dots near the origin.

For nylon, the extrusion was carried out at 230 °C, i. e. above the degradation temperature, 200 °C, for the modified montmorillonites.[6,7] X-ray data for the nylon composites, Figure 8, show common diffraction peaks corresponding to 1.68 nm and 0.83 nm spacing for the three composites; these are assumed to be first and second order of the 1.68 nm spacing. This spacing corresponds to a thermally deformed smectite structure that does not permit the thermodynamic transition to intercalation or exfoliation. The x-ray pattern for 15A clay/nylon also shows a peak at 3.34 nm, an indication that some of the 15A clay did not degrade and adopted an intercalated condition with nylon. This is further supported by the extent of the dielectric dispersion shown in Figure 6, i.e. the board dispersion of nylon/15A clay compared with that of nylon/30B clay and nylon/Na-clay.

References

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[3] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, and D. R. Paul Proc. SPE Ann. Tech. Mtg. May, 2000.
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[7] W. Xie, Z. Gao, W. Pan, D. Hunter, A. Singh and R. Vaia, Chem. Mater. **13***, 2979 (2001).
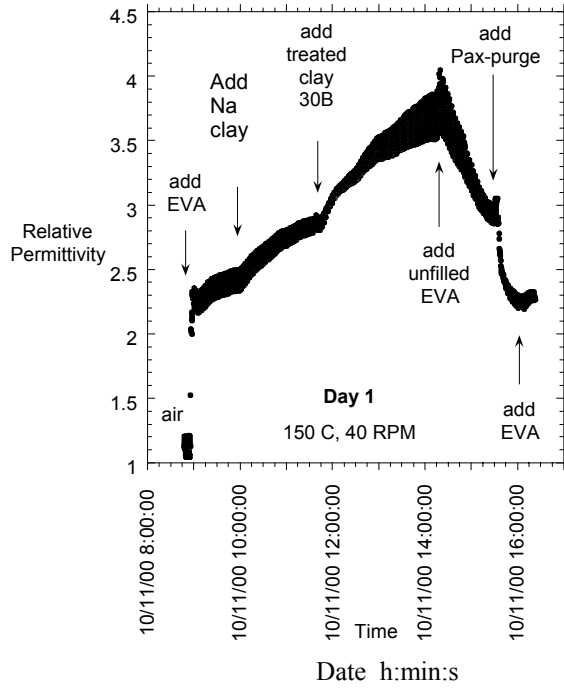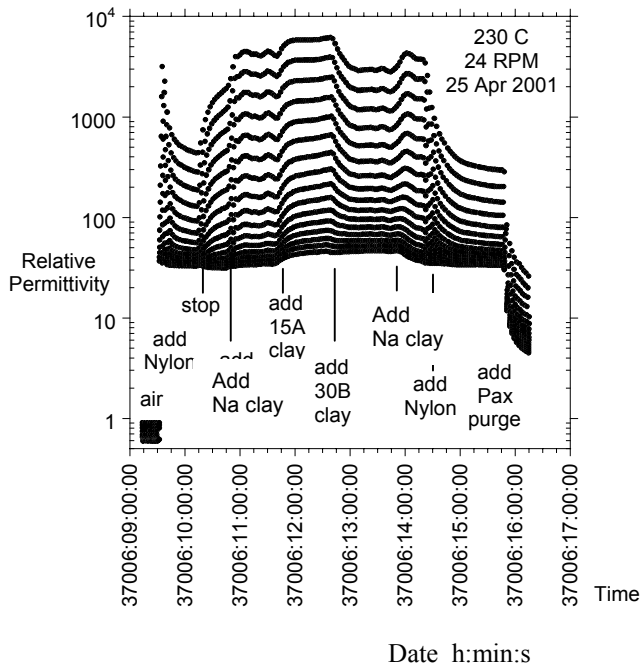
Figure 1. Relative permittivity ε versus time: PE-EVA and clay, frequencies 500 Hz to 10^5 Hz.

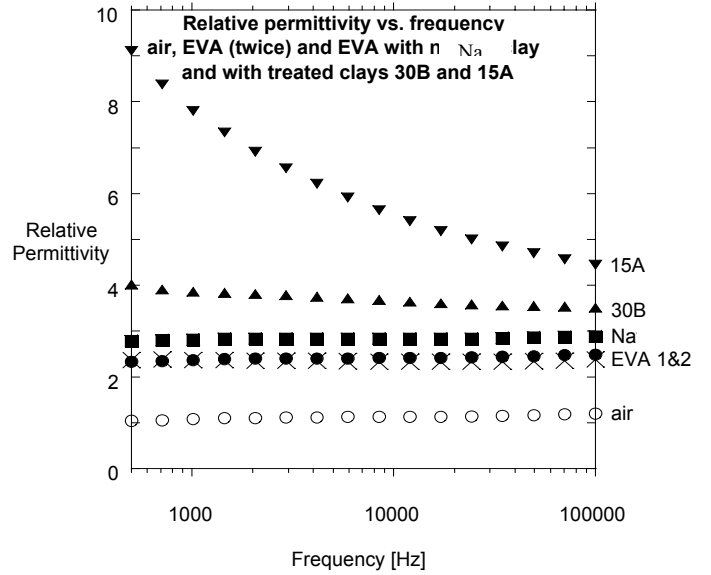
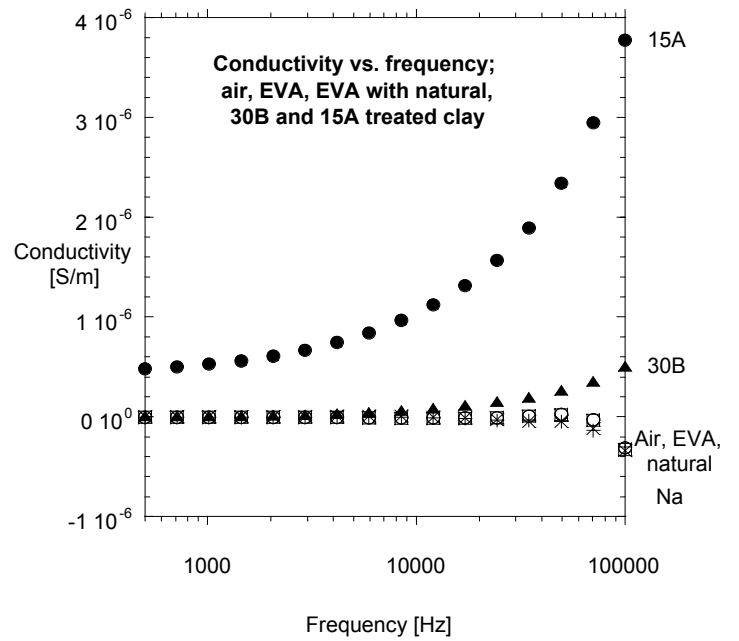Figure 3. Relative permittivity versus frequency: air, PE-EVA, PE-EVA with Na-clay, 30B clay and 15A clay.

Figure 2. Relative permittivity versus time for nylon 6 and clay, frequencies from 500 Hz to 10^5 Hz.

Figure 4. Conductivity versus frequency: air, PE-EVA, PE-EVA with Na-clay, 30B clay and 15A clay

**Loss Factor Vs Relative Permittivity
EVA with Clay
Surface treatments 30B and 15A**

15A

semicircle fit:
center = (7.52, -4.37)
radius = 5.80

30B

Relative Permittivity
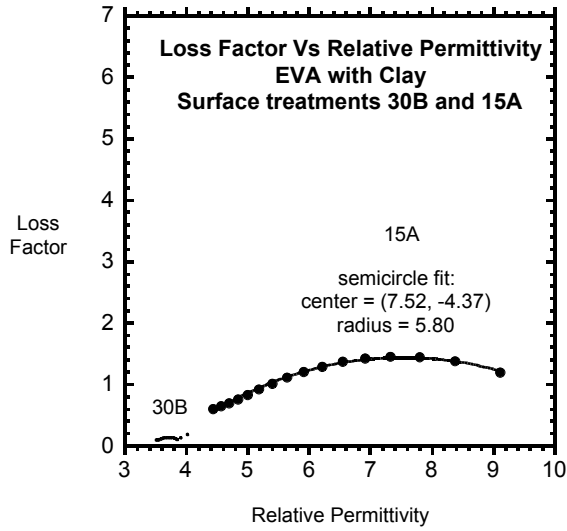
Figure 5. Loss factor versus relative permittivity for
PE-EVA filled with 30B and 15A clays

PE-EVA/Clays

4.7 % Cloisite Na+
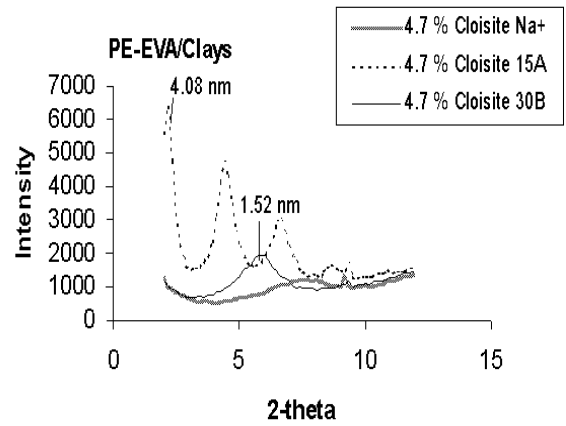4.7 % Cloisite 15A
4.7 % Cloisite 30B

4.08 nm

1.52 nm

2-theta

Figure 7. X-ray diffraction patterns for PE-EVA filled with
Na-Clay, 15A clay and 30B clay

**Loss Factor Vs. Relative Permittivity
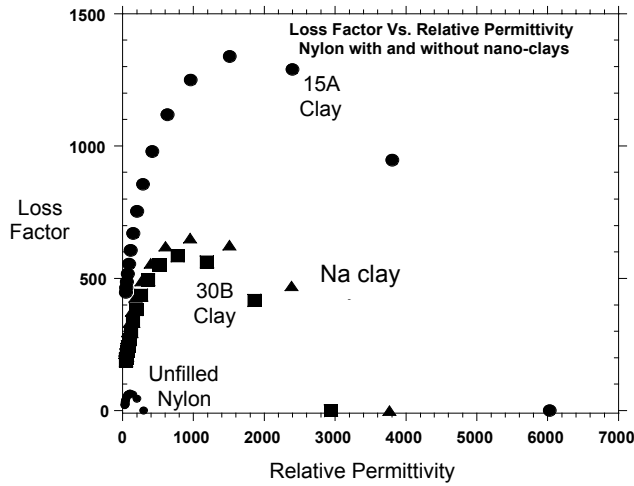Nylon with and without nano-clays**

15A
Clay

Na clay

30B
Clay

Unfilled
Nylon

Relative Permittivity

Figure 6. Loss factor versus relative permittivity for nylon 6,
and nylon 6 filled with Na, 15A and 30B clays

Nylon-Clays

2.9 % cloisite Na+
2.9 % cloisite 15A
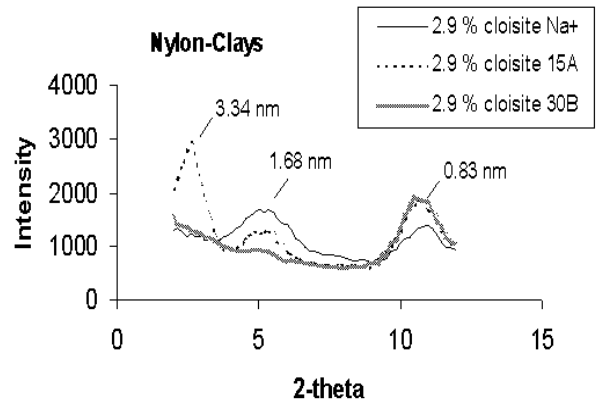2.9 % cloisite 30B

3.34 nm

1.68 nm

0.83 nm

2-theta

Figure 8. X-ray diffraction patterns for nylon 6 filled
with Na clay, 30B clay and 15A clay.