

REAL-TIME DIELECTRIC MEASUREMENTS AND MICROSTRUCTURE OF POLYMER/CLAY NANOCOMPOSITES*

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Abstract

Dielectric measurements were carried out during compounding of nylon/clay nanocomposites using a dielectric slit die that is attached to the end of a twin screw extruder. Contributions to the dielectric properties of nanocomposite melts arise from DC conductivity, dipolar relaxation and interfacial (Maxwell Wagner) polarization. Relationships between clay microstructure and dielectric properties were explored. The magnitude, characteristic frequency and distribution of relaxation times of the Maxwell-Wagner polarization were found to be dependent on the state of microstructure.

Introduction

The principle objective when compounding polymer/clay nanocomposites is to produce a composite with exfoliated or intercalated clay microstructure that yields enhanced properties of the product.(1) Determining microstructure involves off-line X-ray and transmission electron microscope (TEM) measurements.(2) One can minimize off-line characterization by using on-line, real-time measurements from which microstructure can be deduced. The dielectric slit die, an on-line sensor that we have employed in our research, can produce information about clay microstructure through dielectric dispersions that depend on the state of microstructure.

In previous papers, we described the operation of the dielectric slit die, and we presented dielectric data from nylon/clay composites showing that dielectric properties of nanocomposites containing modified montmorillonite clays depend on their microstructure.(3-5) By correlating the dielectric data with off-line X-ray and TEM observations, we showed that there are large differences in the relaxation spectra that arise from the exfoliated and aggregate microstructure, and we have been able to identify dielectric dispersions that correspond to exfoliated and aggregate clay microstructures. These differences were seen in both the α relaxation, associated with segmental motion of the polymer molecule, and in a prominent Maxwell-Wagner (MW) relaxation. The microstructure causes large MW interfacial polarization due to conducting ions that accumulate at the surface of the clay particles. The MW relaxation is associated with an electrical RC time constant of silicate particles immersed in a conducting resin medium.

In this paper we will review recent results and present model concepts concerning dielectric relaxations and their

relationships to clay microstructure. To date, we have focused on a family of nylons: nylon 6, nylon 11 and nylon 12, compounded with modified montmorillonite clays.

Experimental Procedure^a

The dielectric slit die was obtained from Chemical ElectroPhysics Corp. A side view of the sensor is shown in Figure 1. Two semicircular steel pieces, top and bottom halves, form the housing of the sensor. Its overall dimensions are 12.7 cm diameter by 15.24 cm long (5 inches diameter by 6 inches long). The sensor housing contains threaded instrumentation ports of the standard half-inch by 20 threads per inch type in addition to two cut-out chambers for ceramic in-lays that are used for dielectric sensing. The ceramic piece on the bottom is high purity alumina onto which platinum electrodes have been deposited in an interdigitating pattern. The ceramic on top is made from machinable ceramic and is machined with a slit that is 2 mm deep by 2.8 cm wide extending over the length of the piece, approximately 11 cm. A heating jacket surrounds the sensor and temperature is controlled using a thermocouple inserted into the body of the steel housing. A customized interface adapter plate positioned between sensor and extruder establishes the connection to the extruder. The electronics detecting circuitry and the software to operate the dielectric spectrometer were obtained from Chemical ElectroPhysics.(6,7) More details about the slit die are available from a previous publication.(8)

When an alternating voltage is applied across the electrodes, an electric field fringes between neighboring finger electrodes and extends not only through the alumina ceramic but also into the resin media flowing in the slit. By measuring the magnitude and phase of the resultant current and subtracting out the current through the alumina, the relative permittivity and dielectric loss of the resin can be determined.

Simultaneous with the dielectric measurements, light transmission measurements were carried out using an optical fiber sensor that was inserted into the 1/2 inch instrument port. This sensor detected light that traveled through the material in the slit, reflected from the far surface of the slit and reversed its

^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.

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path through the material in the slit. The light sensor is described more fully in another paper.(8)

Below, we will also present some dielectric data taken with off-line instrumentation. We use these data to develop the extent of exfoliation model. The data were obtained using a precision LCR meter (HP 4284 A) and are part of a larger set of experiments that will be described in a future publication.

Materials

Two nylon resins, nylon 6 and nylon 11, were compounded with montmorillonite clays. Nylon 6, capron 8200, was obtained from Honeywell Plastics and nylon 11, Rilsan BESNO, was obtained from Atofina. Three organically modified clays, Cloisite 15A, Cloisite 20A and Cloisite 30B were obtained from Southern Clay Products. The as-received clays contained quaternary ammonium organic surfactant that was incorporated in the gallery between silicate layers by an ion exchange process with natural clay. Both the 15A and 20A clays are treated with the same neutral hydrocarbon surfactant with 15A having 35% more surfactant. The 30B clay has a polar surfactant modifier. The natural clay, Na+, was also used in this study. The powdered clay was compounded with the polymer at 4 % mass fraction of clay in the polymer. Compounding was carried out using an 18 mm Haake Reocord model 9000 twin screw extruder.

The standard uncertainty in relative permittivity measurements is 0.005 and for conductivity it is 1×10^{-10} S/m. Standard uncertainty for temperature measurements is 1 °C. The relative uncertainty in the light transmission measurements is 0.1 %.

Dielectric Measurements

One of the challenges of making measurements on nylon resins in the melt phase is the relatively high conductivity that is encountered. This is the result of operating at high temperature where impurity or surfactant ions are conductive or other conducting mechanisms such as protonic conduction in nylons dominate the dielectric loss. Ions accumulating at the electrode create an electrode impedance in series with the sample impedance. To account for this, we consider an electrode admittance Y_{el} in series with a sample admittance Y_s . The experimental procedure for dealing with this situation and for extracting complex relative permittivity ϵ^* of the material and its real and imaginary parts, $\epsilon^* = \epsilon' - i\epsilon''$, has been described in detail in another publication.(8)

To analyze the data we assume that the material dielectric dispersions can be described by the Cole-Cole equation plus a contribution from the DC conductivity σ_{DC} ,

$$\epsilon^* = -\frac{i\sigma_{DC}}{\omega\epsilon_0} + \epsilon_\infty + \sum_j \frac{(\Delta\epsilon)_j}{[1 + (i\omega\tau_j)^{1-\delta_j}]} \quad (6)$$

where ϵ^* is the complex relative permittivity, ω is radial frequency, ϵ_0 is the permittivity of free space, $\Delta\epsilon$ is the intensity of the j th relaxation, ϵ_∞ is the limiting relative permittivity at high frequency, τ is the characteristic relaxation time of the j th relaxation, and δ is a factor that describes the distribution of relaxation times for the j th relaxation process.(9)

A curve fitting routine has been developed in our laboratory that involves a non-linear regression fit of the Cole-Cole equation to the raw data taking into account the electrode polarization and DC conductivity. The results are reported in terms of σ_{DC} , $\Delta\epsilon$, δ , ϵ_∞ and τ , where $\tau = (2\pi f)^{-1}$ and f is frequency.(8)

Results and Discussion

Figure 2 shows real-time data for extrusion of nylon 11 compounded with 4% mass fraction of 20A, 15A and 30B clays in the resin. Compounding was carried out at 198 °C. Relative permittivity and conductivity are plotted versus time for seventeen frequencies ranging from 50 Hz to 100 kHz. Dielectric sensing started with the neat polymer at $t = 0$ s. After extruding the neat polymer for 1580 s, nylon 11 with 4% mass fraction of 20A clay was added to the feeder. After a transition time extending from 1580 s to 2270 s, the steady state dielectric properties of the nylon 11/20A clay were observed. In the continuation of the experiment, 4% mass fraction of 15A and 30B clays were added at $t = 4000$ s and $t = 6700$ s as indicated in the Figure 2.

We see that the magnitude of the dielectric dispersion (the difference in relative permittivity between low and high frequencies) is greater for the clay/polymer nanocomposite than that for the neat polymer. This is because the introduction of the clay particles to the resin introduces ionic species that contribute to conductivity and polarization over and above that which is present in the neat resin.

Figure 3 is a plot of the relative permittivity versus time for nylon 6 compounded with 4% mass fraction of 15A and 30B clays. The general features of these data and those of Figure 2 are typical of the observations that we made for all nylon composites, namely a large dispersion highlighted by increases in permittivity and dielectric loss at low frequency due electrode polarization and DC conductivity.

Table I gives the results of data analysis on the two nylons and their composites. For all nylons, one relaxation was observed in the neat material and two relaxations were observed in the composites. The single relaxation observed in the neat nylons is associated with segmental motion of the macromolecule, i.e. the α relaxation process. The two relaxations observed in the composites are the α relaxation

and a Maxwell Wagner relaxation associated with interfacial polarization at the polymer/clay interfaces. The Maxwell Wagner polarization is identified by the magnitude of its intensity, $\Delta\epsilon_{MW}$, which is much greater than that for the α relaxation. Large $\Delta\epsilon_{MW}$ is due to ionic conduction that results in an accumulation of ions at the resin/silicate interface.

Table I

	Log $f\alpha$	Log f_{MW}
Nylon 11 at 198 °C	2.48	--
Nylon 11/Na+	2.51	0.74
Nylon 11/20A	2.45	0.24
Nylon 11/15A	2.55	0.16
Nylon 11/30B	2.48	0.62
Nylon 6 at 242 °C	2.40	--
Nylon 6/15A	2.79	1.98
Nylon 11/30B	2.64	1.10

The consequence of adding clay filler to the resin is the creation of a Maxwell Wagner relaxation. In contrast to rotation of dipoles that is the origin of the α relaxation, translation of ions under the influence of an electric field is the basis of MW relaxation. The MW relaxation time τ_{MW} can be viewed as an electrical RC time constant where the resistance R is the resin matrix and the capacitance C is the silicate particle. The concept is illustrated in Figure 4 where ions are shown translating through the resin medium and accumulating at the surface of the silicate particle. We describe the dynamics as follows:

$$RC = \tau_{MW} \quad \text{or} \quad \rho\epsilon = \tau_{MW} \quad (7)$$

where ρ is the resistivity of the resin and $\epsilon = \epsilon_0\epsilon'_s$ is the permittivity of the silicate (ϵ'_s is its relative permittivity). Under the influence of an electric field E an ion with charge q will translate with a drift velocity v according to

$$bv = qE \quad (8)$$

where b is the translation friction constant. Assuming a spherically shaped ion, b is given by the Stokes frictional drag constant $b = 6\pi\eta a$ where η is the viscosity of the resin melt and a is the radius of the spherical ion. The ionic current density J is related to the field E through Ohm's law

$$J\rho = E \quad \text{or} \quad nqv\rho = E \quad (9)$$

where n is the number of ions per unit volume. Combining equations 7, 8, and 9 we obtain

$$\epsilon_0\epsilon'_s = \frac{\tau_{MW}}{\rho} = \frac{nq^2\tau_{MW}}{6\pi\eta a} \quad (10)$$

where $\tau_{MW} = (2\pi f_{MW})^{-1}$ and f_{MW} is the characteristic frequency of the MW relaxation. We will normalize equation (10) with respect to the number of ions n by multiplying both sides by the factor n_0/n where n_0 is a basis

charge density whose value is arbitrarily set equal to 1 m^{-3} . We have

$$\frac{n_0\epsilon'_s}{n} = \frac{n_0C}{nC_0} = \frac{n_0q^2\tau_{MW}}{6\pi\epsilon_0\eta a} \quad (11)$$

where C is the effective capacitance of the silicate, C_0 is its vacuum capacitance and $C/C_0 = \epsilon'$.

We note that the quantities on both sides of equation (11) are dimensionless and we define the quantity $n_0C/(nC_0)$ as the extent of exfoliation. The concept follows from our view of the silicate particle as a capacitor that changes in value as microstructure changes from aggregate to exfoliation. In this model the aggregate particle has a low value of capacitance per surface area and the single exfoliated flake possesses the highest value per surface area. As exfoliation proceeds at a constant temperature, the resistance to ion conduction remains unchanged because the resistance is the drag force due to the resin viscosity, but the capacitance undergoes continuous change. Consequently, the RC time constant of equation 7 is controlled solely by the capacitance of the silicate in the aggregate, intercalated, or exfoliated state, or any combination thereof. 100 % exfoliation will have the highest capacitance, highest τ_{MW} , and lowest f_{MW} . On the other hand, values for the aggregate will be at the opposite extreme. In this manner, we can establish an exfoliation scale, anchored by these two extremes, by which the degree of exfoliation can be quantified.

Considering the right hand side of equation 11, we have $n_0 = 1\text{m}^{-3}$ and $q = 1.6\text{E}-19 \text{ C}$ for singly charged ions. The radius a of the conducting ion is obtained from the X-ray measurement of the gallery between silicate layers for each surfactant and is in the ratio Na+:30B:20A:15A equal to 1:5.0:8.35:8.35. η is the micro or molecular level viscosity of the resin as it expresses drag on the translating ion. One must distinguish between micro and macro viscosity where the macro viscosity is the bulk viscosity that we measure using a pressure drop along the slit die and micro viscosity refers to the local molecular environment. Micro viscosity can be obtained from a measurement of the rotational dielectric relaxation of a polar surfactant, such as Cloisite 30B, in a resin matrix. Using the Stokes relationship for a sphere rotating in a viscous medium, the rotational relaxation time τ_r is

$$\tau_r = \frac{8\pi\eta a^3}{2kT} \quad (12)$$

where T is absolute temperature and k is Boltzman's constant. Eliminating η between equations 11 and 12 yields

$$\frac{n_0C}{nC_0} = \frac{2n_0q^2\tau_{MW}a^2}{3\epsilon_0kT\tau_r} \quad (13)$$

We have not yet obtained direct measurements of τ_r , but we will approximate its value by using the relaxation time of the γ relaxation process of the resin. This is a reasonable approximation considering that the γ relaxation arises from rotation of a small molecular dipole entity on the polymer

chain. From off-line measurements as a function of temperature that were extrapolated to the melt temperature, we obtained $\tau_r = 1.6E-10$ s at 198 °C for nylon 11 and $\tau_r = 1.6E-11$ s for nylon 6 at 242 °C. Off-line measurements, $\log f_r$ versus $1/T$ and the extrapolation to the processing temperatures are shown in Figures 5 and 6 for nylon 11 and nylon 6.

Figure 7 is a linear scale of the extent of exfoliation, $n_oC/(nC_o)$, calculated from equation 13 for nylon 11 and nylon 6 compounded with the Cloisite clays. On this scale, the nylon 11/15A nanocomposite has the highest extent of exfoliation. The scale results are qualitatively in agreement with the results that we have obtained from light transmission and TEM observations.(10)

References

1. E. P. Giannelis, *Advanced Materials*, 8, 29 (1996).
2. A. B. Morgan and J. W. Gilman, *Journal of Applied Polymer Science*, 87, 1329 (2003).
3. A. J. Bur and M. McBrearty, *Proceedings of the Society of Plastics Engineers ANTEC Mtg.*, May, 2003, 3321 (2003).
4. A. J. Bur, S. C. Roth, and M. McBrearty, *Proceedings of the Society of Plastics Engineers ANTEC Mtg.*, May, 2003, 3326 (2003).
5. M. McBrearty, A. J. Bur, and S. C. Roth, *Proceedings of the Society of Plastics Engineers ANTEC Mtg.*, May, 2002, (2003).
6. A. J. Bur, S. C. Roth, and M. McBrearty, *Review of Scientific Instruments*, 73, 2097 (2002).
7. S. Perusich and M. McBrearty, *Polymer Engineering and Science*, 40, 214 (2000).
8. A. J. Bur, S. C. Roth, Y.-H. Lee, and M. McBrearty, *Review of Scientific Instruments*, accepted for publication, (2004).
9. R. H. Cole, *Journal of Chemical Physics*, 23, 493 (1955).
10. Lee Y-H., A. J. Bur, and S. C. Roth, *Proceedings of the Society of Plastics Engineers ANTEC Mtg.*, (2004).

Keywords: clay nanocomposites, dielectric sensor, process monitoring, optical sensor, slit die rheometer

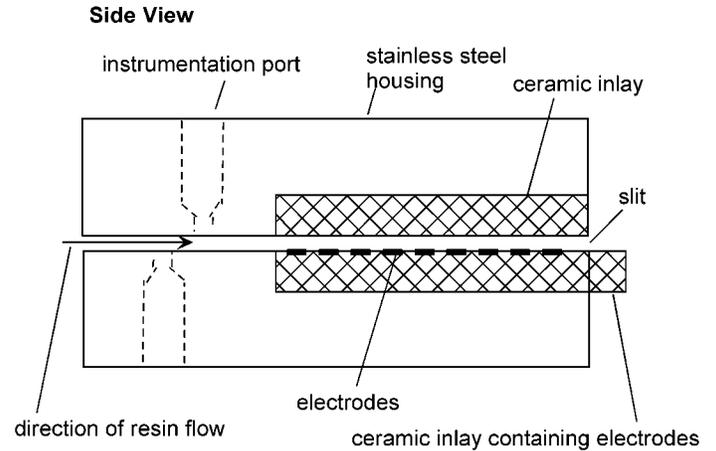


Figure 1. Side view of the dielectric slit die.

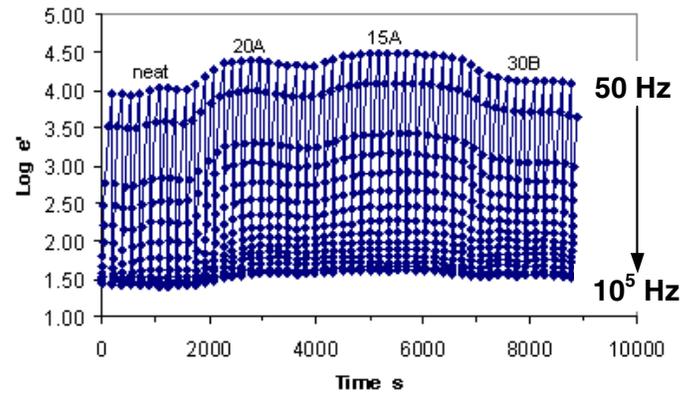


Figure 2. Log ϵ' versus time for nylon 11 compounded with Cloisite clays 20A, 15A and 30B at 198 °C.

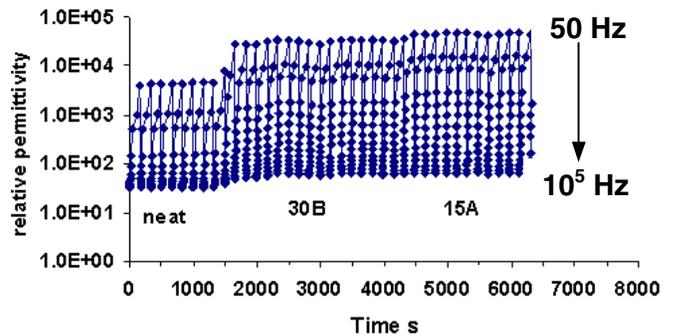


Figure 3. Relative permittivity versus time for nylon 6 compounded with Cloisite 30B and 15A at 242 °C.

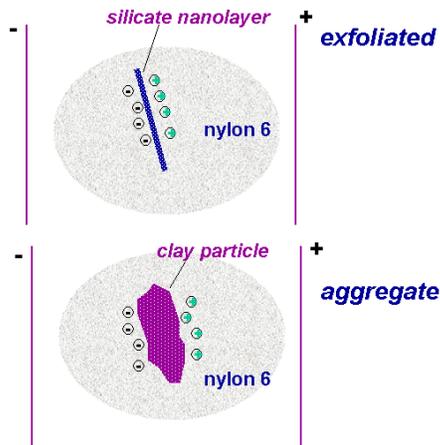


Figure 4. The concept of Maxwell Wagner interfacial polarization is depicted.

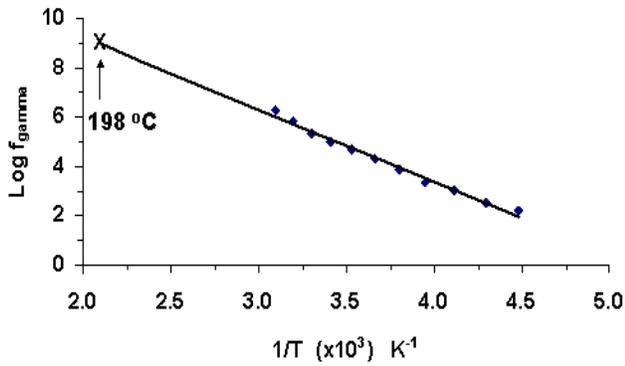


Figure 5. Log f for the γ relaxation of nylon 11 is plotted versus $1/T$ for data taken with off-line instrumentation from -50 °C to 40 °C. Extrapolation extends to 198 °C, the processing temperature for nylon 11.

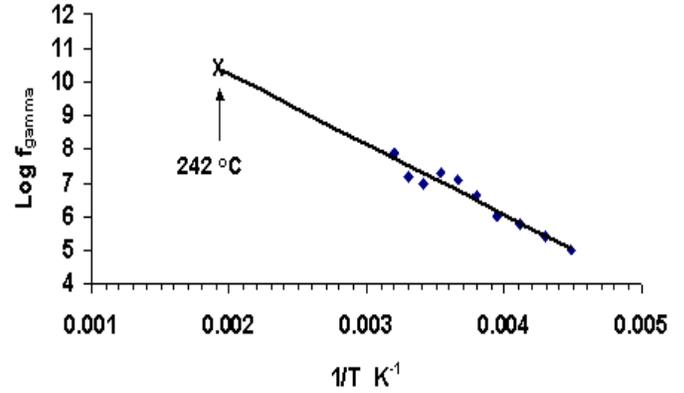


Figure 6. Log f for the γ relaxation of nylon 6 is plotted versus $1/T$ for data taken with off-line instrumentation from -50 °C to 40 °C. Extrapolation extends to 242 °C, the processing temperature for nylon 6.

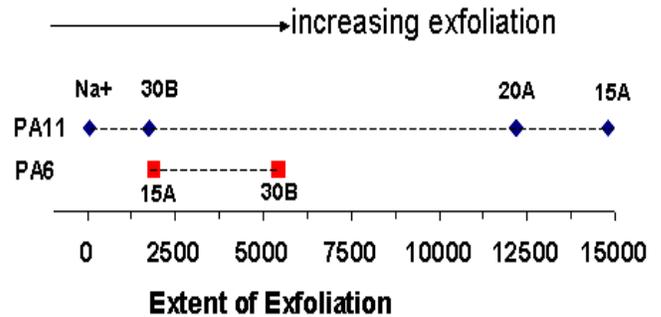


Figure 7. The extent of exfoliation scale.