

# CORRELATION BETWEEN DEGREE OF EXFOLIATION, DIELECTRIC PROPERTIES, AND LIGHT TRANSMISSION OF NYLON 11/ CLAY NANOCOMPOSITES PROBED BY AN ONLINE DIELECTRIC SLIT DIE

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## Abstract

A new dielectric slit die sensor attached to the end of an extruder was designed to examine the melt properties of Nylon 11/ clay nanocomposites. Experimental data were fit with the Cole-Cole relaxation functions corrected for electrode polarization and DC conductivity. Two interesting features were discovered. Firstly, at processing temperature, only one relaxation,  $\alpha$ , was detected in the neat resin and yet two relaxations,  $\alpha$  and Maxwell-Wagner interfacial polarization (MW), were retrieved from the composites. MW was ascribed to the polarization at the polymer/ filler interface. A much broader relaxation time distribution appeared in MW compared to  $\alpha$  as each polymer/ filler interface, bearing various interfacial geometries, is polarized at a distinct time scale. Secondly, the MW relaxation frequency correlated well with the degree of filler dispersion and exfoliation throughout the polymer matrix. A much lower MW frequency was found in the system where a higher extent of silicate exfoliation was obtained. Additional on-line data were obtained from an optical sensor that monitored light transmission through the filled resins. The combination of optical and dielectric data was used to establish a degree of exfoliation scale.

## Introduction

The lack of knowledge of the polymer relaxation in the melt state<sup>1,2</sup> and the fact that there has been no commercially-available instruments suitable for melt state studies led to the development of an innovative on-line dielectric sensor<sup>3-6</sup>. This new device enables real-time monitoring of dielectric properties, light transmission, and viscosities of polymer nanocomposites during extrusion. Interfacial polarization, which originates from the accumulation of ionic charges at the interfaces of two immiscible media having different permittivities and/ or conductivities, depends strongly upon the morphology of the composite<sup>7,8</sup>. This work was initiated under the assumption that the filler, dispersed throughout the polymer matrix, will not only alter the dielectric relaxation of the  $\alpha$  dynamics (rotation of the molecular dipoles) but also create polarization that occurs at the polymer/ filler interfaces. As such, the dielectric spectra of the composites compared to that of the neat should reflect the microstructure of the composites and should correlate closely with the polymer/ filler compatibility.

## Experimental

### (1) Sample Preparation:

Nylon 11 (Capron 8200NL) obtained from Honeywell has a melting temperature of  $T_m = 185^\circ\text{C}$ . Untreated Sodium clay (Na+) and three organically modified clays, obtained from Southern Clay products, Cloisite 15 A, 20 A and 30 B, were used as received and compounded at 4 % mass fraction of clay with Nylon 11. Cloisite 15 A and 20 A are both prepared by ion exchange of naturally occurring sodium with dimethyl, dihydrogenatedtallow, and quaternary ammonium. The only difference between 15 A and 20 A Cloisites is their surfactant concentration which is 1.35 Cation Exchange Capacity (CEC) and 1.03 CEC for 15 A and 20 A, respectively. Similarly, Cloisite 30 B is produced by ion exchange for a methyl, tallow, bis-2-hydroxyethyl quaternary ammonium ion. Cloisite 30 B differs from 15 A and 20 A not only by the surfactant functionality, which is polar for 30 B and non-polar for 15 A and 20 A but also by the surfactant content, which is much lower for 30 B (0.95 CEC). All other properties of the clay are listed in **Table 1**. Polar 30 B was chosen in order to investigate the effect of hydroxyl groups from the surfactants, which could potentially hydrogen bond with the amide groups from the Nylon 11 matrix. Cloisite 15 A, which possesses extra surfactants and yields a much larger X-ray d-spacing compared to 20 A, was selected to understand whether the "pre-swelled" clay galleries which were occupied with a greater number of ionic species will enhance the exfoliation. Prior to extrusion compounding, both resin pellets and the clay powders were dried for 12 h at  $80^\circ\text{C}$ . To prepare 4 % mass fraction of clay in the resin, 200 g batches of dry Nylon pellets and silicate powders were hand mixed in a beaker and transferred to a twin-screw extruder feeder. An 18 mm Haake Record model 9000 twin-screw extruder operating at 30 rpm was used. The residence time for compounding in the extruder was approximately 4 min and the processing temperatures for Nylon 11 and its composites was  $198^\circ\text{C}$ .

### (2) Instrumentation:

The on-line dielectric measurement sensor was recently developed to study dielectric properties of polymer composites in the melt phase<sup>4</sup>. The dielectric cell is connected to a computer-controlled lock-in amplifier, (Stanford Research model SR810), which, in conjunction with instrument software, operates as a dielectric spectrometer (Chemical ElectroPhysics Proceptor) and

yields relative permittivity at fourteen discrete frequencies in the range 50 Hz to  $10^5$  Hz. More details regarding the interdigitating electrode measuring technique and the dielectric slit die design can be found elsewhere<sup>3-5;9;10</sup>. The relative standard uncertainty in the measured  $\epsilon'$  data reported here is 1 % and the standard uncertainty of the temperature, which is regulated by the online heating jacket, is 1 °C. The uncertainty in conductivity is  $10^{-10}$  S/m. The optics sensor used to measure the light transmission has been described in detail elsewhere literature<sup>3;4</sup>. In the transmission mode, one of the fibers transmits light from the light source through a focusing lens, the sapphire window, the flowing resin, reflects off the far stainless steel surface, and reverses its path through the material, sapphire window and lens. The reflected light is collected by the other six fibers and is transmitted to the photomultiplier detector.

### (3) Data Analysis

Molten polymers contain conducting ions that contribute to both DC conductivity and electrode polarization effects<sup>11</sup>. The large increases at low frequencies in both the  $\epsilon'$  and  $\epsilon''$ , observed in most polymers at high temperature, are evidences of these two effects and must be corrected for in order to quantify the material dielectric properties. This is accomplished by modeling the electrode as a capacitance/resistance parallel circuit that is in series with the sample, and DC conductivity as a resistance in parallel with the sample<sup>3;4;6</sup>.

It is known that the frequency dependence of dielectric relaxations can be modeled by Havriliak-Negami function, which reduces to the Cole-Cole equation for symmetric distributions of relaxation times<sup>12;13</sup>. Because Havriliak-Negami fits to the data yielded curves indistinguishable from the results obtained from Cole-Cole equation, the latter was adopted for the data of this paper. A DC conductivity term, proportional to the reciprocal of frequency, was added to a sum of Cole-Cole expressions given as,

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

where  $\sigma_{DC}$  is the DC conductivity,  $\omega$  is the angular frequency,  $(\Delta\epsilon)_j$  is the strength of the  $j^{\text{th}}$  dielectric relaxation,  $\delta_j$  is the  $j^{\text{th}}$  relaxation time distribution parameter,  $\epsilon_0$  is the permittivity of free space (8.854 pF/m),  $\tau_j$  is the characteristic relaxation time of the  $j^{\text{th}}$  relaxation, and  $\epsilon_\infty$  is the high frequency relative permittivity. A global fitting procedure consisting of a least squares non-linear fit to the frequency-dependent data was carried out using 6 fitting parameters as described in the literature<sup>3;4;6</sup>. A fit to the data was considered successful if the calculated values were within 1 % of the measurements, i.e. within the nominal experimental uncertainty of the observations. If the 1 % criterion for a good fit was not obtained, then additional

relaxation dispersions were added to the fitting function one at a time until the 1 % criterion was satisfied.

## Results and Discussion

### (1) Microstructures of the Silicate:

Morphological characterization of the composites was carried out by transmission electronic microscopy (TEM) and X-ray diffraction (XRD) and the results are summarized in **Table 1**. Cloisite 30 B silicate, which bears a CEC less than the untreated Cloisite Na+, yielded a degree of swelling of 58 % upon the incorporation of long chain amino surfactants. For Cloisite 20 A, which possesses a CEC slightly higher than that of the neat Cloisite Na+, caused the silicate to expand 107 %. The highest degree of swelling due to surfactant (169 %) was found in Cloisite 15 A, in which excess amount of surfactants was added.

The degree of exfoliation was estimated from the optical sensor data. Light transmission intensity versus time during processing of Nylon 11 and its composites is plotted in **Figure 1**. The neat polymer, which yielded the highest light transmission among all samples, represents 100 % light transmission. It is assumed that composites with 100 % degree of exfoliation will have the same light transmission as the neat resin because the exfoliated particles are too small to scatter light. As for the Nylon 11 composite filled with untreated Cloisite Na+, the lowest intensity of light was transmitted and its degree of exfoliation is known to be zero. Relative degree exfoliation was then computed when compared with these two reference points (100 % and 0 %) and the results were listed in **Table 2**. Nylon 11 generated the highest degree of exfoliation when compounded with Cloisite 15 A, followed by 20 A, 30 B and the lowest extent of exfoliation was found in untreated Na+ composite which agrees well with the TEM results. **Figure 2** shows the TEM of the best-exfoliated 15A/ NY11 composite.

The incorporated long chain organic surfactants serve to expand the clay galleries prior to compounding yet the complete delamination process is still governed by the thermodynamics<sup>14</sup>. If the polymer/ clay pair is compatible enough to trigger the clay delamination, which is the case of polyamide 11, the degree of exfoliation should be determined by the amount of macromolecular chains that occupy the silicate galleries. More Nylon 11 chains were able to diffuse into the widely pre-swelled gaps of Cloisite 15 A and delaminate the silicate stacks even more, consequently, the most thorough exfoliated state was produced compared to 20 A and 30 B.

### (2) Microstructures of the Composites:

**Figure 3 (A)** exhibits the measured online dielectric data for the Nylon 11/ 20 A composites taken at  $T = 195$  °C. An increase in  $\epsilon''$  in the low frequency regime, resulting from ionic conduction in the melt state is observed. The monotonic rise of  $\epsilon'$  with descending frequency is due to the electrode polarization *i.e.* conducting ions accumulated at the

electrode surfaces. The solid lines in both  $\epsilon'$  and  $\epsilon''$  are the fits to the measured data using the Cole-Cole function corrected for ionic conduction and electrode polarization and the dotted line is the relative permittivity of the material that is obtained from the fit. The large discrepancy between the solid line and the dotted line in  $\epsilon'$ , seen in the low frequency regime, is attributed to the electrode polarization. This large deviation supports our contention that the Cole-Cole function must be used in conjunction with the electrode admittance correction.

No relaxation is visualized from either  $\epsilon''$  or  $\epsilon'$  raw data, yet two relaxations along with a DC conductivity were retrieved from the fitting procedure as illustrated in **Figure 3 (B)**. Two relaxation modes in the Nylon 11/ 20 A composite, centered at  $\log f = 0.24$  (Hz) and  $\log f = 2.45$  (Hz), are ascribed to Maxwell-Wagner (MW) interfacial polarization and  $\alpha$  relaxation, respectively. The low frequency relaxation, MW, shows a much broader relaxation time distribution ( $\delta_{MW} = 0.53$ ) than the higher frequency  $\alpha$  relaxation ( $\delta = 0.08$ ) as listed in **Table 2**. The presence of filler/ polymer interfaces broadens the MW relaxation time distribution as each interface, bearing various interfacial geometries, is polarized at a distinct time scale. On the other hand, a narrower  $\alpha$  relaxation in the polymer melt originates from the segmental dynamics of amorphous chains that exhibit a relative homogeneity for temperature well above  $T_g$  of the Nylon 11 matrix (50 °C). Much greater dielectric intensity was generated in MW ( $\Delta\epsilon_{MW} = 4944$ ) than in  $\alpha$  relaxation ( $\Delta\epsilon = 2934$ ) as the effect of mobile ions being translated to an interfacial surface was much greater than the polarization of molecular dipoles being aligned.

All the fitting parameters are summarized in **Table 2**. For all the composites, two relaxations were obtained from the fitting procedure, however, for the neat resins, only one relaxation was observed. The composites exhibited greater DC conductivity than the neat polymers, owing to the presence of additional ions from the clays. The only relaxation in the neat Nylon is associated with the  $\alpha$  relaxation of segmental motion in the melt. Besides  $\alpha$  relaxation, the additional relaxation observed in the composites is attributed to Maxwell-Wagner (MW) polarization<sup>7,8</sup>. MW dispersion is identified by its lower characteristic frequency and a large intensity,  $\Delta\epsilon$ . Conducting ions accumulated at the rigid resin/ filler interface that move slowly through the molten Nylon under the influence of an applied voltage are responsible for the lower frequency and a large  $\Delta\epsilon$ .

#### (3) Effect of Microstructures on Maxwell-Wagner (MW):

To elucidate the impact of clay microstructures on the MW dielectric behavior of the polymer matrix, the Cole-Cole plot and the fitted  $\epsilon''$  for Nylon 11 filled with four types of clays were overlapped and displayed in **Figures 4**

**(A)** and **4 (B)**. The dynamics of interfacial polarization can be simplified and modeled by an effective resistance-capacitance time constant ( $\tau = RC$ ) of the resin/ silicate medium under the assumption that the resin behaves as the conducting resistance (R) and the silicate particles act as the capacitance (C). R can be approximated by the reciprocal of the ionic conductivities of the composites ( $\sigma_{DC}$ ) and  $\tau$  is the reciprocal of MW characteristic frequency. As such, the value of  $f_{MW}$  can be estimated approximately by  $\sigma_{DC}/ C$ . Since all the  $\sigma_{DC}$  values appeared to be very similar for all the composites samples, it is the silicate capacitance that expresses the degree of exfoliation. In other words, a lower filler capacitance should lead to a higher MW frequency. For Na+/ Nylon 11 with the lowest degree of exfoliation, 0 %, the highest MW frequency ( $\log f_{MW} = 0.74$  Hz) was found. The slowest MW dynamics ( $\log f_{MW} = 0.16$  Hz), which infers the highest capacitance, was detected in Nylon 11/ 15 A composite with the greatest extent of exfoliation, 57 %, on the light transmission scale. The value of MW frequency decreased monotonically with the extent of exfoliation. The enhanced electric capacity of the exfoliated composites is ascribed to the generation of numerous nano-capacitors upon silicate delamination

#### (4) Effect of Microstructures on $\alpha$ Relaxation:

To explore the impact of clay microstructures on the dielectric behavior of the  $\alpha$  relaxation, the arc plot and the fitted  $\epsilon''$  for Nylon 11 filled with four types of clays were overlapped and displayed in **Figures 5 (A)** and **5 (B)**. All the  $\alpha$  frequency and the relaxation time distribution appeared to be similar, yielding  $\log f = 2.5$  (Hz) and  $\delta \approx 0.08$ . Nylon filled with untreated Na+ exhibited a similar  $\alpha$  characteristic frequency compared to the neat resin, as the bulk matrix was not disturbed when the fillers remained in an immiscible aggregate state. The consistent  $\alpha$  dynamics in the exfoliated composites is explained by the following. Rigid silicate plates served as “molecular dividers” therefore the intermolecular cooperativity is diminished and the  $\alpha$  dynamics is accelerated. On the other hand, intimate contacts between the polymer and the filler surfaces hampered the mobility of amorphous chains and thus slowed down the  $\alpha$  dynamics. As the dividing effect and the reinforcement effect occur in concert and they change the characteristic frequency in opposite directions, offsetting each other and yielding a consistent  $\alpha$  frequency in all composites samples.

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**Keywords:** relaxation, dielectric, exfoliated, Maxwell-Wagner, nanocomposites, microstructure, polyamides

**Table 1:** Summary of three types of organically-treated Cloisite and untreated Cloisite. The d-spacing of the silicate were determined using XRD by the manufacture. The degree of swelling due to surfactants and polymer were calculated and are also listed.

Type of Clay	Na+	15 A	20 A	30 B
d-spacing* (nm)	1.17	3.15	2.42	1.85
Degree of Swelling Due to Surfactants (%)	N/A	169	107	58
CEC (meq/100g)	92.6	125	95	90
Relative Surfactant Concentration (CEC)	N/A	1.35	1.03	0.97

\*XRD data supplied by the manufacture.

\*\*DOS<sub>s</sub> (%) = 100\*(d'-d)/d in which d and d' is the d-spacing for the untreated Cloisite Na+ and the organically treated Cloisite, respectively.

**Table 2:** Summary of on-line curve-fitting results including frequency (f), dielectric strength (Δε), width of relaxation time distribution (δ), and DC conductivity (σ<sub>DC</sub>).

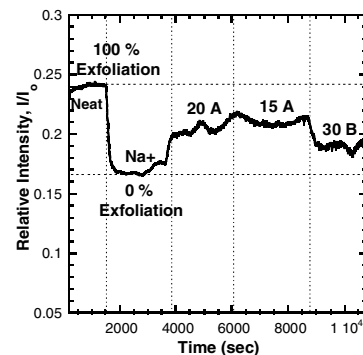
	Neat	Na+	20 A	30 B	15 A
Structures*	N/A	A**	E <sup>+</sup>	E <sup>+</sup>	E <sup>+</sup>
E <sup>+</sup> (%)	N/A	0	50	31	57
Log f (Hz)	2.48 ±0.03	2.51 ±0.02	2.45 ±0.01	2.48 ±0.03	2.55 ±0.01
Log f <sub>MW</sub> (Hz)	N/A	0.74 ±0.04	0.24 ±0.09	0.65 ±0.03	0.16 ±0.03
Δε	1218 ±150	2679 ±100	2934 ±100	2146 ±100	3107 ±50
Δε <sub>MW</sub>	N/A	3166 ±50	4944 ±100	3350 ±350	5285 ±15
δ	0.08 ±0.01	0.06 ±0.01	0.08 ±0.01	0.07 ±0.01	0.09 ±0.01
δ <sub>MW</sub>	N/A	0.52 ±0.02	0.53 ±0.01	0.51 ±0.01	0.52 ±0.01
σ <sub>DC</sub> × 10 <sup>4</sup> (S/m)	8.91 ±0.13	15.4 ±0.3	13.6 ±0.07	11.14 ±0.4	15.58 ±0.07

\*Determined by both TEM and XRD

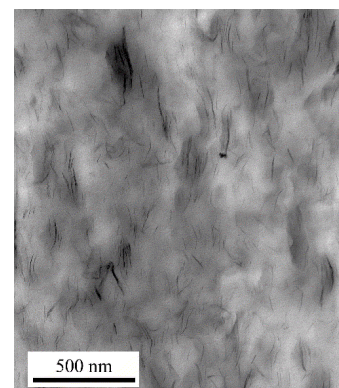
\*\* A-Aggregated

+ E-Exfoliation

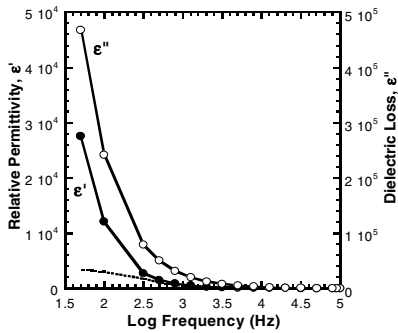
**Figure 1:** Relative light transmission intensity recorded by online optical sensor.



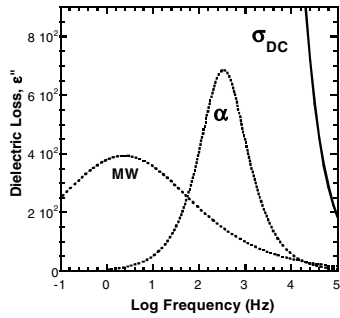
**Figure 2:** TEM micrographs of Nylon 11 composites filled with Cloisite 15 A clay.



**Figures 3(A), 3(B):** (A) Permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) is plotted against frequency in the logarithmic scale for the Nylon 11/ 20 A at 198 °C. Solid symbols are the measured data, dashed lines represent curves fitted by the original Cole-Cole equation, and the solid line illustrates results fitted by the Cole-Cole function corrected for DC conductivity and electrode polarization. (B) Two relaxation modes, Maxwell-Wagner polarization (MW) and  $\alpha$  relaxation, along with DC conductivity extracted from the fitted  $\epsilon''$  are plotted as a function of frequency.

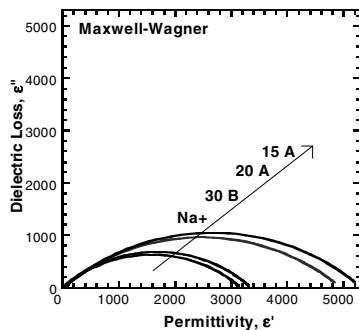


(A)

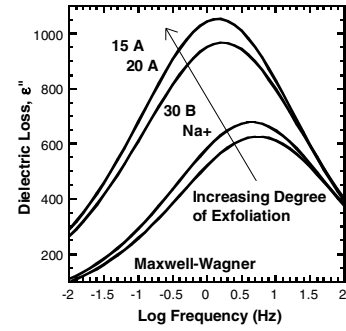


(B)

**Figures 4(A), 4(B):** Maxwell-Wagner polarization for Nylon 11 and its composites filled with 4 % mass fraction Na+, 15 A, 20 A, and 30 B. (A) Arc plot, dielectric loss ( $\epsilon''$ ) extracted from the corrected Cole-Cole fit is plotted against permittivity ( $\epsilon'$ ). (B) Dielectric loss ( $\epsilon''$ ) retrieved from curve fitting is plotted as a function of experimental frequency in the semi-logarithmic scale.

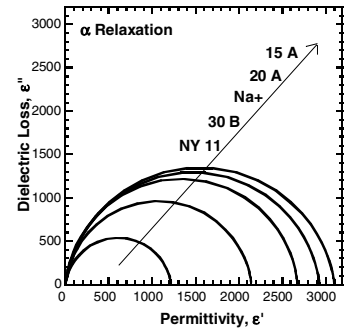


(A)

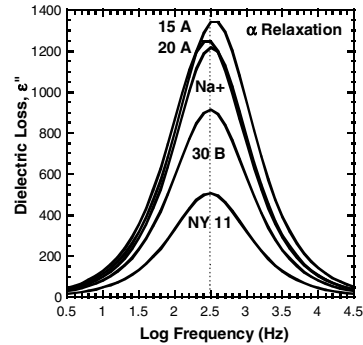


(B)

**Figures 5(A), 5(B):**  $\alpha$  relaxation for Nylon 11 and its composites filled with 4 % mass fraction Na+, 15 A, 20 A, and 30 B. (A) Arc plot, dielectric loss ( $\epsilon''$ ) extracted from the corrected Cole-Cole fit is plotted against permittivity ( $\epsilon'$ ). (B) Dielectric loss ( $\epsilon''$ ) retrieved from curve fitting is plotted as a function of experimental frequency in the semi-logarithmic scale.



(A)



(B)