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Dielectric spectroscopy during extrusion processing of polymer nanocomposites: a high throughput processing/characterization method to measure layered silicate content and exfoliation ☆

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Abstract

Dielectric spectroscopy was conducted during extrusion processing of polyamide-6 (PA6) and layered silicate/polyamide-6 nanocomposites. Dielectric dispersion parameters were identified that appear sensitive to layered silicate concentration and degree of exfoliation. Specific to measuring layered silicate concentration is that the Maxwell–Wagner strength of dispersion, $\Delta\varepsilon_{mw}$, increases linearly with the % mass fraction layered silicate content. This relationship is independent of exfoliation resulting in nanomorphology-averaged $\Delta\varepsilon_{mw}$ values that reflect layered silicate concentration; i.e. $12,800\pm519$ indicates 1.29% mass fraction of a layered silicate in PA6. The nanomorphology is primarily reflected in the Maxwell–Wagner characteristic relaxation frequency value, f_{mw}, where, for example, 80.4 ± 5 Hz indicates a mixed intercalated/exfoliated nanomorphology. However, following the nanomorphology with the f_{mw} value can in some cases be complicated because different nanomorphologies can yield the same f_{mw} value. In these cases we have found that there is a significant difference in the conductive resistance and segmental mobility of these polymers, as indicated by the σ_{DC} and f_α values. For example, the intercalated and exfoliated nanocomposites have a f_{mw} value of about 5.1 Hz, but the exfoliated nanocomposites have σ_{DC} and f_α values that are much larger than determined for the intercalated nanocomposites.
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1. Introduction

Using a dielectric spectrometer attached to an extruder (extrusion-dielectric spectrometer), Bur et al. monitored the dielectric response of organoclay filled poly (ethylene-co-vinyl acetate) (PE-EVA) [1], polyamide-6 (PA6) [2] and polyamide-12 (PA12) [3] nanocomposites during extrusion

compounding. Using a non-linear global fitting routine, the electrode polarization and direct current (DC) conductivity contributions were removed from the complex relative permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$). The result was the dielectric loss (ε'', imaginary component) and relative permittivity (ε', real component) of the materials that were associated with molecular dipole rotation and ion accumulation at the organoclay/polymer interface. In each of these polymers the incorporation of organoclay caused an additional relaxation dispersion due to this interfacial polarization at the organoclay/polymer interface, Maxwell–wagner relaxation.

Relevant to our research presented in this manuscript, the previous extrusion-dielectric spectroscopy research was

conducted on pure PA6 and two organoclay/PA6 nanocomposites that contained the same organoclay concentration but very different nanomorphologies, aggregated and exfoliated [2]. This research was combined with off-line dielectric spectroscopy to identify and better understand the material dielectric relaxations as a function of temperature. Insufficient data was obtained to suggest a relationship of the dielectric dispersion parameters with organoclay exfoliation and concentration.

Presented here are possible correlations of layered silicate mass fraction (0, 1.29, 2.59, and 3.26%) and the level of layered silicate exfoliation (intercalated, mixed intercalated/exfoliated, highly exfoliated) with specific dielectric dispersion parameters of layered silicate filled PA6 nanocomposites obtained during extrusion compounding. The end goal of this research is to develop a simultaneous processing/characterization method (a High Throughput method) that allows for real-time measurement of additive concentration and mixing.

It is important to remember that the following discussions are about PA6 nanocomposites and without first studying other polymers it is inaccurate to believe the dielectric dispersion values are universal for all polymer nanocomposites. However, we believe the trends discussed here will still exist; i.e. linear relationship between $\Delta\varepsilon_{mw}$ and layered silicate mass fraction.

2. Experimental[1]

2.1. Materials

Two quaternary ammonium modified montmorillonites (organoclays), Cloisite 20A and Cloisite 30B [4], and pure PA6 (UBE Industries, Japan) were melt compounded at various layered silicate contents (Table 1). Prior to compounding, these organoclay powders were dried under high vacuum at $90\pm2\,^{\circ}C$ for 3 h and pure PA6 was dried for 4 h under high vacuum at $70\pm2\,^{\circ}C$. Transmission electron microscopy (TEM) analyses indicate that 20A in 20A/PA6 nanocomposites has a mixed intercalated/exfoliated nanomorphology and 30B in 30B/PA6 nanocomposites has a well-exfoliated nanomorphology, Fig. 1.

In addition to compounding pure PA6 with Cloisite clays, commercially available PA6 nanocomposites (UBE Industries, Japan) were extrusion processed after drying under high vacuum at $70\pm2\,^{\circ}C$ for 4 h; see Table 1 for layered silicate contents. TEM analyses indicate these nanocomposites have an aggregated/intercalated nanomorphology (Fig. 1). These materials are commonly referred to

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Table 1
Percentage mass fraction of layered silicates in PA6 as measured by TGA

Averaged layered silicate content (% mass fraction)	Measured layered silicate content (% mass fraction)		
	In situ/PA6	20A/PA6	30B/PA6
1.29	1.31 ± 0.10	1.28 ± 0.12	1.29 ± 0.09
2.59	N/A	2.56 ± 0.15	2.61 ± 0.12
3.26	3.32 ± 0.11	3.17 ± 0.04	3.28 ± 0.02

The average layered silicate content refers to the nanomorphology averaged layered silicate concentration, where in situ/PA6, 20A/PA6, and 30B/PA6 have different nanomorphologies. (1σ uncertainty).

as in situ polymerized PA6 nanocomposites (in situ/PA6) because polymerization of ε-caprolactam (PA6 monomer) occurs in the presence of the organoclay. Normally this method generates highly exfoliated nanocomposites, however, it is our understanding modifications may have been made by the company to improve the organoclay thermal stability and we speculate that these modifications may have caused the poor dispersion.

2.2. Material processing

Melt processing was conducted on a B and P Process Equipment and Systems twin-screw extruder (co-rotating, intermeshing, 25:1 L:D). Operating conditions were 36.7 rad/s (350 rpm) screw speed and $250\pm3\,^{\circ}C$ barrel temperature for all zones except the feed ($190\pm3\,^{\circ}C$). All organoclay powders and resin pellets were gravimetrically fed (2.5 kg/h total discharge rate, 60 s residence time) using Brabender Mass Loss feeders.

2.3. Dielectric measurements and curve fitting

Extrusion-dielectric spectroscopy was performed using a Chemical ElectroPhysics (CEP) slit channel, multi-sensor, and heated dielectric spectrometer called Proceptor [1,2,5, 6]. This sensor was attached to the exit end of the extruder using a customized adapter plate to interface with B and P extruder. Dielectric, optic and pressure sensors were used to monitor the polymer as it flowed through the dielectric sensor cell. A jacket heater was used to control the cell temperature to $250\pm5\,^{\circ}C$. A single dielectric experiment took 90 s during which the 'measured' relative permittivity (ε'_{meas}) and dielectric loss (ε''_{meas}) of the material was measured at 15 frequency points over a frequency sweep of $500–10^5$ Hz.

In the molten state these polymeric materials contain conducting ions that contribute to both direct current (DC) conductivity and electrode polarization effects; as evidenced by a large increase at low frequencies for both the measured ε' and ε'' [1,2]. Separating out these conducting ion effects was accomplished by modeling the electrode polarization as a capacitance/resistance parallel circuit that
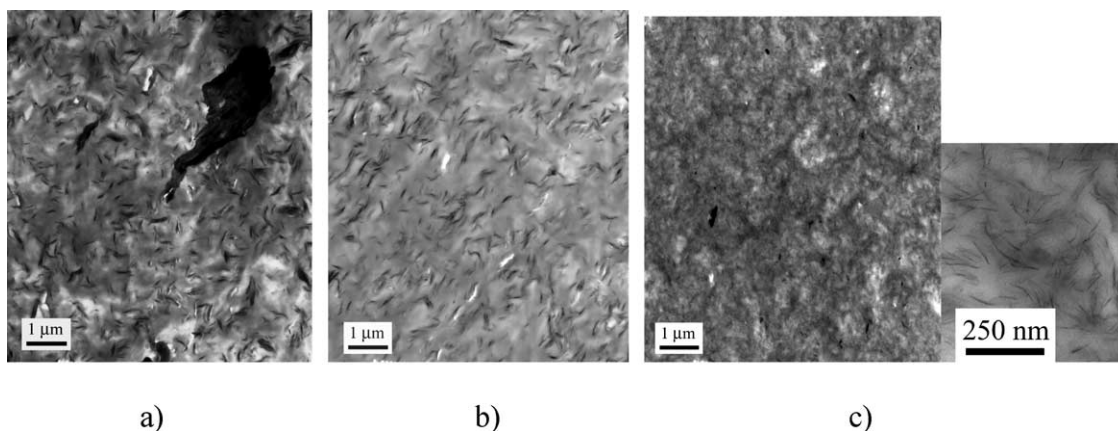
Fig. 1. TEM of intercalated 3.32%-in situ/PA6 (a), mixed intercalated/exfoliated 3.17%-20A/PA6 (b), and well-exfoliated 3.28%-30B/PA6 (c).

is in series with the sample and the DC conductivity as a resistance in parallel with the sample [7]. This scenario can be described as electrode (ele) admittance, Y_{ele}, in series with the sample (s) admittance, Y_s Eqs. (1) and (2). These admittances yield the apparent (app) admittance, Y_{app} Eq. (3), where G_{app} and C_{app} refer to the apparent conductance and capacitance, respectively.

$$Y_s = G_s + i\omega C_s \tag{1}$$

$$Y_{ele} = G_{ele} + i\omega C_{ele} \tag{2}$$

$$Y_{app} = G_{app} + i\omega C_{app} = \frac{Y_{ele}Y_s}{Y_{ele} + Y_s} \tag{3}$$

Sample dielectric properties were obtained from Eq. (1). In practice, sample relative permittivity (ε'_s) and dielectric loss (ε''_s) values Eqs. (4) and (5) were extracted from Y_{app} by a non-linear curve fitting routine, where C_o is the sample capacitance in a vacuum and ε'_s and ε''_s are defined as

$$\varepsilon'_s = \frac{C_s}{C_o} \tag{4}$$

$$\varepsilon''_s = \frac{G_s}{\omega C_o} \tag{5}$$

Specific to the curve fitting routine, it is known that the frequency dependence of dielectric relaxations can be modeled by the Havriliak–Negami function, which reduces to the Cole–Cole equation for symmetric distributions of relaxation times [7,8]. Indistinguishable curves resulted from fitting the dielectric data using the Havriliak–Negami equation compared to the Cole–Cole equation, therefore the latter was adopted for the dielectric data analysis. To account for DC conductivity in these equations, a DC conductivity term (σ_{DC}) that was proportional to the reciprocal of frequency was added to a sum of Cole–Cole expressions Eq. (6). The dielectric fitting parameters are defined in Table 2 and an example of a curve fitting graph is provided in Fig. 2.

$$\varepsilon_s^* = -i\frac{\sigma_{DC}}{\varepsilon_o\omega} + \varepsilon_\infty + \sum_j \frac{(\Delta\varepsilon)_j}{[1 + (i\omega\tau_j)^{1-\delta_j}]} \tag{6}$$

To analyze the data, the real and imaginary parts of Eq. (6) were substituted into Eq. (3) using the definitions in Eqs. (4) and (5). The global fitting procedure consisted of using a least squares non-linear fit to the frequency dependent data, which was accomplished by adjusting the fitting parameters defined in Table 2 and Y_{ele} until the calculated values match, at less than 1% difference, the measured values; fitting always began by initial fitting σ_{DC} and Y_{ele} in conjunction with one dielectric relaxation. If the error was greater than 1% then additional relaxation dispersions were added to the fitting function until less than 1% error was obtained. For all materials studied there were no more than two relaxations; i.e. j was equal to 1 or 2. For a more extensive explanation of the data analysis protocol see publications by Bur et al. [1] and Noda et al. [2].

2.4. Characterization

TEM specimens were cut from extruded samples using a Leica cryo-ultramicrotome, equipped with a diamond knife. Sectioning was performed at -80 ± 2 °C. Sections were collected from the knife edge and placed onto 400 µm mesh

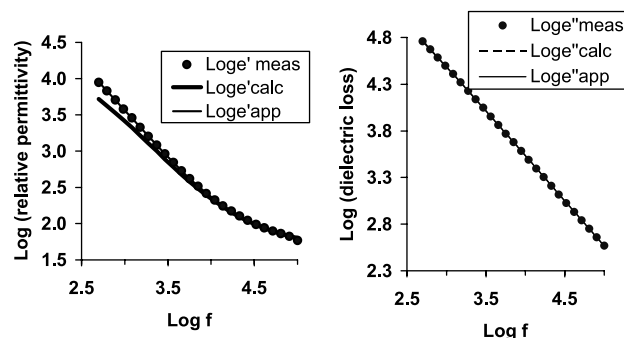Fig. 2. Curve fitting graphs of the calculated relative permitivitty (ε') and dielectric loss (ε'') terms to the measured values for 3.2%-30B/PA6 sample. The calculated curve reflects the dielectric property of the material.

Table 2
Descriptions of the dielectric dispersion parameters used in the global fitting routine

Symbol	Name	Description
C_{ele}	Capacitance (electrode)	Reduced capacitance resulting from charge accumulation on the electrode surface (F), not a material property
G_{ele}	Conductance (electrode)	Reduced conductance resulting from charge accumulation on the electrode surface (S/m), not a material property
f	Frequency	Characteristic relaxation frequency for each relaxation dispersion (Hz); inversely proportional to relaxation time (τ)
ω	Radial frequency	$\omega = 2\pi f$
σ_{DC}	Direct current conductivity	Associated with diffusion of unbound ions (S/m)
$\Delta\varepsilon$	Strength of dispersion	Strength of a dielectric relaxation (no units)
δ	Breadth of dispersion	Distribution of relaxation times about a characteristic relaxation time (no units)
ε_o	Permittivity of free space	$8.854 \times 10{-}12$ F/m, permittivity in vacuum
ε_∞	Unrelaxed permittivity	Relative permittivity in the high frequency limit where all relaxation processes cannot follow the alternating current (F/m)

copper–rhodium grids. Electron micrographs were taken with a Philips EM400C at an accelerating voltage of 120 kV.

Layered silicate concentrations were measured using a Thermal Analysis Q500 equipped with a 16-sample auto sampler. Nanocomposite samples (20 ± 5 mg) were heated to 900 ± 3 °C at 20 °C/min in breathing quality air. The TGA results of the nanocomposites are provided in Table 1 with layered silicate contents reported with 1σ standard uncertainty.

3. Results and discussion

Interpretation of TEM images was used to qualitatively rank these nanocomposites based on the level of layered silicate exfoliation. Fig. 1a shows that the 3.32%-in situ/ PA6 contains large aggregates (2–5 μm) and numerous small aggregates of approximately 1 μm. There are no individual exfoliated layered silicate sheets visible in any TEM images of in situ/PA6 and tactoids sizes range from 12 to 24 layered silicate sheets thick. Fig. 1b shows that 3.17%- 20A/PA6 contains few layered silicate particles near 1 μm and the norm being tactoid sizes ranging from 6 to 14 layered silicate sheets thick. All 20A/PA6 nanocomposites contain numerous individual exfoliated layered silicate sheets. Fig. 1c shows that 3.28%-30B/PA6 is highly exfoliated. Based on TEM interpretation we have classified the nanocomposite nanomorphologies as intercalated (in situ/PA6), mixed intercalated/exfoliated (20A/PA6), and well exfoliated (30B/PA6). Since the nanomorphology was independent of organoclay concentration only the highest organoclay content TEMs are provided (Fig. 1) as representatives of the three different nanomorphologies.

3.1. Differentiating pure polymer from nanocomposite

Pure PA6 has a single dielectric relaxation, r_α, that has been previously identified as reflecting macromolecular segmental motion (rotation of dipoles) and termed α

relaxation (Table 3) [1,2]. All PA6 nanocomposites contain two relaxations, r_α and r_{mw} (Table 3), where r_{mw} is the Maxwell–Wagner relaxation. The Maxwell–Wagner relaxation refers to the frequency dependence of interfacial polarization (ion accumulation) that occurs at the interface between materials with differing dielectric constants, such as polymer and layered silicates. Characteristic of a Maxwell–Wagner relaxation is a large $\Delta\varepsilon$ value. Assigning the second relaxation in the nanocomposites as a Maxwell–Wagner relaxation was based on that the polymer and layered silicates have quite different dielectric constants and the large $\Delta\varepsilon_{mw}$ values (12,000–33,000). We believe that the dielectric dispersion parameters contained in the Maxwell–Wagner relaxation are sensitive to layered silicate content and level of exfoliation. These relationships are the focus of the discussion below. The dielectric fitting parameters are defined in Table 2 and optimum fitting parameters that are relevant to the discussions of this paper are provided in Table 3 (1σ uncertainty). The $\Delta\varepsilon_{mw}$ and f_{mw} parameters are
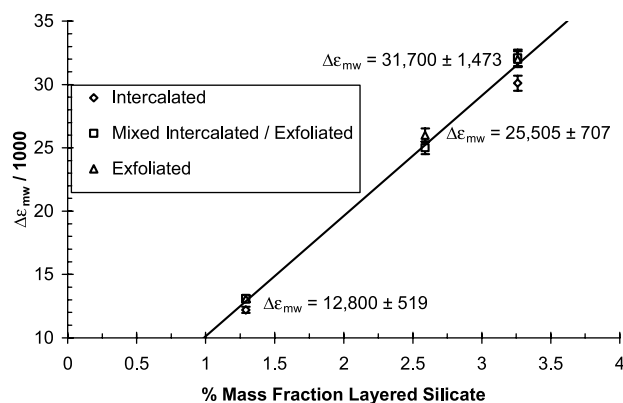
Fig. 3. The $\Delta\varepsilon_{mw}$ values appear to quantitatively indicate the layered silicate concentration and are independent of nanomorphology. We suggest the nanomorphology averaged $\Delta\varepsilon_{mw}$ values (provided in the figure) indicate a (1.29, 2.59, and 3.26%) mass fraction of layered silicate loading. The equation that represents the linear relationship (solid line) between the nanomorphology averaged $\Delta\varepsilon_{mw}$ value and the layered silicate content is provided in the text as Eq. (7).

Table 3
Values of the dielectric dispersion parameters that resulted from the global fitting of the real-time dielectric data

Material	Fitting parameters						
	$\sigma_{DC}/10^{-4}$ (S/m)	Relaxations					
		r_α			r_{mw}		
		$\Delta\varepsilon/1000$	f (Hz)	$\delta/100$	$\Delta\varepsilon/1000$	f (Hz)	$\delta/100$
Pure PA6	2.54 ± 0.11	1.25 ± 0.16	588 ± 5	13.2 ± 1	N/A	N/A	N/A
In situ/PA6 (intercalated)							
1.31%	2.66 ± 0.14	0.40 ± 0.05	601 ± 11	5.0 ± 1	12.2 ± 0.6	5.0 ± 0.3	40.1 ± 10
3.32%	2.68 ± 0.11	0.31 ± 0.02	603 ± 15	5.1 ± 0.3	30.1 ± 1.5	9.2 ± 0.6	27.1 ± 9
20A/PA6 (mixed intercalated/exfoliated)							
1.28%	8.90 ± 0.42	1.58 ± 0.06	739 ± 10	5.2 ± 2	13.1 ± 0.7	78 ± 2.0	15.0 ± 3
2.56%	11.4 ± 0.55	1.14 ± 0.06	1171 ± 23	7.9 ± 1	25.0 ± 1.3	80 ± 2.8	13.8 ± 1
3.17%	12.9 ± 0.60	1.13 ± 0.07	1400 ± 30	12.0 ± 1	32.1 ± 1.4	83 ± 2.0	15.8 ± 2
30B/PA6 (well-exfoliated)							
1.29%	9.77 ± 0.49	1.34 ± 0.08	765 ± 10	4.5 ± 2	13.1 ± 0.7	3.0 ± 0.1	41.1 ± 8
2.61%	12.2 ± 0.72	2.06 ± 0.09	986 ± 13	2.7 ± 2	26.0 ± 1.3	2.7 ± 0.9	39.6 ± 9
3.28%	13.5 ± 0.86	1.00 ± 0.05	1016 ± 64	3.5 ± 1	32.0 ± 2.0	1.6 ± 1.0	43.4 ± 2

Dielectric dispersion parameters are reported with 1σ uncertainty, which is determined from five on-line dielectric experiments.

plotted against nanomorphology and/or layered silicate content in Figs. 3 and 4 (1σ uncertainty), respectively.

3.2. Correlation of $\Delta\varepsilon_{mw}$ with concentration

There is a linear relationship between the Maxwell–Wagner strength (intensity) of relaxation, $\Delta\varepsilon_{mw}$, and layered silicate content (Table 3 and Fig. 3). As shown in Fig. 3, the layered silicate concentration results in a characteristic $\Delta\varepsilon_{mw}$ value and that value is independent of nanomorphology. The nanomorphology averaged $\Delta\varepsilon_{mw}$ values are $12,800\pm519$, $25,505\pm707$ and $31,700\pm1473$ and indicate layered silicate concentrations of (1.29, 2.59 and 3.56) % mass fraction, respectively. This linear relationship between the nanomorphology averaged $\Delta\varepsilon_{mw}$ and layered
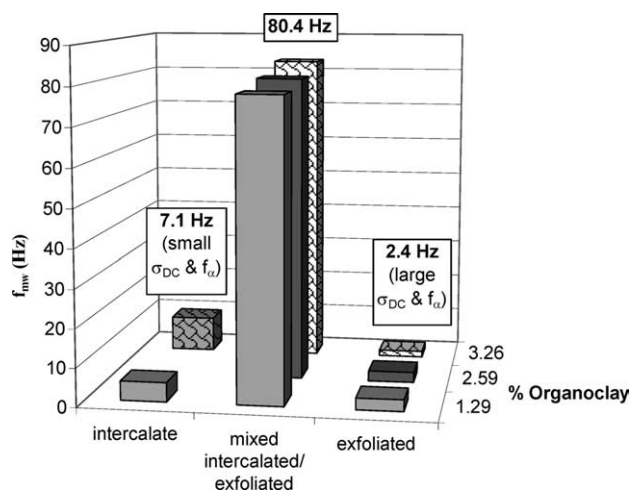

Fig. 4. The f_{mw} values appear to indicate the nanomorphology and are independent of layered silicate concentration. Provided in the figure is the concentration averaged Δf_{mw} values. When the f_{mw} value is small, as is the case for the intercalated and exfoliated samples, then the value of the σ_{DC} and f_α parameters will indicate the nanomorphology.

silicate content, $c_{\text{layered silicate}}$, can be defined by Eq. (7) ($R^2=0.99998$).

$$\Delta\varepsilon_{mw} = 9.48 * 10^4 * c_{\text{layered–silicate}} + 0.6453 \qquad (7)$$

The $\Delta\varepsilon_{mw}$ observations are interpreted as follows. During the dielectric experiment polymer dipoles are oriented, and ions are displaced, by an applied electric field. When the electric field is alternated the dipoles reorient and the ions reposition/translate to maintain alignment with the electric field. These translating ions can accumulate at the layered silicate/polymer interface (contributors to the Maxwell–Wagner relaxation, r_{mw}), accumulate at the electrode interface (electrode polarization), or freely diffuse in the matrix (direct-current conductivity, σ_{DC}). The $\Delta\varepsilon_{mw}$ value reflects the amount of ion accumulation at the layered silicate/polymer interface (Maxwell–Wagner relaxation). The increase in the $\Delta\varepsilon_{mw}$ value with increasing layered silicate content could result from either an increase in the amount of ions and/or layered silicate surface. However, the independence of exfoliation on the $\Delta\varepsilon_{mw}$ value suggests that the dielectric strength of the Maxwell–Wagner relaxation is dominated by the amount of ions and not the layered silicate surface area.

3.3. Correlation of f_{mw} with nanomorphology (degree of exfoliation)

The Maxwell–Wagner characteristic relaxation frequency values, f_{mw}, are strongly influenced by nanomorphology (Table 3 and Fig. 4). The f_{mw} values are independent of layered silicate concentration resulting in concentration averaged f_{mw} values of 7.1 ± 5 Hz, 80.4 ± 5 Hz, and 2.40 ± 1 Hz that appear to indicate an intercalated, mixed intercalated/exfoliated, and exfoliated nanomorphologies, respectively. However, the similarity between the f_{mw} values of the intercalated and exfoliated samples requires

using an additional parameter to differentiate these nanomorphologies, σ_{DC} and/or f_α. The σ_{DC} and f_α values are similar for the intercalated samples (2.67×10^{-4} S/m$\pm$ 0.2×10^{-4} S/m and 600 Hz$\pm$12 Hz, respectively) and the pure polymer (2.54×10^{-4} S/m$\pm 0.1 \times 10^{-4}$ S/m and 588 ± 10 Hz, respectively) and significantly different from those of the mixed and exfoliated samples (12.1×10^{-4} S/m$\pm 5.0 \times 10^{-4}$ S/m and 1012 ± 350 Hz, respectively). We suggest that for PA6 nanocomposite an f_{mw} value of $80.4 \pm$ 5 Hz indicates a mixed intercalated/exfoliated nanomorphology and the researcher should strive to minimize this value. Because the intercalated and exfoliated nanomorphologies yield similar f_{mw} values the researcher should simultaneously strive to increase the σ_{DC} and f_α values, as compared to the pure polymer. We suggest a small f_{mw} value in conjunction with large f_α and σ_{DC} values indicate an exfoliated nanomorphology, where as a small f_α and σ_{DC} values indicate an intercalated nanomorphology. Before proceeding with an explanation of what is physically occurring it is important to understand the following background information.

The f_{mw} value is related to the kinetics of ion accumulation at the interface between the differing dielectric constant materials. Interpretation of f_{mw} is best explained if one thinks of the dynamics of this interfacial polarization in terms of a resistance (polymer)-capacitance (layered silicates) time constant with a relationship expressed as $\tau = R \times C$, where τ (relaxation time) is the time it takes to reach a new equilibrium as a result of applying an alternating current. The direct current (DC) conductivity term, σ_{DC}, reflects the ability of free ions to diffuse through the polymer matrix, where the free ions can be unbound, bound and/or degraded organic modifiers [9, 10], ion exchange by-products [10], and/or other ions. Resistance (R) is the opposition the polymer offers to the flow of these free ions, therefore the conducting resistance of the resin can be approximated by the ionic conductivity of the nanocomposite, $R \cong 1/\sigma_{DC}$. Since τ can also be expressed as $\tau = 1/2\pi f$ then the f_{mw} values can be discussed in terms of the resistance (R) and capacitance (C) behavior of the nanocomposites using these relationships, $\tau_{mw} = 1/2\pi f_{mw} \cong \sigma_{DC}/C$.

The f_α value is related to the rotational mobility of the PA6 peptide linkages. To better understand the following discussion of f_α one may consider reviewing the publications of Nagi and coworkers [11,12], who have extensively studied the concept of intermolecular cooperative effects. As the concept applies here, in order for polymer segmental motion to occur adjacent polymer chains must move, which causes additional chains to move and this process continues to three dimensionally translate to some volume, which is referred to as the cooperativity domain size. Many factors affect the frequency/relaxation rate of the segmental mobility, such as the strength of intermolecular interactions and polymer density. Our assumption is the layered silicates reduce the intermolecular cooperativity

domain size and with increased exfoliation comes a greater decrease in cooperativity. However, one must also keep in mind that layered silicate/polymer interactions could restrict segmental mobility so that with increased exfoliation could come a greater restriction in segmental mobility. Therefore, the magnitude of the f_α value reflects the outcome of this 'tug-of-war', where a smaller f_α value can be an indication of either increased restricted segmental mobility due to increased layered silicate/polymer interactions (increased exfoliation) or increased cooperativity domain size due to decreased exfoliation.

Even though the in situ/PA6 is a nanocomposite the layered silicate dispersion is quite poor and based on the σ_{DC} and f_α value it appears the layered silicate has a minimal impact on the polymer conductive resistance and intermolecular cooperativity. Think of the in situ/PA6 nanocomposites as pure PA6 with isolated layered silicate chunks. In comparison think of the mixed and exfoliated nanocomposites as a single material where there is an extensive amount of polymer/layered silicate interactions that significantly alter the polymer conductive resistance and intermolecular cooperativity. As discussed earlier the incorporation of the layered silicate creates capacitors where the time it takes to charge the capacitors is τ_{mw} and the conductive resistance of the polymer and the capacitance of the layered silicates influence this relaxation time, $\tau_{mw} = R \times C$. The conductive resistance of the mixed and exfoliated nanocomposites is similar, as suggested by the similar σ_{DC} value, and since the capacitance is independent of ion concentration but directly proportional to surface area the decreased f_{mw} value with an increased exfoliation can be explained as a result of an increased amount of layered silicate surface area. Physically speaking, it takes longer for negative and positive charges to accumulate at the interface of the same layered silicate particle when a significant amount of particles are present (Fig. 5). On the other end of the nanomorphology spectrum, the capacitance of the intercalated nanocomposites decreases due to decreased surface area, but the conductive resistance is simultaneously increasing as indicated by the decreasing σ_{DC} value. The impact of the increased resistance is greater than the decreased capacitance, therefore the f_{mw} value decrease
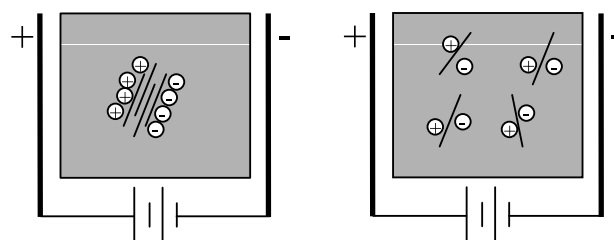

Fig. 5. An illustration of layered silicate filled polymer in an applied electric field. The ions accumulate at the organoclay surfaces creating a charged capacitor. The capacitance of any capacitor is directly proportional to surface area; therefore the capacitance of the nanocomposite increases with exfoliation. We believe the decreasing f_{mw} with increasing exfoliation is a result of this increased capacitance.

from the mixed to the intercalated nanomorphologies is due to a change in conductive resistance where as a similar change in f_{mw} value from the mixed to exfoliated nanomorphologies is due to a change in capacitance. A change or similarity in conductive resistance implies a difference or similarity in segmental mobility, which would come out in the f_α value. The f_α values (Table 3) support our assumption that the polymer dielectrics are similar for the intercalated nanocomposite and pure PA6 and similar for the mixed and exfoliated nanocomposites, but significantly different from each other.

3.4. Dielectric sensor has a HT method

At this point in the research the dielectric sensor is not an efficient HT characterization method because off-line curve fitting is required to extract the dielectric responses that correlate with layered silicate concentration and exfoliation. As our research expands to other polymers and additives so will our understanding of the relationship of all the dielectric responses (obtained through curve fitting) with the type of polymer and additive being processed. Incorporating these relationships as constraints in the curve fitting protocol could result in reduced curving fitting time and a better fit of the calculated to the experimental values. From this study we observed that the r_α term always had a higher relaxation frequency (f), a lower dielectric strength ($\Delta\varepsilon$), and smaller distribution of relaxation frequencies (δ) compared to the values of the corresponding parameters of the r_{mw} term. In the future, these relationships between r_α and r_{mw}, and between the dielectric dispersion parameters and layered silicate concentration and exfoliation will be used as a starting point as we expand to other polymer and additive combinations.

4. Conclusion

A dielectric spectrometer was attached to the end of an extruder and used for monitoring the dielectric responses of PA6 and PA6 nanocomposites during extrusion processing of these materials. All nanocomposites had two dielectric relaxations, α and Maxwell–Wagner, associated with rotational mobility of PA6 amide linkages and ion accumulation at the layered silicate/polymer interface, respectively. The pure polymer had only the α relaxation. We propose that the $\Delta\varepsilon_{mw}$ value quantitatively indicates the layered silicate concentration. We propose that the f_{mw}, f_α, and σ_{DC} values are needed to qualitatively indicate the level of layered silicate exfoliation.

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