Dielectric Spectroscopy During Extrusion Processing of Polyamide-6 Nanocomposites: A High Throughput Method

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INTRODUCTION

Using HT methodologies developed in our laboratory we have rapidly generated and tested the flammability of additive filled polymers in significantly less time than achieved using conventional methods.[1,2 3] However, interpretation of test data is still slow because we rely on time-consuming characterization techniques, i.e. TEM, to qualitatively evaluate additive concentration and degree of additive mixing. A viable approach to decrease characterization time is to determine additive mixing and concentration during processing, which could be possible using an on-line dielectric spectrometer.[4,5,6] Over the last few years, Bur and McBrearty have been using an on-line dielectric spectrometer to monitor the dielectric response of poly (ethylene-co-vinyl acetate) (PE-EVA),[7] polyamide-6 (PA-6)[5] and polyamide-12 (PA-12)[4,6] nanocomposites during compounding on a twin screw extruder. These researchers reported that incorporation of organoclay into a polymer caused an additional relaxation dispersion due to polarization at the organoclay/polymer interface.

Thinking that this additional relaxation dispersion may correlate with additive mixing and/or concentration, we began using a similar on-line dielectric spectrometer to monitor, in real-time with extrusion processing, the dielectric properties of organoclay filled polymers (nanocomposites).[6] The focus of the research has been to identify a correlation between the organoclay nanomorphology and concentration with the real-time dielectric data. Presented here are possible relationships between the dielectric dispersion parameters and the organoclay concentration and nanomorphology in polyamide-6 (PA6) nanocomposites. A more extensive publication is currently being prepared for submission.[6]

EXPERIMENTAL[8]

Cloisite 20A and Cloisite 30B[9] were melt compounded with PA6 (Ube Industries), at various concentrations, using a twin screw extruder operating at 36.7 radian/s (350 rpm) screw speed and 250 °C ± 5 °C barrel temperature. The materials studied are referred to as pure PA6, 20A/PA6, and 30B/PA6.

Transmission electron microscopy (TEM) specimens were cut from extruded samples using a Leica cryo-ultramicrotome, equipped with a diamond knife. Sectioning was performed at –80 °C ± 2 °C. Sections were collected from the knife edge and placed onto 400 mesh copper-rhodium grids. Electron micrographs were taken with a Philips EM400C at an accelerating voltage of 120 KV.

On-line dielectric spectroscopy (CEP Proceptor) was performed using a slit channel, multi-sensor, heated dielectric cell manufactured by Chemical ElectroPhysics (CEP). Complete details of this spectrometer and data processing are published elsewhere.[4,5,6] A jacket heater was used to maintain the polymer flow temperature in the cell at 250 °C ± 5 °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 values over a sweep from 500 Hz to 10^5 Hz.

A consequence of high temperature dielectric spectroscopy of polymers is the dielectric data contains contributions from dissociated ions as well as the polymer dielectric dispersion parameters. The dissociated ions contribute to electrode polarization effects and to DC conductivity. Separating out the dissociated ion contributions is necessary to yield information about the material dielectric relaxation processes. Our approach was to describe the dielectric dispersions using the Cole-Cole relaxation expression (provided below) plus a DC conductivity term and to model the electrode effect as an impedance in series with the sample.[7] The dielectric data analysis consisted of using a non-linear fitting routine, where the relaxation parameters plus the electrode factors are adjusted until the calculated values match, at less than 1 % difference, the experimental values. All the fitting parameters are defined elsewhere[4,5,6]. Important to the discussion here is j represents the number of relaxations, ω is the radial frequency (equal to $2\pi f$), τ is the relaxation time ($1/f$), f is the characteristic relaxation frequency, and $\Delta\varepsilon$ is the strength of dispersion.

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

RESULTS AND DISCUSSION

Based on TEM interpretation we have classified the nanocomposite nanomorphologies as mixed intercalate/exfoliate (20A/PA6) and well exfoliated (30B/PA6).
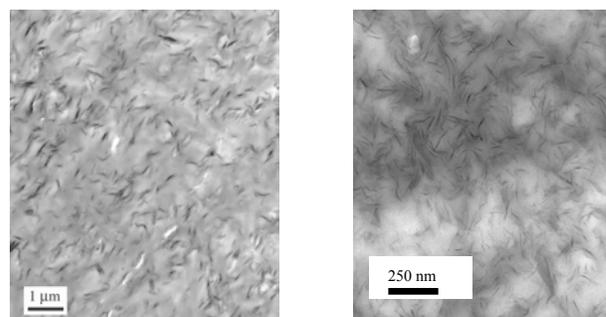

Figure 1. TEM Images of 20A/PA6 and 30B/PA6 Nanocomposites.

The pure PA6 has a single relaxation, r, which has been previously identified as reflecting macromolecular segmental motion (rotation of dipoles) and termed the α relaxation (Table 1).[5] All organoclay filled PA6 nanocomposites (Table 1) contain two relaxations, r and r_{mw}, where r_{mw} is an interfacial Maxwell-Wagner relaxation. The latter assignment was based on the observed large dielectric strength, $\Delta\varepsilon_{mw}$, which indicates a polarization dominated by ion translation to the filler/polymer interface; behavior indicative of an interfacial Maxwell-Wagner relaxation.

The Maxwell-Wagner strength of relaxation, $\Delta\varepsilon_{mw}$, appears to correlate with organoclay content (Table 1). Specifically, a factor of 2.5 increase in 20A mass fraction content (from 2 % mass fraction to 5 % mass fraction) gives a 2.5 times larger $\Delta\varepsilon_{mw}$ value (13,100 to 32,000). A similar incremental relationship between $\Delta\varepsilon_{mw}$ value and organoclay content was also observed in the 30B/PA6 sample series. (Table 1).

Additional information may also be extracted from the relaxation frequency data. The Maxwell-Wagner characteristic relaxation frequency, f_{mw}, appears to be sensitive to the organoclay nanomorphology. Specifically, a mixed intercalate/exfoliate nanomorphology (20A/PA6) has a concentration averaged f_{mw} value of

80.4 Hz $\pm$ 5 Hz and a well exfoliated nanomorphology (30B/PA6) has a concentration averaged f_{mw} value of 2.43 Hz $\pm$ 1 Hz (Table 1).

Table 1. Pertinent Fitting Parameter Values for PA6 and 20A/PA6; i/e=intercalate/exfoliate, e=exfoliate (1 sigma uncertainty)

Material	Relaxations				TEM
	r		r_{mw}		
	$\Delta\varepsilon$/1000	f (Hz)	$\Delta\varepsilon$/1000	f (Hz)	
Pure PA6	1.25 $\pm$ 0.16	588.2 $\pm$ 0.21	none	none	
2%-20A/PA6	1.58 $\pm$ 0.06	738.8 $\pm$ 16	13.2 $\pm$ 0.17	78.2 $\pm$ 2.0	i/e
5%-20A/PA6	1.13 $\pm$ 0.17	1400 $\pm$ 141	32.1 $\pm$ 1.4	83.4 $\pm$ 1.0	
2%-30B/PA6	1.34 $\pm$ 0.08	664.7 $\pm$ 31	13.1 $\pm$ 0.7	1.34 $\pm$ 0.08	e
5%-30B/PA6	1.00 $\pm$ 0.05	1016 $\pm$ 62	32.0 $\pm$ 2.0	1.00 $\pm$ 0.05	

CONCLUSION

The dielectric dispersion parameters were calculated from off-line curve fitting of dielectric data, which was collected during extrusion processing. The $\Delta\varepsilon_{mw}$ and f_{mw} values appear sensitive to organoclay, therefore may be used to monitor the concentration and exfoliation of organoclay, respectively. With additional research this sensor could be used to characterize material composition during processing, therefore allowing for "on the fly" changes to yield the desired product and circumventing the need to conduct off-line characterization.

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8. This work was carried out by the National Institute of Standards and Technology (NIST), an agency of the U. S. government, and by statute is not subject to copyright in the United States. Certain commercial equipment, instruments, materials, services, or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.
9. Cloisite is a registered trade name of Southern Clay Products (www.nanoclay.com/). 20A is N,N-dimethyl-N,N-dihydrogenatedtallow quaternary ammonium exchanged montmorillonite and 30B is N-methyl-N-tallow-N,N-bis-2-hydroxyethyl quaternary ammonium exchanged montmorillonite.