MONITORING POLYMER/CLAY NANOCOMPOSITES COMPOUNDING USING A DIELECTRIC SLIT DIE

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Abstract

A new in-line process monitoring instrument, a dielectric slit die, was used to examine the compounding of polymer/clay nanocomposites. The instrument is a multipurpose sensing device for measuring dielectric, rheological, and optical properties during extrusion compounding. We report results of compounding nylon 12 and polyethylene ethyl vinyl acetate copolymer with organo modified clays.

Introduction

Processing and compounding of polymers with fillers and pigments requires either off-line or on-line evaluation in order to determine the quality of the compounded product. On-line monitoring techniques are advantageous because they present immediate results that can be used to adjust process parameters. On-line monitoring of polymer/clay nanocomposites compounding is of special interest because current practice involves extensive off line measurements (X-ray diffraction and TEM) to determine the extent of exfoliation and/or intercalation of the clay. An on-line method to deduce microstructure would provide desirable and efficient feedback that can be used to control product quality.

In the past several years, our work has focused on the development and application of instrumentation for process monitoring. This has involved optical, spectroscopic and dielectric monitoring equipment. A first generation dielectric sensor that we used for on-line monitoring of resin compounding was described earlier.[1,2] That sensor consists of a ceramic ring with interdigitating electrodes deposited on its inside surface. As an extruded resin flows through the ring, its dielectric properties are monitored by a fringing electric field that extends into the resin melt. Using this sensor, we reported the results of compounding resins with inorganic fillers and resin/nanoclay composites. We observed that dielectric properties are significantly impacted by filler content and microstructure.[2]

The subject of this paper is the results of real-time monitoring of nanocomposites compounding using a new multifunctional sensor. A diagram of the dielectric slit die sensor showing the slit configuration is presented in Figure 1. The slit channel, with approximate dimensions of 2 mm high by 2.8 cm wide by 15 cm long, defines a constant geometry sample cell in which the processed material is characterized by on-line sensing devices. The primary sensor in the channel is the dielectric sensor consisting of interdigitated electrodes that are deposited and fired onto a ceramic substrate that forms one surface of the slit. In addition to the dielectric sensor, the design allows for a number of sensors to be placed in-line along the slit. At this time, pressure, optics and dielectrics sensors are being employed. Other sensors can be added in accordance with the needs of the experiment. The details of the design and construction of the sensor are presented in another paper from this conference.[3]

Dielectric measurements yield information about two electrical parameters: the capacitance and resistance of the material under investigation. When measurements are made as a function of temperature and frequency, the dynamics of molecular relaxation processes can be evaluated. In the case of composites whose components have dielectric contrast, such as polymer and clay, the composite electrical properties reflect the dynamics of capacitive/resistive networks associated with the composite microstructure.

Dielectric measurements are expressed as

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{1}$$

where ε^* is the complex relative permittivity and ε' and ε'' are the real and imaginary parts. ε' is the capacitive or polarization property and ε'' is the conductivity property of the material. As a function of frequency, DC conductivity and microstructural relaxations will be exhibited. At processing temperatures, we can expect that the dielectric properties of polymer/clay composites will contain significant ionic conductivity because, at elevated temperatures, the ions in the clay dissociate and become conductive under the influence of an electric field. Ionic conduction also contributes to the real part of the relative permittivity as interfacial polarization or electrode polarization. Both of these phenomena usually occur at low frequency when ions can follow in phase with the applied electric field and accumulate at the electrode or, in a heterogeneous mixture, at the interface between components of different dielectric constant. The frequency dependence of interfacial polarization is known as Maxwell-Wagner relaxation.[4] For composite materials with a distribution of permittivities and conductivities, a distribution of relaxation times results. These effects are the focus of our research on the dielectric properties of polymer/clay nanocomposites.

Experimental Procedure[a]

Two polymer resins were used in this study, nylon 12, Grilamide L16 from EMS-Chemie, and polyethylene ethyl vinyl acetate (PE-EVA) copolymer, Equistar UE630-000 with 17 % vinyl acetate. The smectite clays were obtained from Southern Clay products; they are Cloisite Na+, Cloisite 15A and Cloisite 30B. The 15A and 30 B clays have been organically modified to be more compatible with organic polymers. The modification is achieved through an ion exchange process that exchanges the Na ions in the galleys between silicate layers with ammonium ions having organic appendages.(5)

The clay was compounded with the polymer at 4 % mass fraction of clay in the polymer. Compounding was carried out using an 18 mm Haake Rheocord model 9000 twin screw extruder. Figure 2 shows the experimental setup with the dielectric sensor attached to the end of the extruder. A lock-in amplifier is used to detect the in-phase and out-of-phase components of the current through the processed composite from which the real and imaginary parts of the relative permittivity are calculated.

Standard uncertainties for the measurements reported here were 1 °C for temperature and 70 kPa (10 psi) for pressure. The standard uncertainty in relative permittivity is 0.01 and for conductivity it is 1×10^{-10} S/m.

Results and Discussion

Figure 3 shows real-time dielectric data for extrusion of nylon 12 (neat) and for nylon 12 compounded with 4 % Cloisite clay 30B. Compounding was carried out at 195 °C. Relative permittivity and conductivity are plotted versus time for fifteen different frequencies ranging from 500 Hz to 100 kHz. Each line in the plot of Figure 3 is at a constant frequency. At t = 0, the neat polymer entered the electrode region of the dielectric sensor and was extruded for approximately 25 min, at which time resin pellets mixed with 4 % mass fraction of clay were added to the feeder. Permittivity and conductivity began to increase as the mixture filled the slit region. After significant transition time, the data reached a plateau value. The transition is associated with the time it takes the clay/polymer mixture to completely fill the sensing region, particularly at the surface near the electrodes. At t = 4200 s, the neat resin was extruded for the second time and relative permittivity values returned to their original values.

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[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.

For both the neat and clay/resin mixture we observed large dielectric dispersion which is distinguished by the change in permittivity and conductivity over the frequency range of observation, 500 Hz to 100 kHz. To analyze the dispersion, we focus on the conductivity or imaginary term. When measuring the dielectric properties of a polymer melt at elevated processing temperatures, ion conductivity becomes a prominent feature of the behavior. This is particularly true when fillers containing ionic species are compounded with a resin matrix. In some cases ionic conductivity is so large that it dominates the contribution from molecular dipolar and microstructural relaxation processes. In general the 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,

$$\sigma = \sigma_{DC} + \sigma_r \tag{2}$$

and

$$\varepsilon'' = \frac{\sigma_{DC}}{\omega \varepsilon_o} + \varepsilon_r'' \tag{3}$$

where the first term is the DC loss due $\sigma_{DC,}$ the DC conductivity, ω is 2π x frequency, ε_o is the permittivity of free space and ε_r'' is loss associated with relaxation processes. If ε_r'' is small, then the total dielectric loss ε'' is dominated by the ionic conductivity, and ε'' plotted versus frequency will have a slope of –1 on a log-log plot. This is seen in Figure 4 where data for both the neat and clay filled polymers are plotted. For neat nylon 12, the slope is –0.9893 and for the clay composite, it is –0.979. Thus, for the neat polymer the dielectric loss can be attributed solely to DC conductivity and for the clay composite whose slope differs significantly from –1, a small dielectric dispersion is present. In this case, ionic conductivity is so prominent that it is difficult to separate out the relaxation effects.

Figure 5 displays dielectric data for PE-EVA copolymer compounded with 15A clay at 154 °C. The data are plotted versus time for a compounding run that started with the neat resin. At t = 3200 s, a mixture of 4 % mass fraction of clay in nylon was added. After a transition time that extended over 35 min, a plateau region signaled the steady state for the nanocomposite melt. In the neat resin, we observed that the relative permittivity was 2.56 over the entire frequency range, i.e. no dielectric dispersion is seen in these data. Upon the addition of the 15A clay, a large dispersion develops. The sources of this dispersion are both the dc ionic conductivity and dielectric mixture dynamics of the Maxwell-Wagner type.[4]

Analysis of the 15A/PE-EVA dielectric dispersion involves fitting ε'' versus frequency with a function of the following type:[6]

$$\varepsilon^* = \frac{\sigma_{DC}}{\varepsilon_o \omega} + \varepsilon_\infty + (\varepsilon_l - \varepsilon_\infty)/\left[1 + (i\omega\tau)^{1-\alpha}\right] \qquad (4)$$

where ε_l and ε_∞ are the low and high frequency limits of the dispersion, τ is the characteristic relaxation time of the dispersion and α is a parameter that broadens the distribution of relaxation times for the process. If $\alpha = 0$, then the dispersion is Debye-like with only a single relaxation time. α is constrained to values between 0 and 1.

The result of fitting the dielectric loss curve is shown in Figure 6 and the table below shows the optimum fitting parameters:

ε_l - ε_∞ = 17.8
τ = 2.86 x 10^{-4} s
σ_{DC} = 1.10 x 10^{-6} S/m
α = 0.58

The value of τ corresponds to a frequency of 553 Hz, i.e. there is a dielectric dispersion (second term of equation (4)) whose maximum loss occurs at 553 Hz in the same frequency regime for which the $1/\omega$ DC conductivity term is significant. $\alpha = 0.58$ indicates that the dispersion is quite broad operating over four to five decades of frequency. The fitting procedure generates quantitative parameters that can be used to characterize the dispersion and establish correlations with off-line characterizations of the nanocomposite microstructure. For example a broad dielectric dispersion is associated with a broad distribution of relaxation times. In dielectric terms this corresponds to a distribution relaxation entities such as a distribution of the spatial dimensions of the nanocomposite microstructure. Establishing the correlation between microstructure and dielectric properties will be the main focus of our future research.

References

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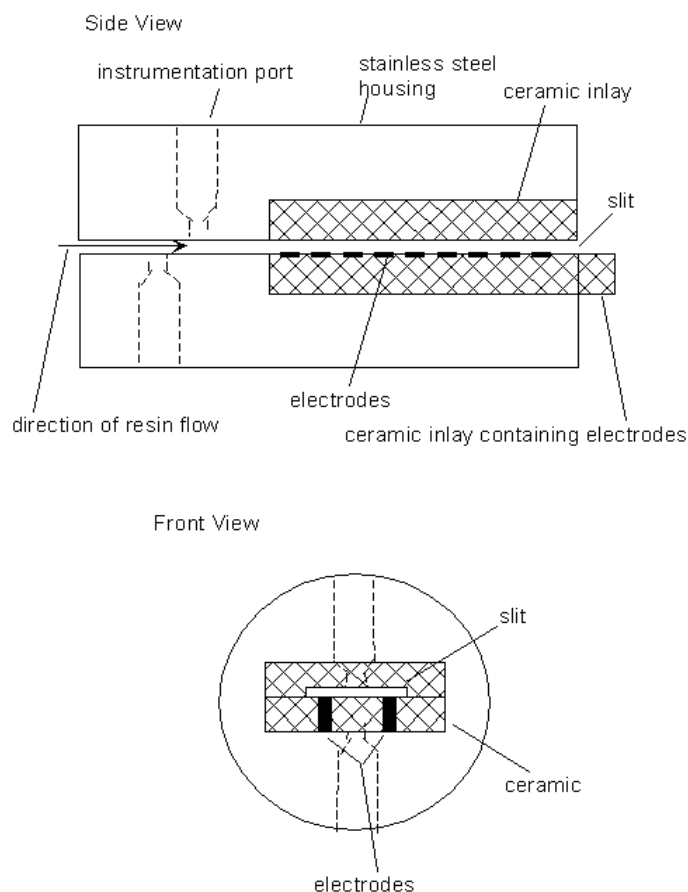6. R. H. Cole, J. Chem. Phys. **23**, 493 (1955).

Figure 1. A schematic diagram of the dielectric slit die is shown.

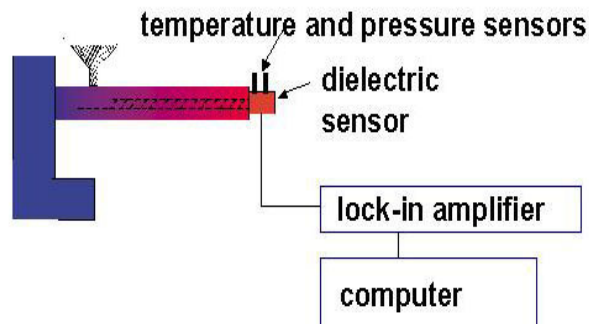

Figure 2. Dielectric slit die connected to extruder and lock-in amplifier.

Nylon 12 w 30B

nylon 12

y = -0.9893 x + 5.8984
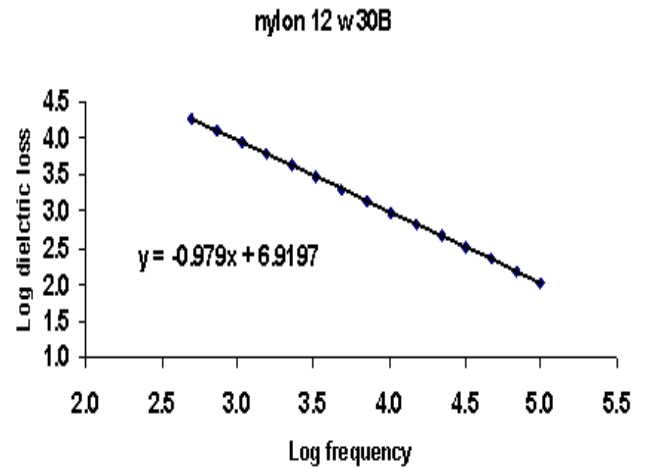
Nylon12 w 30B

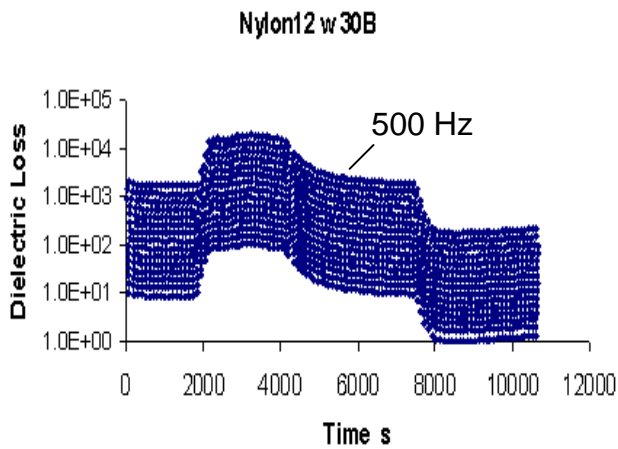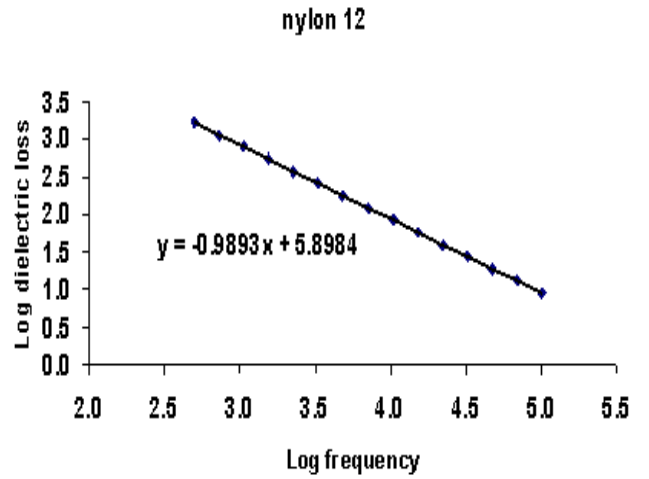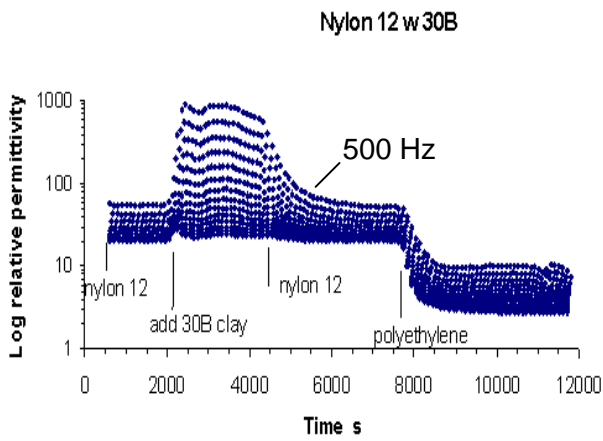nylon 12 w 30B

y = -0.979x + 6.9197

Figure 3. The relative permittivity (top) and the dielectric loss (bottom) are plotted versus time for nylon 12 and 30B clay compounding. Changes are noted in top plot. The lines are for constant frequency lines for 17 frequencies between 500 Hz and 10^5 Hz.

Figure 4. Log dielectric loss versus log frequency shows that the dielectric behavior is dominated by the DC conductivity.
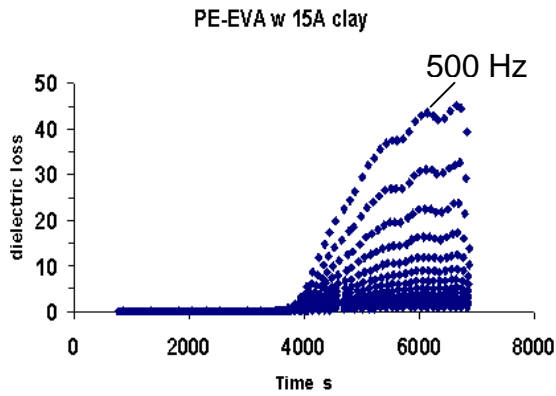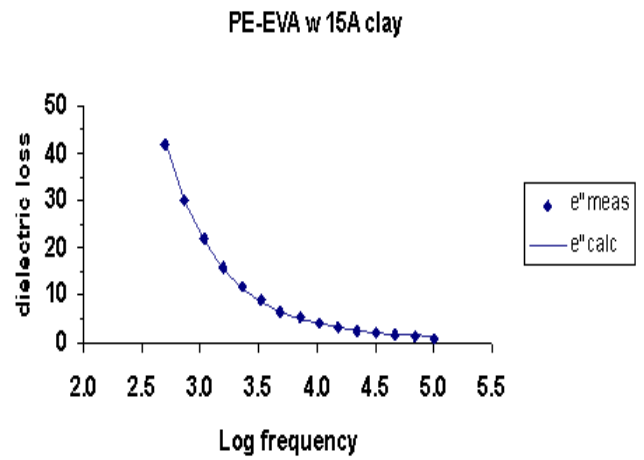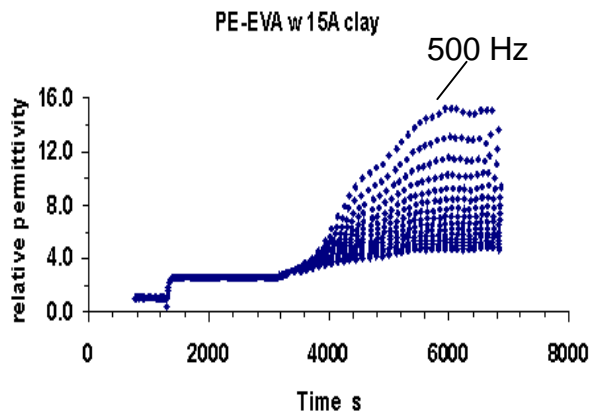
Figure 5. Relative permittivity (top) and dielectric loss (bottom) are plotted versus time for 15 frequencies between 500 Hz and 10^5 HZ. PE-EVA copolymer compounded with 15A clay.

Figure 6. Measured (points) and calculated (line) dielectric loss versus log frequency for PE-EVA compounded with 15A clay.