

REAL-TIME DIELECTRIC MEASUREMENTS DURING EXTRUSION OF FILLED POLYMERS

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Abstract

Mineral fillers are added to polymers to extend and modify physical properties, and their concentrations should be carefully controlled to obtain the desired end-use properties. To achieve this control, real-time measurements are very useful. Previous work has shown that in-line dielectric sensors can measure the concentrations of fillers in non-polar polymers. This work extends the measurements to polar polymers.

Introduction

Loss-in-weight feeders provide open-loop control, but variations in the consistency of the filler material and the conditions in the feeders can cause fluctuations in filler concentrations. For demanding applications, in-line measurements are desired for real-time quality monitoring and closed-loop control. Dielectric sensors are among the few in-line instruments that can measure chemical concentrations in opaque liquids. A previously reported [1], ring shaped sensors with interdigitated electrodes on their inside surfaces quantitatively determine filler concentrations in non-polar polymers. Accuracy increases with contrast in relative permittivity between the additive and primary material. This work reports and compares in-line dielectric measurement with filled and unfilled polar and non-polar polymers.

Theory

The relative permittivity ϵ of a non-polar polymer can be estimated by adding the empirically determined and literature tabulated contributions P_{LL} to the molar dielectric polarization from each of the chemical groups, e.g. $-\text{CH}_2-$ that comprise its monomer repeat unit [2].

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\sum_i P_{LL,i}}{V} \quad (1)$$

where V is the molar volume, which can be estimated by the van der Waals volumes of the molecular groups or calculated as a function of temperature and pressure from the polymer's equation of state [3]. The contributions P_{LL} represent only the dipole moments formed by nuclei and electrons within the small chemical groups. The relative permittivity of a mixture containing volume fraction ϕ_A of non-polar polymer A with relative permittivity ϵ_A and volume fraction ϕ_B of additive material B with relative permittivity ϵ_B is given approximately by, among others, the Landau-Lifshitz-Looyenga mixing rule [4]

$$\epsilon^{1/3} = f_A \epsilon_A^{1/3} + f_B \epsilon_B^{1/3} \quad (2)$$

To estimate accuracy in candidate applications, relative permittivities of polymers and additives can be measured, found in the literature, e.g. [5], or calculated using Equation (1). The precision of the determinations depends on the standard uncertainty of the relative permittivity measurements, which for the in-line analyzer is within 0.01, and the amount of contrast between the relative permittivities of the additive and polymer. In polar polymers like nylon, dipoles associated with larger segments of the molecules can orient in applied fields and increase the relative permittivity [6]. Dielectric relaxations are frequency and temperature dependent and provide revealing information about molecular structure. Polar polymers have higher conductivities and they can exhibit electrode polarization [7] at low frequencies. In this process, ions pile up at the electrodes in screening layers having characteristic thicknesses or Debye lengths $1/k$ approximately equal [8] to

$$\frac{1}{k} = \left(\frac{\epsilon_0 e k T}{\sum_i (z_i e)^2 c_i} \right)^{1/2} = \frac{\epsilon_0 e}{\Delta C / A} \quad (3)$$

where $\epsilon_0 = 8.854 * 10^{-12}$ F/m is the permittivity of free space, $k = 1.38 * 10^{-23}$ J / K is the Boltzmann constant, T is the temperature in Kelvin, z_i is the valency of the i^{th} species of ions, $e = 1.602 * 10^{-19}$ C is the electronic charge, c_i is the number of the i^{th} species ions per cubic meter, ΔC

is additional capacitance generated by the double layer and A is the electrode area. The middle expression is a result of the Gouy-Chapman theory, and the expression on the right is an approximation obtained by linearizing the Poisson-Boltzmann equation.

Equipment

A single in-line dielectric sensor, that was described in a previous paper, was used for the experiments presented here.[1] The sensor has a 45 mm ID by 38 mm long ceramic ring with no moving parts. On its inner surface are interdigitated electrodes that apply weak electric fields that fringe a few millimeters into the process materials. There are 27 finger pairs. Finger widths and spacings are 1.3 mm, and finger lengths are 29 mm. The effective area of each electrode is 10^{-3} m^2 . The sensor is encased in a steel housing and, for the work described here, it was installed at the exit of a 12 mm diameter Haake twin screw extruder. The transition from the 12 mm diameter flow stream exiting the extruder to the 45 mm ID of the sensor was facilitated using a 15.3 cm long adapter piece whose diameter expanded smoothly from 12 mm to 45 mm in a conical shape.

In early work, when the composition of the material in the extruder was changed, long delays were experienced before the sensor responded. It was reasoned that the new composition material followed the relatively higher velocity flow at the center of the conical adapter and sensor, only slowly renewing the material at the surface in the peripheral measurement annulus. To accelerate sensor response to composition change, a flow diversion bullet was installed in the center of the flow stream. The bullet's diameter was tapered to maintain a constant cross sectional flow area along the length of the conical adapter piece. In the sensor it had a constant 25 mm diameter and left a 10 mm radial flow gap between the outside of the bullet and the inside of the sensor.

The dielectric sensor assembly was temperature controlled and included melt temperature and pressure transducers. Remotely located instruments determined the relative permittivity and electrical conductivity of the process fluids at frequencies between 200 Hz and 100,000 Hz. Standard uncertainties in the measurements were: 0.01 for relative permittivity, 10^{-10} S/m for conductivity, 1 °C for temperature and 35 kPa (5 psi) for pressure. Polystyrene was Dow Styron 613 26 CLR W. Nylon 6 was Allied Signal Capron 8202. Alumina was Buehler 14.5 micron. Clays were Southern Clay Products Cloisite 15A and 30A nanoparticles of alkyl-quatarnary ammonium montmorillonite.^a

Procedures

Excitation voltage was 1.0 V. Relative permittivity and conductivity were measured at sixteen

point frequencies between 200 Hz and 100,000 Hz in continually repeating sweeps that took about two minutes each. Data was automatically archived in a database with time stamps. The addition of the flow diversion bullet increased the capacitance between the electrodes and ground, so the calculations were appropriately adjusted to correctly determine the sensor capacitance and resistance from the electrical measurements. Using an off-line test stand, the capacitance C of the sensor with the bullet was measured when it was filled with reference solvents of known permittivity and when it was empty, i.e. filled with air. This data was used to determine the sensitivity dC/de of the sensor. In air, the capacitance and resistance of the sensor were then measured over the full range of temperature and frequency for subsequent baseline calibration. The accuracy of the relative permittivity calibration procedure was verified by separate measurements with reference solvents, and the accuracy of the conductivity calibration procedure was checked by measurements with potassium chloride salts.

Polystyrene melts with and without 20 wt. % alumina powder were processed through the extruder (running at 1.0 revolution / s), the conical adapter and sensor at 180 °C and a mass flow rate of $1.18 * 10^{-3} \text{ kg / s}$. Nylon and clay fillers were dried at 100 °C under vacuum for at least an hour before use. Nylon melts with and without clay filler were processed through the extrusion equipment at 228 °C and more slowly at 0.67 revolutions / s and $4.7 * 10^{-4} \text{ kg / s}$. The volume fractions of solid fillers were controlled to within 0.2 % by manual weighing in small batches.

Results

In air, the relative permittivity measured 1.00 [Figure 1]. The relative permittivity of the unfilled molten polystyrene at 180 °C and 1 MPa measured about 2.6 over the full frequency range [Figure 3]. The relative permittivity of the polystyrene increased when the filler was added [Figure 1]. The increase was very slow, however, with the signal still not fully steadied after 6000 s (100 minutes) with the new material. The conductivity increased slightly when the filler was introduced, but for both filled and unfilled polystyrene the conductivity was very low; everywhere less than 10^{-6} S / m . Unfilled polystyrene was added and the relative permittivity began dropping, but again the rate of change was slow.

In an initial, exploratory experiment, nylon 6 was extruded over the range of temperatures from 228 °C to 275 °C. Over this range, the permittivities were approximately constant and conductivities fell slightly as the temperature was reduced. Subsequent experiments with nylon were run at 228 °C, at which temperature the measured relative permittivity [Figures 5 and 7] of unfilled molten nylon was 90 at 100 KHz. The relative permittivity of the unfilled nylon increased with

decreasing frequency to 7000 at 200 Hz. The capacitance difference between high and low frequencies was 3×10^{-8} F. When clay filler was added, the relative permittivity and conductivity went down dramatically and promptly, in contrast to our observation with PS filled with alumina. As the feed material was alternately switched between filled and unfilled nylon, the measured relative permittivity and conductivity changed and stabilized to repeatable new readings in approximately 40 minutes.

Analysis

The measured relative permittivity of the non-polar polystyrene melt (2.6) was slightly above but reasonably close to the prediction (2.5) from Equation 1. When the filler was added, the relative permittivity increased in accordance with Equation 3. The slow transitions between readings with filled and unfilled polystyrene were likely due to the large system volume and surface area.

In the more polar nylon melts, even at the highest frequencies, the relative permittivity was much higher ($\epsilon = 90$ at 100 KHz) than the prediction (about 4.1) from Equation 1. It is well known that dipoles associated with hydrogen bonding likely that molecular relaxations contributed to the large high frequency permittivity. The relative permittivity was even larger at low frequencies, increasing to $\epsilon = 7000$ at 200 Hz. The conductivity was more than two orders of magnitude greater than that of the polystyrenes, reaching as high as 8×10^{-4} S/m. These high values of permittivity and conductivity suggest that mobile ions are contributing to interfacial polarization that significantly enhance the dielectric constant at both low and high frequencies. Considering the high temperature of the measurements, 228 °C, which is well above the melting temperature (165 °C), it is not surprising that high conductivity is observed for this medium because its relatively low viscosity permits increased ion mobility.

At the low frequencies, the high conductivity and the apparent extremely high relative permittivity suggest that electrode polarization was occurring. Equation 3 can be used to estimate the thickness of the charge layer associated with such an electrode polarization. Using for the relative permittivity the lowest, high frequency value and for the difference in capacitance the measured capacitance variation between low and high frequency, Equation 3 gives a Debye length of 2.6×10^{-5} m. Only minor variations in relative permittivity were observed as the temperature was varied from 228 °C to 275 °C. Equation 3 indicates that this temperature variation would cause a 4.5% change in screening length and capacitance increment.

The addition of a relatively small amount of clay substantially, consistently and promptly decreased the relative permittivity and conductivity. The transitions

between materials were much quicker with nylon/clay than with polystyrene/alumina, even though the extrusion rate was lower with nylon. The data indicate that clay particulate migrates to the surface faster than does alumina in the PS.

Conclusions

As demonstrated elsewhere with other non-polar polymers, Equations 1 and 2 are reliable for polystyrene and its compounds and the in-line dielectric analyzer is generally useful for measuring filler concentrations in non-polar polymers. With nylon, a polar polymer, electrode polarization occurs at low frequencies. Fortunately the temperature dependence of the electrode polarization is minor by calculation and experiment and the process can be avoided by working at high frequencies. The addition of a relatively small amount of filler causes large, repeatable changes in relative permittivity and electrical conductivity. Dielectric measurements may also be useful for measuring filler concentrations in polar polymers.

^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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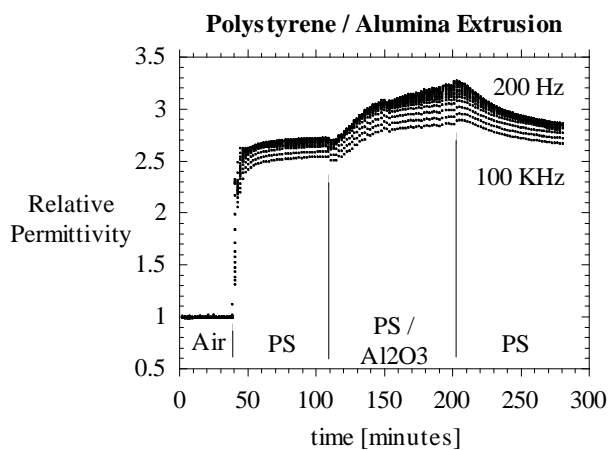


Figure 1. Relative permittivity vs. time measured with the in-line dielectric sensor as polystyrene melts with and without 20 wt. % alumina were processed through the system at 180 °C.

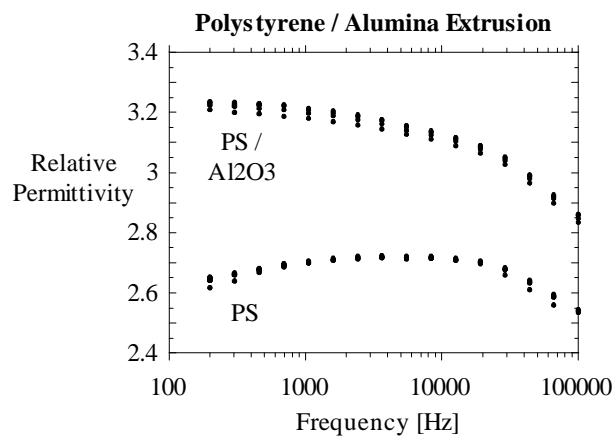


Figure 3. Relative permittivity vs. frequency measured with the in-line dielectric sensor as polystyrene melts with and without 20 wt. % alumina were processed through the system at 180 °C.

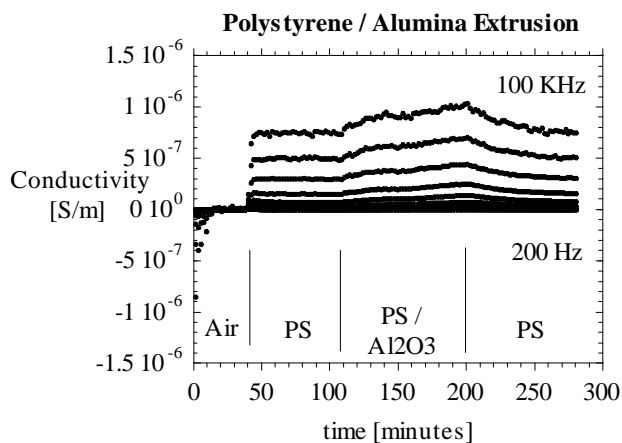


Figure 2. Conductivity vs. time measured with the in-line dielectric sensor as polystyrene melts with and without 20 wt. % alumina were processed through the system at 180 °C.

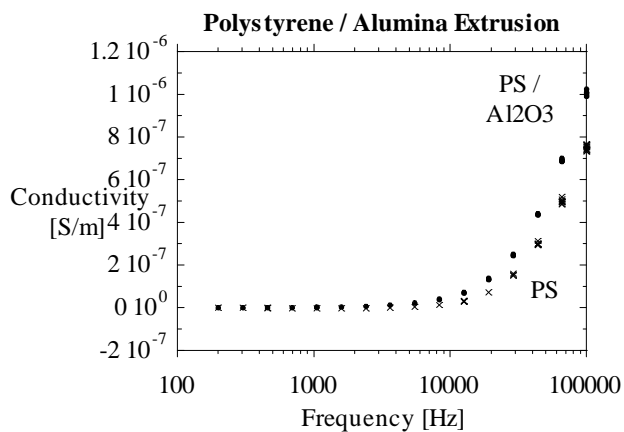


Figure 4. Conductivity vs. frequency measured with the in-line dielectric sensor as polystyrene melts with and without 20 wt. % alumina were processed through the system at 180 °C.

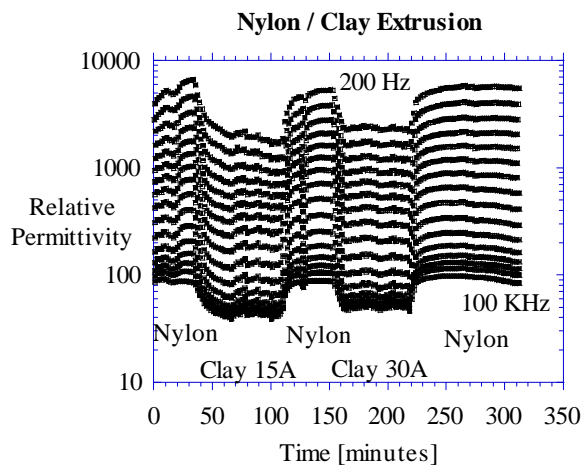


Figure 5. Relative permittivity vs. time measured with the in-line dielectric sensor as nylon 6 melts with and without 5 wt. % clay additives were processed through the system at 228 °C.

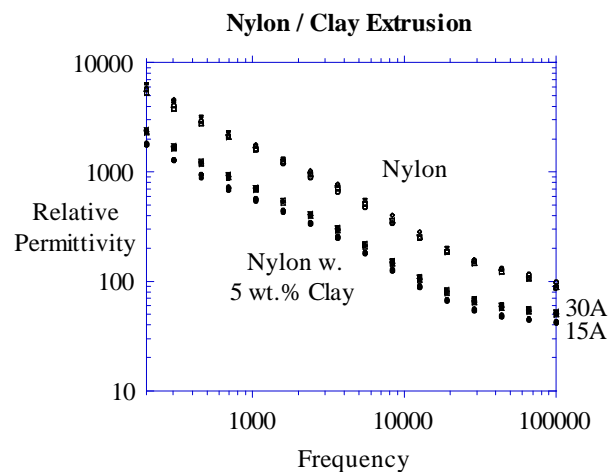


Figure 7. Relative permittivity vs. frequency measured with the in-line dielectric sensor as nylon 6 melts with and without 5 wt. % clay additives were processed through the system at 228 °C.

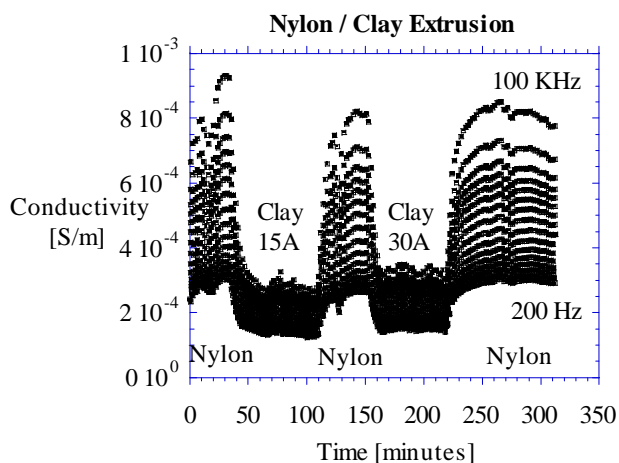


Figure 6. Electrical conductivity vs. time measured with the in-line dielectric sensor as nylon 6 melts with and without 5 wt. % clay additives were processed through the system at 228 °C.

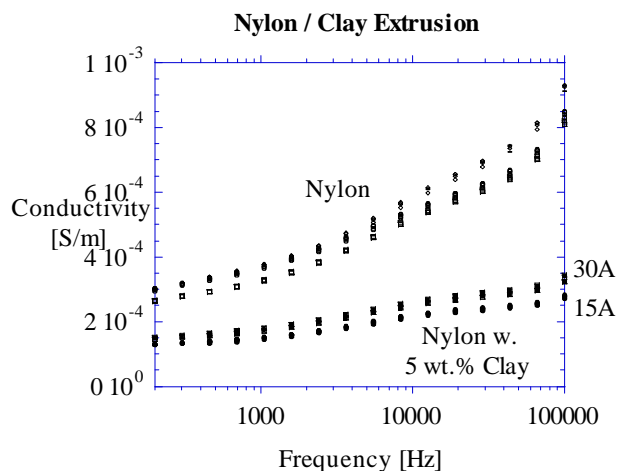


Figure 8. Electrical conductivity vs. frequency measured with the in-line dielectric sensor as nylon 6 melts with and without 5 wt. % clay additives were processed through the system at 228 °C.

Keywords: dielectric, sensor, in-line, analyzer