IN-LINE DIELECTRIC SENSOR FOR CHEMICAL COMPOSITION MEASUREMENTS IN MOLTEN POLYMERS

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Abstract

Resin producers and compounders use additives to extend and modify the properties of their polymers, and they increasingly use rugged dielectric sensors to measure additive concentrations in-line for automatic process control and quality monitoring. They need to control the concentrations of the additives they use as processing aids and to modify properties in plastics, elastomers, fibers, adhesives and coatings. This helps them meet demanding product quality specifications and ensure strong prices and market shares. Theory and experiments described here indicate that dielectric measurements in melts can quantitatively determine individual or total additive concentrations with an accuracy that depends on electrical contrast and can exceed 0.1 volume percent (1000 ppm) with polymers and compounds having one or possibly two dominant additives. In-line measurements of additive concentration facilitate automatic process control, which helps maintain product quality and manufacturing efficiency. In multi-component mixtures the measurements indicate on-aim conditions, provide automatic quality monitoring and accelerate transitions.

Introduction

Today's resin producers and compounders need to satisfy demanding product quality specifications within runs, from lot to lot, and from site to site to maintain profitable prices and market share. They also need to deliver a broad range of products on tight schedules, so they need to change their manufacturing operations often and quickly. Maintaining quality with frequent transitions is a significant challenge. Material producers use additives as processing aids and to extend and modify the properties of their polymers. They receive or prepare the additives in solid or liquid carriers, often as masterbatches containing multiple additives, and dose the carriers into the polymers. Additives significantly affect important end-use properties of the materials. To meet quality specifications, makers of resins and compounds need to control the concentrations of additives. With insufficient additives the full effects are not realized, and with excess additives other undesirable properties can result. Additive concentrations can fluctuate in response

to disturbances in either the carrier preparation or the dosing process. The concentrations of additives are key process variables that should be carefully controlled to obtain the desired product properties.

Permittivity (dielectric constant) measurements in melts quantitatively determine individual or total additive concentrations with polymers and compounds that can be treated as two component mixtures. This includes multi-component resins and compounds in which one additive dominates in concentration or permittivity contrast, and materials with additives or primary materials that are by themselves mixtures (such as masterbatches or co-polymers). Procedures are given for predicting the precision of the method in prospective applications. Accuracy increases with contrast in permittivity between the additive and primary material. Work in progress extends the method to three-component mixtures. In-line measurements of additive concentration facilitate automatic process control, which helps maintain product quality and manufacturing efficiency. Electrical measurements can also be used for automatic quality monitoring, even in multi-component mixtures. The electrical properties of a given desired product have specific values, and in-line measurements can verify onaim operation and help achieve quicker product transitions. Dielectric measurement can facilitate process control and quality monitoring to improve product quality and maximize manufacturing efficiency.

Theory

The permittivity ε of a 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. -CH₂that comprise its monomer repeat unit [1].

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\sum_{i} P_{LL,i}}{V}$$

(1)

where V is the molar volume and can be calculated as a function of temperature and pressure from the polymer's equation of state [2]. Mathematically equivalent to Equation 1 is the Clausius-Mossotti mixing rule,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \phi_A \frac{\varepsilon_A - 1}{\varepsilon_A + 2} + \phi_B \frac{\varepsilon_B - 1}{\varepsilon_B + 2}$$
(2)

which gives the permittivity of a homogeneous mixture containing volume fraction ϕ_A of primary material A with permittivity ε_A and volume fraction ϕ_B of additive material B with permittivity ε_B . Like Equation 2, the Landau-Lifshitz-Looyenga mixing rule

$$\varepsilon^{1/3} = \phi_A \varepsilon_A^{1/3} + \phi_B \varepsilon_B^{1/3}$$
⁽³⁾

and others [3] involve mixing by volume fraction of functions of permittivity. For any such function $f(\varepsilon)$, the concentration of additive can be determined from in-line permittivity measurements as

$$\phi_{B} = \frac{f(\varepsilon) - f(\varepsilon_{A})}{f(\varepsilon_{B}) - f(\varepsilon_{A})}$$
(4)

To estimate accuracy in candidate applications, permittivities of polymers and additives can be measured, found in the literature, e.g. [4], or calculated using Equation (1). The precision of the determinations, expressed as an uncertainty +/- $\Delta \varphi_B$, depends on the uncertainty $\Delta \epsilon$ of the permittivity measurements (which for the in-line analyzer is within 0.01) and the magnitude of the contrast between the permittivity functions of the additive and primary materials:

$$\Delta \phi_{B} = \frac{1}{\left| f(\varepsilon_{B}) - f(\varepsilon_{A}) \right|} \frac{df}{d\varepsilon} \Big|_{\varepsilon_{A}} \Delta \varepsilon$$
(5)

Work is underway to extend the determinations to threecomponent mixtures. In some materials [3], conductivity mixes by volume fraction according to the "refractive index" mixing rule

$$\sigma^{1/3} = \phi_A \sigma_A^{1/2} + \phi_B \sigma_B^{1/2}$$
(6)

The present authors have determined individual concentrations of methanol, isopropanol and water in three-component mixtures using simultaneous solutions of Equation (6) and various mixing rules for permittivity including Equation (3).

Equipment

The in-line dielectric sensor [1] is a ceramic ring (Figure 1) with electrodes on its inner surface. Process fluid flows through the sensor, which applies weak alternating electric fields that extend deeply even into opaque materials, avoiding surface fouling and stagnation problems. The sensor fits between two steel housing pieces to form a flow-through assembly (Figure 2) with no moving parts or flow diversions. The assembly attaches easily to various types of melt processing equipment; in extruders it typically attaches just beyond the screw(s) and before the die piece (Figure 3). The dielectric sensor assembly is temperature controlled and includes melt temperature and pressure transducers. Similar sensors can be made with inside diameters ranging from 13 mm to 300 mm. Remotely located instruments determine the permittivity and electrical conductivity of the process fluids at frequencies typically between 500 Hz and 100,000 Hz. Ethylene - vinyl acetate was from DuPont. Polyethylene and polystyrene were from Dow. Calcium carbonate (Acros) is an inexpensive mineral antiblocking agent that reduces sticking between film layers, and common filler that adds mechanical stiffness and lowers moisture permeability. Alumina (EM Scientific) is another widely used mineral filler that improves physical properties and increases thermal conductivity.

Procedures

Sensors were calibrated with air. The accuracy of the 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. Sensors were attached to extruders processing different ethylene copolymers and polyethylene and polystyrene melts containing graduated concentrations of calcium carbonate and alumina powder. Permittivity and conductivity were repeatedly measured at thirteen frequencies between 500Hz and 100,000 Hz. Temperature and pressure were measured, and data was automatically archived in a database with time stamps.

Results

Measured permittivities of non-compounded PE and PS melts were consistent with Equation 1. The measured permittivity of molten polystyrene at 180 C and 10 bar was 2.51 over the full frequency range. The permittivities of ethylene copolymers increased with vinyl acetate concentration (Figure 4), the permittivities of the polystyrene compounds increased with filler concentration (Figure 5), and all data sets correlated well with Equation 2 but gave coefficients that overestimated the permittivities of the pure mineral fillers. Equation 3 correlated equally well (e.g. Figure 6) and gave permittivities for the pure additives in approximate agreement with published values (e.g. Figure 7). The precision of the composition determinations was consistent with the uncertainty formula in Equation 5 and its graphical representation in Figure 8. For alumina in polystyrene, the formula indicates better than 0.5 volume % uncertainty, and Figure 6 shows that in the experiments 0.4 % was achieved.

Analysis

Simple functions of permittivity varied linearly with additive concentration in these co-polymers and compounds, consistent with mixing Equations (2) and (3). The numerical values of coefficients that best fit the latter equation agreed with the known permittivities of the components. The 0.4% accuracy of the experiments was consistent with Equation 5 and Figure 8, which indicate that the precision of the measurements increases with the amount of contrast between the permittivities of the additives and the other materials. Successive measurements at a single frequency once every two seconds could be averaged over three minutes to yield nearly one hundred measurements, reducing the uncertainty by a factor of ten. Quantitative measurements of additive concentration and real-time verification of product quality should benefit resin producers, compounders, molders and extruders.

Conclusions

In-line dielectric sensors successfully measured the concentrations of these typical fillers and comonomers, so they could likely measure other additives and fillers in other polymers and copolymers during processing. The feasibility of a prospective application can be determined by calculating the measurement precision from Equation 5 and comparing to the requirements of the application. Alternately, Figure 8 can be used. The figure shows contours of constant uncertainty calculated from Equation 5 on a plot of additive permittivity versus primary material permittivity. The permittivites of the materials are used to locate an operating point, and the labeled zones are used to read off the accuracy. If the indicated resolution meets the application requirements, then dielectric measurements can be effectively used for in-line composition determinations. With these measurements, resin producers and compounders can implement automatic process control of concentrations. Composition control ensures accurate additive concentrations and enables producers to satisfy demanding product quality specifications. It also helps maintain and strengthen prices and market share. Composition control promptly corrects for any process disturbances and thereby reduces vield losses. Automatic composition control also allows less frequent lab testing, thereby reducing production expenses, safety hazards and environmental impact. Even in multi-component mixtures and compounds, the electrical properties and concentrations of the ingredients control the frequency dependent permittivity and conductivity signatures of the mixtures. Therefore electrical measurements can be used for on-aim verification to set alarms if product quality deviates and to accelerate product transitions. Resin producers and compounders use additives to extend and modify the properties of their polymers, and dielectric sensors enable them to measure additive concentrations in-line for automatic process control and quality monitoring.

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Keywords: dielectric, permittivity, sensor, analyzer, inline, polymer, compound, copolymer, melt, additive, filler, composition





Figure 1. Photograph of an in-line dielectric sensor, showing the flow passage and the interdigitated electrodes on its inside surface.

Figure 3. Photograph of an in-line sensor in its housing, surrounded by a band heater and attached to an extruder.



Figure 2. Cross section view showing an in-line dielectric sensor installed in its two piece steel housing which forms a flow-through assembly which bolts onto extruders or into transfer lines.



Figure 4. Permittivity vs. time measured with the in-line dielectric sensor as various ethylene copolymers with different concentrations of vinyl acetate were processed through the extruder.



Figure 5. Permittivity vs. time measured with the in-line dielectric sensor as polystyrene melts with increasing levels of alumina were processed through the extruder. The system was drained between successive materials.



Figure 7. Experimental data (dots) and best fit to Equation 3. The point at 100% CaCO₃ is a literature value included here to illustrate the numerical accuracy of the fit coefficients.



Figure 8. To estimate precision in a prospective application, locate a point horizontally at the permittivity of the primary material and vertically at the permittivity of the additive, then read the accuracy from Figure 8.



Figure 6. Experimental data (dots) and best fit to Equation 3. Fit parameters: $e_PS = 2.53$ (cf. 2.51) and $e_Al2O3 = 9.01$ (cf. 11). RMS error in $e^{(1/3)} = .003$ RMS error in volume fraction estimates = .004.