High Throughput Methods For Rapidly Developing Additive Filled Polymers

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Introduction

The high throughput (HT) concept began with Hanak and coworkers at RCA Corporation in the early 1970s.[1] Specific to the point of these first high throughput papers was the rapid processing methods for sample preparation, characterization methods, and inherent greater efficiency of Hanak's "multiple-sample concept".[2] Today the sample architecture described by Hanak is referred to as "composition-spread" or "gradient" composition.

In BFRL, we are simultaneously utilizing three approaches to develop rapid polymer compounding, characterization, and analysis methods. One approach is to increase the efficiency of a technique. Often experiments are still sequential, but the time required to complete a material set significantly decreases. For example, compounding a gradient of additive concentrations rather than multiple single compositions decreases the compounding time by three or four fold. Another approach is to conduct measurement methods in parallel rather than in series. For example, simultaneously compounding and measuring polymer microstructure combines synthesis and characterization in a single experiment. The last approach is to automate experiments. This is similar to the idea of conducting experiments in parallel because while an instrument is taking measurements on a material set the operator can run other experiments on the same matrix of samples. All of these approaches significantly increases the volume of data, however, data is not the final goal. The final goal is to strive for the opportunity to more completely explore the infinite number of permutations and combinations of research ideas, with the ultimate output being the rapid generation of useful knowledge.

The purpose of this document, and presentation, is to briefly discuss how we are applying a HT approach to rapidly generate knowledge about additive filled polymers; informatics is not discussed. The techniques presented are gradient extrusion, in-line (with the extruder) dielectric and optic sensors and Flooring Radiant Panel flammability tests.

Experimental[a,b]

Extrusion and In-Line Sensors

Compounding of additive filled polymers is performed in a B and P Processing twin-screw extruder (co-rotating, intermeshing, 25:1 L:D, 145.7 radians/s to 47.1 radian/s (150 rpm to 500 rpm)) (Figure 1). Polymer pellets and powder additives are gravimetrically fed using three Brabender Mass Loss feeders. The feeder discharge rate is dependent on material density, and therefore varies significantly. In general, the total compounded polymer output is between 2.0 kg/h to 3.0 kg/h, however, the system can be operated between 1.0 kg/h to 10 kg/h. At normal operating conditions (36.6 radian/s (350 rpm), 2.5 kg/h) the residence time is 90 s and residence sample length is 1.5 m long (3.2 cm x 0.2 cm, width by thickness).

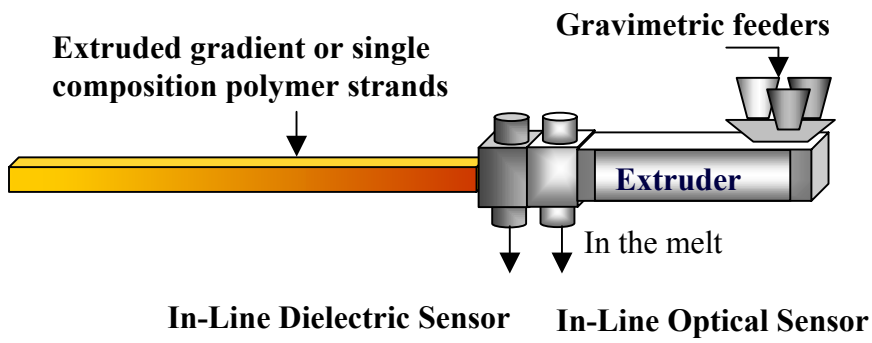

Figure 1. Illustration of a twin–screw extruder with in-line sensors.

Gradient additive compositions were produced by turning on or off the additive discharging gravimetric feeder (add-feeder). Gradients are generated because the add-feeders do not immediately reach their set discharge rate. Compositional "up gradients" are generated when the add-feeder is turned on, which results in gradients from 0 % mass fraction to a programmed value. Compositional "down gradients" are generated when the add-feeder is turned off, producing gradients from a programmed value to 0 % mass fraction. The length of a gradient and length of time to produce a gradient is approximately equal to the residence length and time. The length and time will vary based on processing conditions and the programmed add-feeder value. For example, decreasing the residence time will stretch out the gradient because the time it takes the add-feeder to reach its programmed value is independent of the processing conditions.

A heated cell attached at the end of the extruder houses the optic and dielectric sensors (Figure 1); this multipurpose sensing device is manufactured by Chemical

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[a] 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. In addition, NIST is not liable for the accuracy of the results from experiments not conducted at NIST.

[b] The policy of the National Institute of Standards and Technology (NIST) is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document, however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

ElectroPhysics.[3] The sensors provide information about the polymer microstructure during polymer/additive compounding. The cell also contains a melt flow thermocouple and pressure transducer; therefore, the cell can be used to measure apparent viscosity. (Minimal information about the cell design is provided due to pending patents.)

The optic sensor provides, in real-time, information about additive content, dispersion and distribution. A schematic of the optic sensor is provided in Figure 2. A bandpass filter narrows the incident whitelight frequency to 632 nm. A portion of the light is continuously monitored by a reference photomultiplier tube detector (PMT) and the remaining light travels through the polymer melt, reflects off the opposing side of the sensor housing, and the reflected photon counts are measured by another PMT. Photon counts are measured every 1 s and represent an average of 10 values over that 1 s.

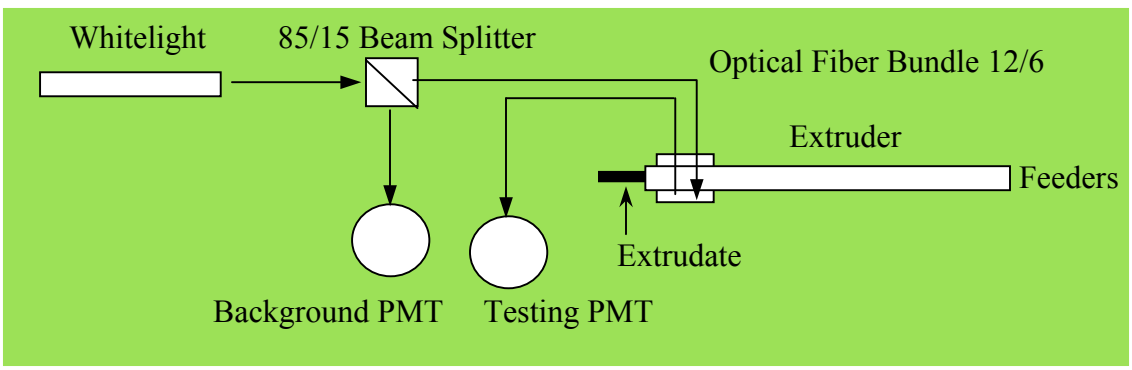

Figure 2. Schematic of in-line optic sensor set-up.

The dielectric sensor provides information about the dynamics of molecular relaxation processes, which are associated with polymer/additive microstructure and additive concentration.[4] Currently, we are taking a conventional dielectric spectroscopy approach to measuring polymer dielectric properties and to interpreting the data. This includes measuring permittivity (ε') and dielectric loss (ε") at 15 frequency values over a frequency sweep of 500 Hz to 10^5 Hz. A single frequency sweep takes approximately 90 s, thus the current dielectric sensor methodology is designed for single composition compounding only. From the frequency sweep, values of relaxation variables characteristic of the polarized moieties in the dielectric are determined by curve fitting the experimentally measured ε" with the Cole Arc Dispersion Function (Figure 3).[4] These characteristic values can be graphically presented using a Cole-Cole plot (Figure 4). Initial experiments indicate that the Δε value is dependent on additive content, dispersion and distribution. Since the Δε value is determined from post processing curve fitting, the dielectric sensor is not currently a real-time measurement device.

$$\varepsilon'' = \frac{\sigma_{DC}}{\omega\varepsilon_o} + \frac{1}{2}\left(\varepsilon_0 - \varepsilon_\infty\right) \times \left[\frac{\cos\left(\frac{\pi}{2}\alpha\right)}{\cosh\left(\left(1-\alpha\right)\ln\left(\omega/\omega_0\right)\right) + \sin\left(\frac{\pi}{2}\alpha\right)} \right]$$

Figure 3. Curve fitting portion of the Arc Dispersion Equation

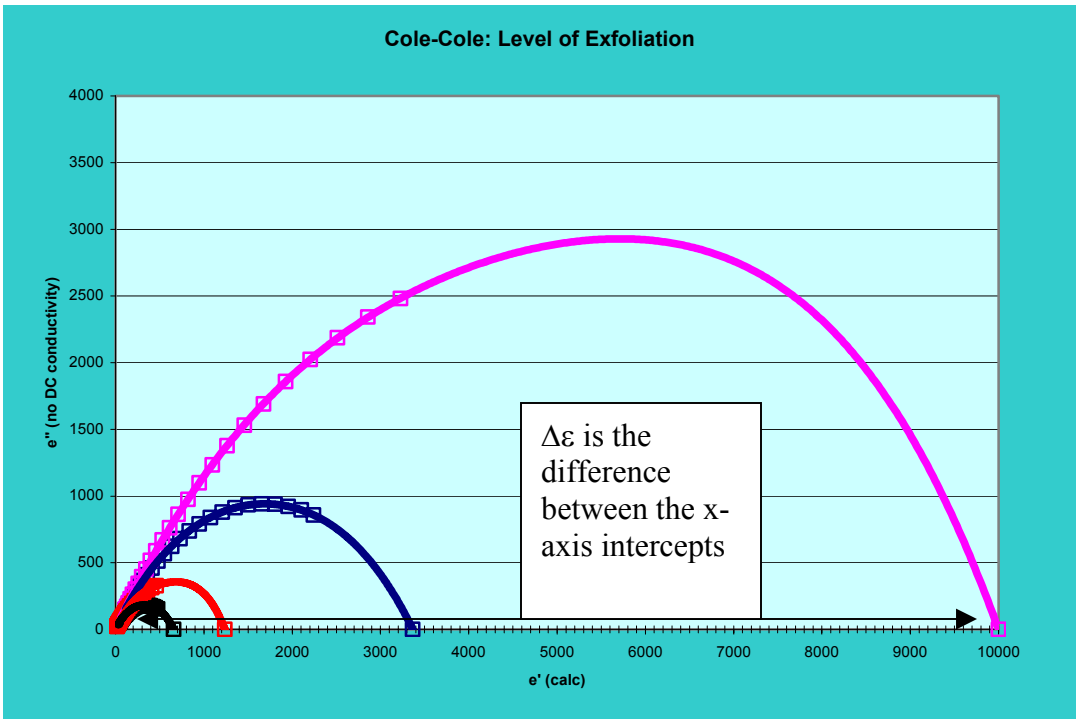

Figure 4. An example of a Cole-Cole plot, which graphically represents characteristic dielectric relaxation variables

The following filled polymers will be discussed in reference to the high throughput projects.

- Polystyrene was compounded with 1) ammonium polyphosphate (APP) and pentaerythritol (PER) (APP/PER-PS), 2) Cloisite 15A[5] (15A-PS), and 3) various concentrations of both additives (15A-APP/PER-PS). The processing conditions were 36.6 radians/s (350 rpm), 2.5 kg/h and barrel temperature zones were all set at 190 °C. A UL-94[6] V0 rating is achieved with 29 % mass fraction of a 3:1 APP/PER loading.[7] The purpose of this project was to determine the optimal relative 15A and APP/PER concentration that would give V0 behavior with keeping the total additive content below 30 % mass fraction.[8]
- Polyamide-6 was compounded with Cloisite 30B[9] (30B-PA6) and Cloisite 20A[5] (20A-PA6) at 350 rpm, 2.5 kg/h and all barrel temperature zones were set at 250 °C. Two in-situ polymerized organically modified-MMT-PA6 nanocomposites (is-MMT-PA6) were provided from a commercial source (the same source that provided the virgin PA-6) and were extruded at the same conditions as the melt compounded nanocomposites. These nanocomposites were used to explore a possible relationship between the data generated from in-line extruder sensors and the amount of om-clay, the degree of om-clay dispersion, and the level of om-clay distribution.
- Polypropylene with various POSS compounds were melt mixed at 350 rpm, 2.5 kg/h, and all barrel temperature zones set for 240 °C. The purpose was to

determine which POSS compounds improved the flammability and mechanical properties of PP and what were the optimal POSS concentrations.

Flammability Testing

Two flammability testing methods are being developed using the Flooring Radiant Panel[10] (Figure 5): 1) measuring the minimum flux needed for a flame to spread across a material and 2) measuring the velocity of a flame spreading across a material (Figure 6).

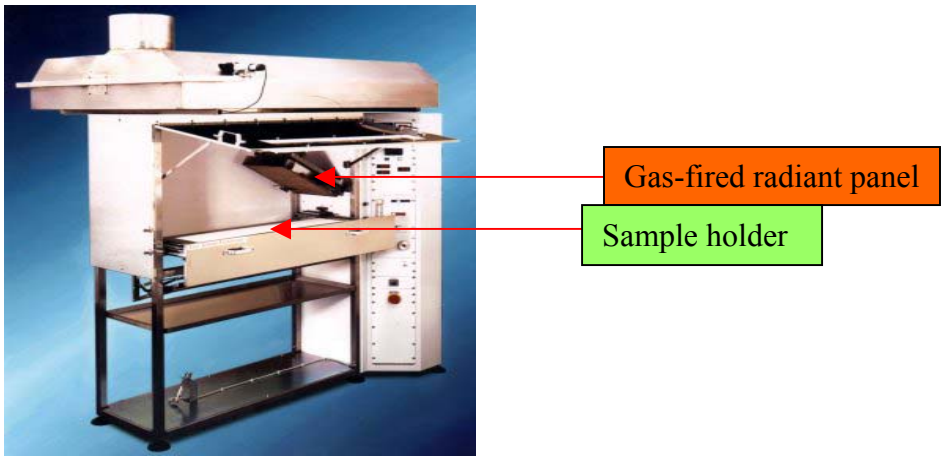

Figure 5. Flooring Radiant Panel

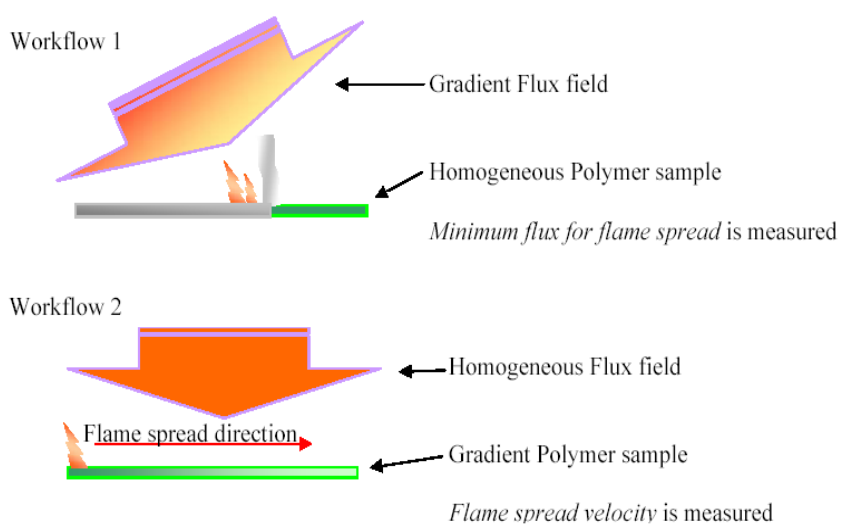

Figure 6. An illustration of the two different flame spread approaches: one where the sample is homogenous and the flux field has a gradient intensity (Workflow 1), and the other utilizing a compositional gradient within the sample and a homogenous flux field (Workflow 2).

Workflow 1-Gradient Heat Flux and Constant Composition

The purpose of this experiment is to measure the minimum external flux needed to self sustain burning of polymeric materials, minimum flux for flame spread (MFFS). The gradient flux provides a high throughput opportunity to determine in one experiment

what the MFFS for a single additive/polymer concentration over a range of heat fluxes. A non-high throughput approach is to independently measure each additive concentration at each of the heat flux values.

The Floor Radiant Panel (FRP) is shown is Figure 5 and Figure 7. A gas burner panel can be horizontal to the ceramic sample holder, creating a constant heat flux over the entire sample, or positioned at an angle, creating a gradient heat flux over the sample. The sample is always ignited at the highest heat flux end. For the constant composition PS samples, the heat flux was 25 $kW/m^2 \pm 0.5$ kW/m^2 at the ignition site and the samples burned like a candlewick toward the low flux end (2 kW/m^2 at approximately 75 cm from ignition site). When the external source was insufficient to maintain polymer burning the flame extinguished. This heat flux is the MFFS for that polymer composition. The higher the heat flux when the polymer self extinguishes, the higher the MFFS, and therefore the polymer is considered more flame resistant.

Figure 7. FRP used for measuring MFFS. Notice that the panel is angled to create a gradient flux and the samples are ignited at the highest flux end. The samples burn like a wick away from the igniter.

Workflow 2-Constant Heat Flux and Gradient Composition

The purpose of this experiment is to measure the rate of flame spread across a polymer sample. Higher flame velocities indicate lower flame resistance; i.e., the propensity for a fire to spread to other portions of a room, for example. The radiation panel of the FRP is aligned horizontal to a gradient composition sample. For the gradient composition filled PS samples the heat flux was set at 19 kw/m^2 and the gradient sample was generally 1.5 m to 2.5 m in length. The sample was ignited and feed into the FRP using a conveyer belt. The sample feeding velocity was altered to keep the flame in the same position. The velocity of the sample feeding is a direct measure of flame velocity. In other words, the faster the flame spreads the faster the sample is fed into the FRP.

Results and Discussion

Gradient Extrusion and In-Line Sensors

In one workday we compounded 13 different compositions strands of a POSS-ABS, POSS-PP, and POSS-(FR)PP (flame retarded, FR). The strands were standard POSS-polymer compositions (0 % mass fraction and 9 % mass fraction), and gradients (0 % mass fraction to 9 % mass fraction). Gradients were generated by turning on or off the add-feeder. If we assume we can dstinguish between 1 % mass fraction additive content, then each gradient strand contains 9 different compositions. Therefore at least 30 compositionally different materials were compounded.

We were able to follow the generation of gradient compositions using the optic sensor (Figure 8). The test photon signal normalized to the background photon signal (T/B) increases as additive content increases. A T/B value of 0.216 is the virgin PP and 0.236 is nearly 9 % mass fraction POSS filled PP. A POSS-PP gradient was generated in approximately 170 s (strand length is 1.5 m). The up and down gradients appear to have similar composition profile (Figure 8). By increasing the rpm value we can increase the length of the sample composition gradient to 2.5 m in approximately the same amount of time. Automated TGA (Figure 9) of a 2.5 m gradient strand compounded in 200 s, performed after extrusion, shows the down gradient is steeper than the up gradient. The gradient sample characterized by TGA (Figure 9) and the gradient sample represented by the third optical up and down peak (Figure 9) is the same PP/POSS gradient sample.

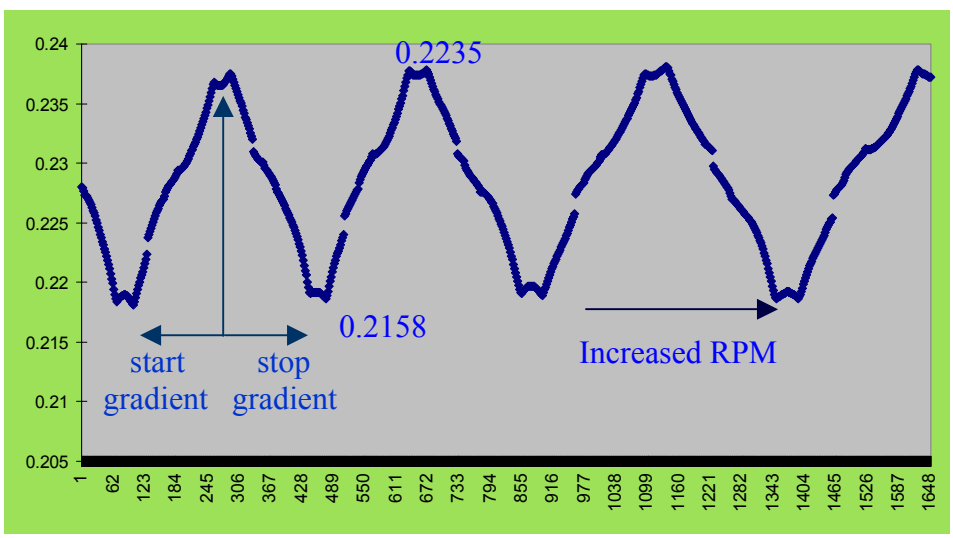

Figure 8. Optic sensor of PP with gradient concentrations of polyvinyl-POSS (0 % mass fraction to 9 % mass fraction). Gradients produced by turning on and off the POSS feeder. Y-axis = T/B and X-axis = time (s).

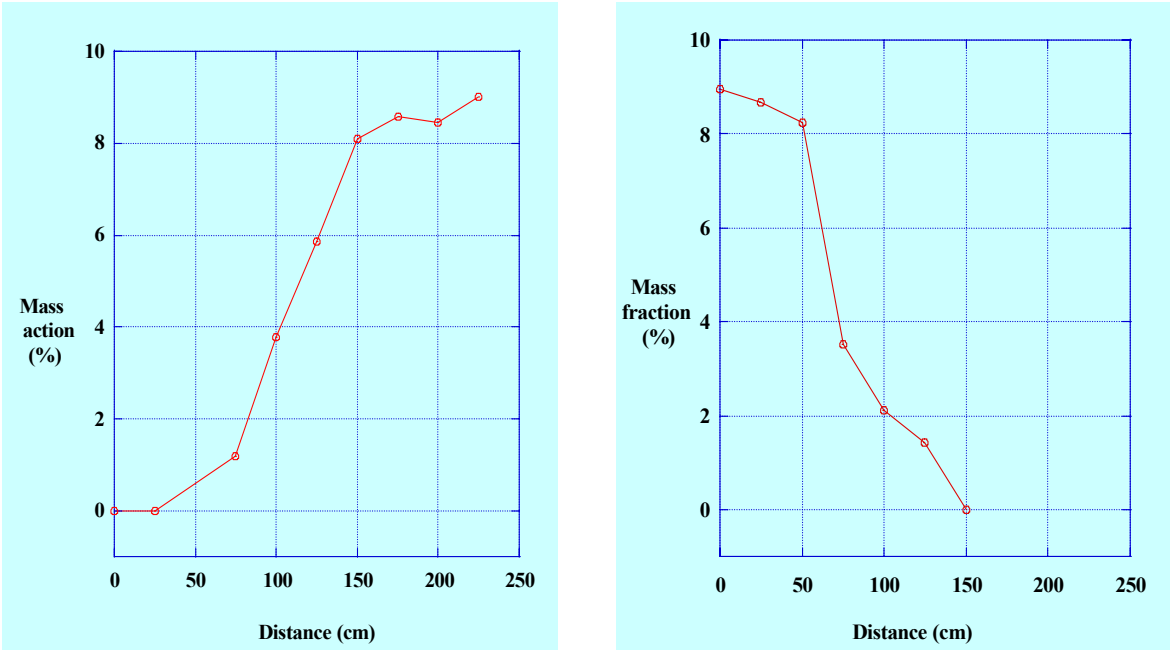

Figure 9. Gradients of POSS in PP generated by turning on and off the POSS feeder. TGA residual yields in air are used to determine the amount of POSS in PP relative to the extrudate position.

Two real-time analytical techniques are being developed to monitor additive content and degree of mixing during melt compounding with polymers in an extruder, dielectric and optic sensors. As these methods are developed the sensor results are continuously compared to conventional off-line techniques, such as TEM. Provided below are the comparisons of conventional technique results and real-time sensors results for om-clay/PA-6 nanocomposites.

Transmission electron microscopy revealed very important relationships between the PA-6 nanocomposites.

- is-MMT-PA6 was highly delaminated (dispersed) and homogeneously mixed (well dispersed)
- 30B-PA6 and 20A-PA6 are both well delaminated, however, is-MMT-PA6 is better delaminated and 30B-PA6 is better than 20A-PA6 (is-MMT >> 30B > 20A).
- 30B-PA6 and 20A-PA6 are inhomogeneously mixed. Clear polymer and clay rich regions.

Based on the microstructure characteristics observed by TEM and TGA, we were able to associate trends between the sensors and these microstructural differences.

The dielectric data is graphically represented in the Cole-Cole style plots; an example is provided in Figure 10. The difference between the x intercept values is the $\Delta\varepsilon$ value and the magnitude of the $\Delta\varepsilon$ value depends on additive content, dispersion and distribution. Two regions stick out. The inhomogeneously mixed nanocomposites have $\Delta\varepsilon$ values larger than the virgin PA6 and the homogeneously mixed nanocomposites have $\Delta\varepsilon$ values

less than the virgin PA6. Within the inhomogeneously mixed region (Δε values greater than virgin PA6), the Δε values increase as delamination increases. These trends were observed regardless of clay content. In regard to clay content, there is a significant decrease in Δε value with decreasing clay content. For example, 30B-PA6 Δε value is approximately 10,000 pF at 5 % mass fraction clay and approximately 4,900 pF at 2 % mass fraction clay. However, the fact that the Δε value is linked to all these factors makes it impossible that this parameter can provide a complete understanding of an unknown polymer microstructure. In other words, if you were given Figure 10 and asked why is the Δε value increasing from the black arc to the blue arc, the best answer you could provide is it is due to 1) increasing additive content, or 2) increasing additive dispersion, or 3) it may result from differences in dispersion.

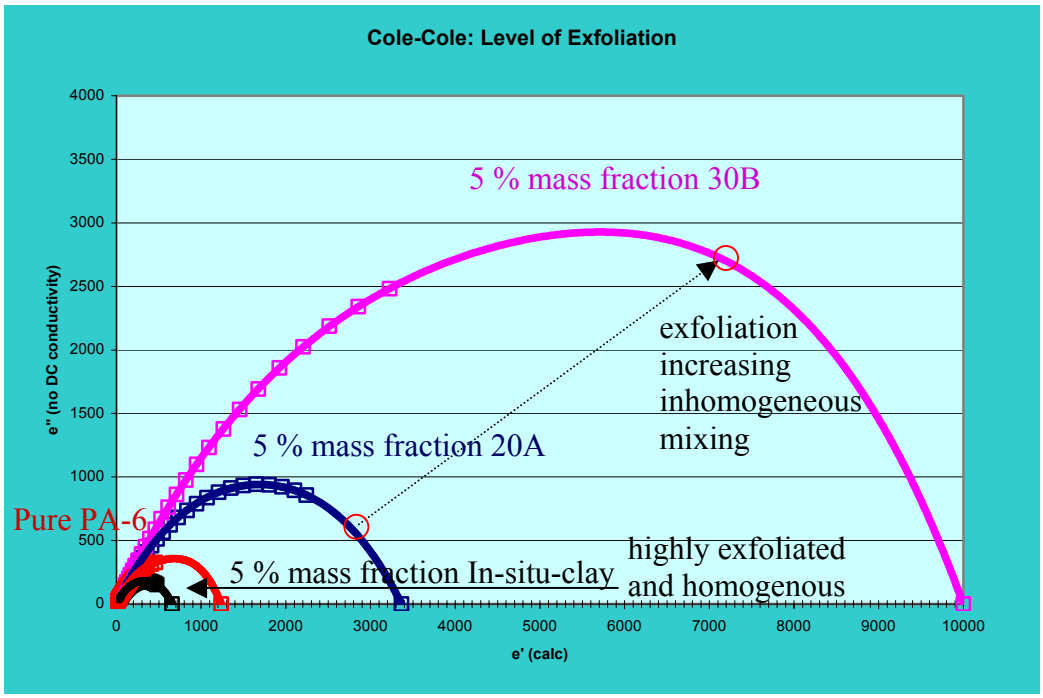

Figure 10. Cole-Cole plot of PA6 filled with 3 different om-MMTs. Inhomogeneous and homogeneous distribution regions are observed. Inhomogeneous region: as Δε increases, dispersion increases.

The dielectric and optic sensors are sensitive to surface area. The more additive surface area in a molten polymer, the more light is scattered, therefore the photon count for the optic sensor decreases. For the dielectric sensor, there is more polymer/additive interface, therefore, a greater change in the material's capacitor and resistor behavior. In nanocomposites, clay surface area can increase by adding more clay or, by improving clay dispersion/delamination. Therefore, a 2 % mass fraction of well-delaminated clay can have the same optic and dielectric signals as a 4 % mass fraction of a lesser delaminated clay.

Flammability Experiments-Workflow 1

The goal of this experiment was to determine if a combination of 15A-APP/PER in PS could lead to V0 behavior at a lower total additive loading than the pure APP/PER-PS V0 material. The high throughput aspect of this test is that in one experiment the MFFS can be determined for a single composition, rather than conducting several experiments at several heat fluxes, using several single composition strands, 10 to 20 experiments rolled into one. As an example, the MFFS results from testing PS filled with various amounts of APP-PER and organically modified layered silicate (15A) is provided in Figures 11 and 12. Using this MFFS HT method we were able to investigate the synergistic/antagonistic systems, which involved over 30 formulas and 120 tests in 6 to8 days. This includes both extrusion and MFFS testing. The important point to remember is that the higher the heat flux when a material self extinguishes, the more flame resistant is the material. The curve in Figure 12 represents the MFFS values for APP/PER-PS. All other points represent 15A-APP/PER-PS composites MFFS values. We concluded that combining APP/PER with 15A in PS might lead to antagonistic flame resistance results. In other words, adding clay decreases the MFFS. However, synergistic effects were observed for all 10 % mass fraction APP/PER and 15A combinations, 15 mass fraction-% APP/PER with 2 % mass fraction 15A, and 20 % mass fraction APP/PER with 2 % mass fraction 15A. Since the V0 PS (30 % mass fraction APP/PER-PS) self extinguished at 13.7 kW/m^2 and no APP/PER and 15A combination self extinguished at heat fluxes at or above this value, we believe that no combination of 15A-APP/PER will result in a V0 PS.

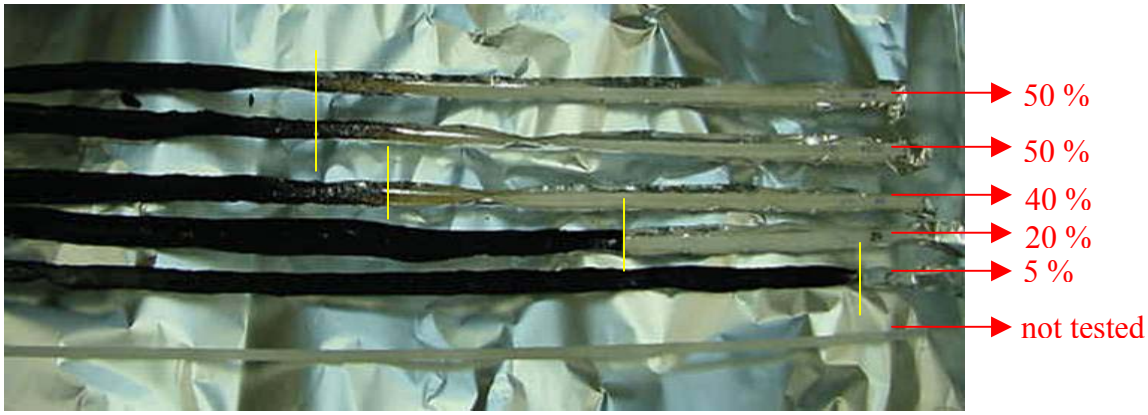

Figure 11. Extruded strips of PS with various % mass fraction APP/PER after measuring MFFS. Yellow line indicates the position of self-extinguishment. Notice the lower the flame retardant content the further the flame travels from the ignition site.

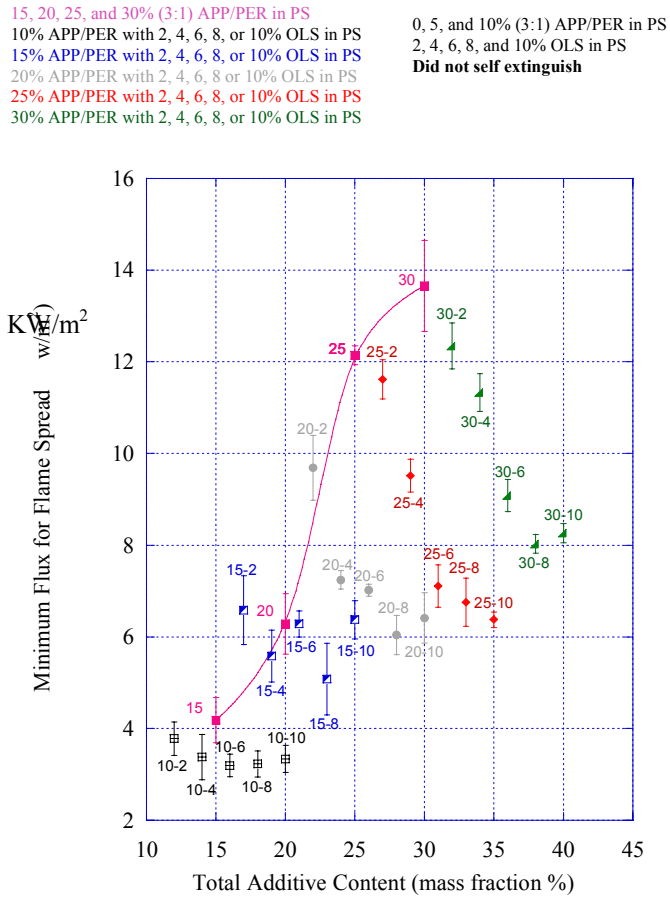

Figure 12. Plot of MFFS versus total additive content in PS samples. Error bars reflect the reproducibility of five experiments. Average error is ± 5 of MFFS value.

Flammability Experiments-Workflow 2

The gradient composition and constant heat flux FRP experiments provides an opportunity to measure the flame velocity of several additive concentrations in a single experiment. The gradient composition APP/PER-PS samples were ignited at the 0 % mass fraction additive end, where the radiant panel heat flux was set at 19 kW/m^2. After ignition, the flame burns across the sample (from lower to higher APP/PER content) while the flame position is kept constant (Figure 13). For APP/PER-PS samples the first few % mass fraction of APP/PER usually burns rapidly and the researcher is unable to keep the flame at the ignition position, however, from 5 % mass fraction to 40 % mass fraction the material displays fuse-like burning behavior that is extremely well behaved and easy to monitor. As shown in Figure 13, the flame velocity decreases from 2.4 mm/s at sample position 0 mm (5 % mass fraction APP/PER) to 1.1 mm/s at a sample position of 1410 mm (V0 formulation). At sample position greater than 1420 mm (> 30 % mass fraction) the flame velocity further decreases. At sample lengths greater than 1500 mm the velocity increases due to decreasing additive content, the APP/PER feeder was turned off.

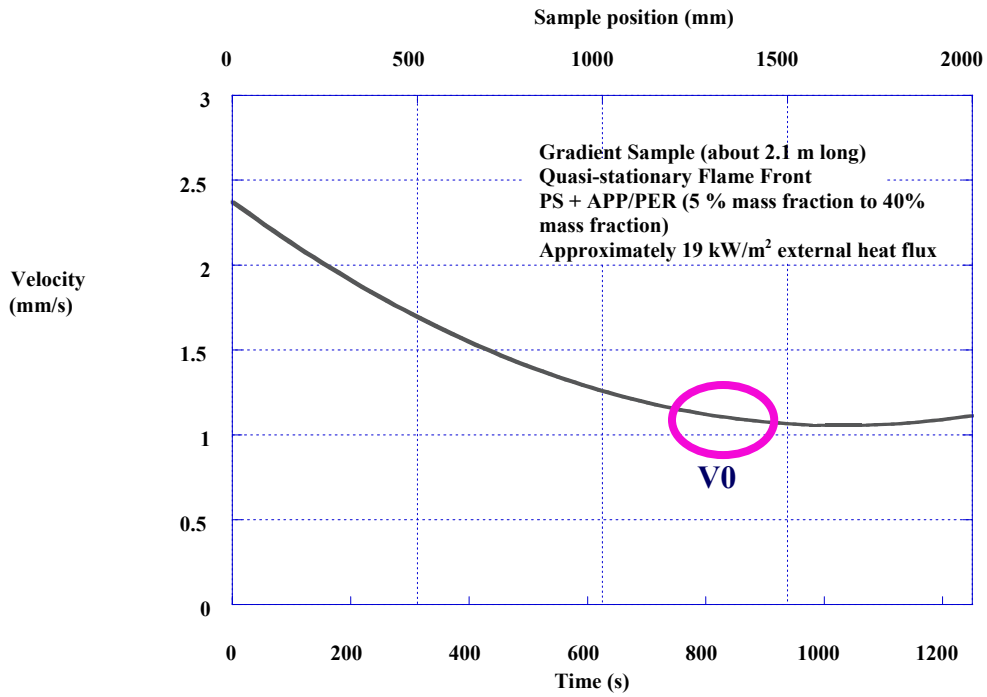

Figure 13. Flame velocity as a function of additive concentration measured in a constant heat flux of 19 kW/m^2 with a 5 % mass fraction to 40 % mass fraction APP/PER gradient in PS.

Conclusions

We are developing several HT methods that will decrease the time to develop new additive filled polymers with desired mechanical and physical properties. Presented here was our initial research with a single flame retardant and two layered silicates, however we have already begun to explore a larger variety of other flame retardants and nano-additives, such as nanotubes and POSS. In addition, we are using other polymer matrices, such as PC/ABS, PP, and HIPS. In addition to the HT methods discussed here (gradient extrusion, in-line sensors, and flammability test methods) we are also developing HT mechanical testing, composition characterization, and gradient coating synthesis methods.

References

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[5] N,N-dimethyl-N,N-dioctadecyl quaternary ammonium treated montmorillonite provided by Southern Clay Products under the trade name of Cloisite 20A and Cloisite 15A. The

difference is 15A contains approximate 30 mass fraction-% of excess unbound organic modifier.

[6] UL-94: The standard for flammability of plastic materials for parts in devices and appliances. http://www.ul.com/services/flame/html

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[10] See http://www.fire-testing/.com/frp.htm for additional information about the Floor Radiant Panel.