Summary
This application note describes analysis techniques to assess the distribution and quantity of inorganic fillers in thermoplastics using scanning electron microscopy with energy dispersive spectroscopy, along with thermogravimetric analysis.

Background
Inorganic fillers are often added to thermoplastics to provide increased rigidity, hardness, impact strength, thermal conductivity, pigmentation, radiopacity, as well as reduced mold shrinkage. Filler, in the form of a powder, is normally compounded into the thermoplastic resin with an extruder, with filler contents ranging up to 60 wt.% depending on the application.

Procedure and Results
Polymethyl methacrylate (PMMA), a transparent thermoplastic, is used in applications ranging from safety glass to dental composites. Fillers such as barium sulfate and zirconium oxide are often added for radiopacity for medical use.[1]

In this application note, 10 wt.% of zirconia oxide was compounded into PMMA using a twin screw extruder. The uniformity of dispersion and weight percent of filler in the final product was assessed with scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and thermogravimetric analysis (TGA). SEM-EDS provides structural and elemental information about the materials. TGA provides mass change in the sample as it is heated to high temperatures.

Scanning electron microscopy was performed on a Zeiss EVO L15 SEM equipped with an Oxford Instruments EDS X-ray detector. The analysis was conducted in variable pressure mode, allowing the sample to be analyzed without gold-coating. A backscattered detector was used, and an accelerating voltage of 15 kV. The SEM image is shown in Figure 1. In backscatter mode, higher atomic number species scatter incoming electrons with a higher amount of energy compared to lower atomic number species, and hence appear brighter compared to materials with a lower atomic number. The bright particles are thus likely the zirconium oxide. The dark shadows are air pockets in the sample, where backscattered electrons are less likely to escape to the detector. The SEM image suggests good dispersion of the zirconium oxide, with minimal agglomeration and particle sizes less than 10 μm. To confirm the composition of the individual particles, EDS maps were created of the image in Figure 1. The overall composition map is shown in Figure 2. The small bright particles do appear to be associated with zirconium. This observation is confirmed by the individual element maps shown in Figure 3. Given that oxygen is contained in both PMMA and zirconium, the oxygen map does not track with the zirconium map.

Thermogravimetric analysis was performed on a TA Instruments Q500, with a temperature sweep from 30 to 800ºC. The carrier gas was air, which allows the polymer matrix to oxidize and combust, leaving behind the inorganic filler. The residual weight after complete combustion of the polymer matrix is therefore the filler content, along with any additional inorganic residue. As shown in Figure 4, a final percent mass of 9.4% was found for the specimen. This material was compounded with 10 wt.% zirconia dioxide. To obtain a statistical representation of the overall filler content, multiple specimens should be run, as there could be pellet to pellet variation.

These two types of analysis can therefore show uniformity of filler content, identity of filler, and concentration of filler.

[1] Akinci et al, Composites Part B, vol 56, 42-47 (2014); Motaung et al, Express Polym. Lett., Vol 6, 871 (2012).

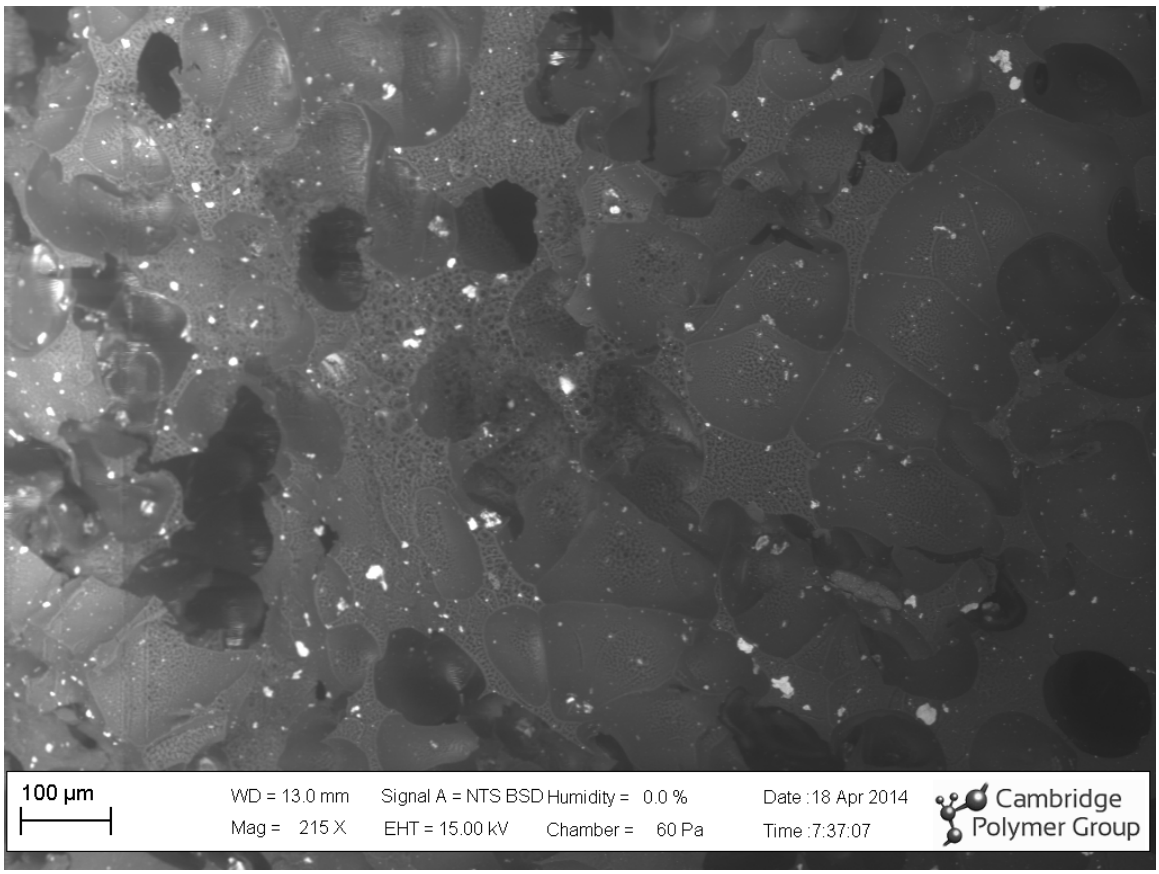

Figure 1: Scanning electron micrograph of sectioned PMMA sample in backscatter mode. The bright particles indicate higher atomic number species compared to the darker carbon-based matrix of the PMMA.

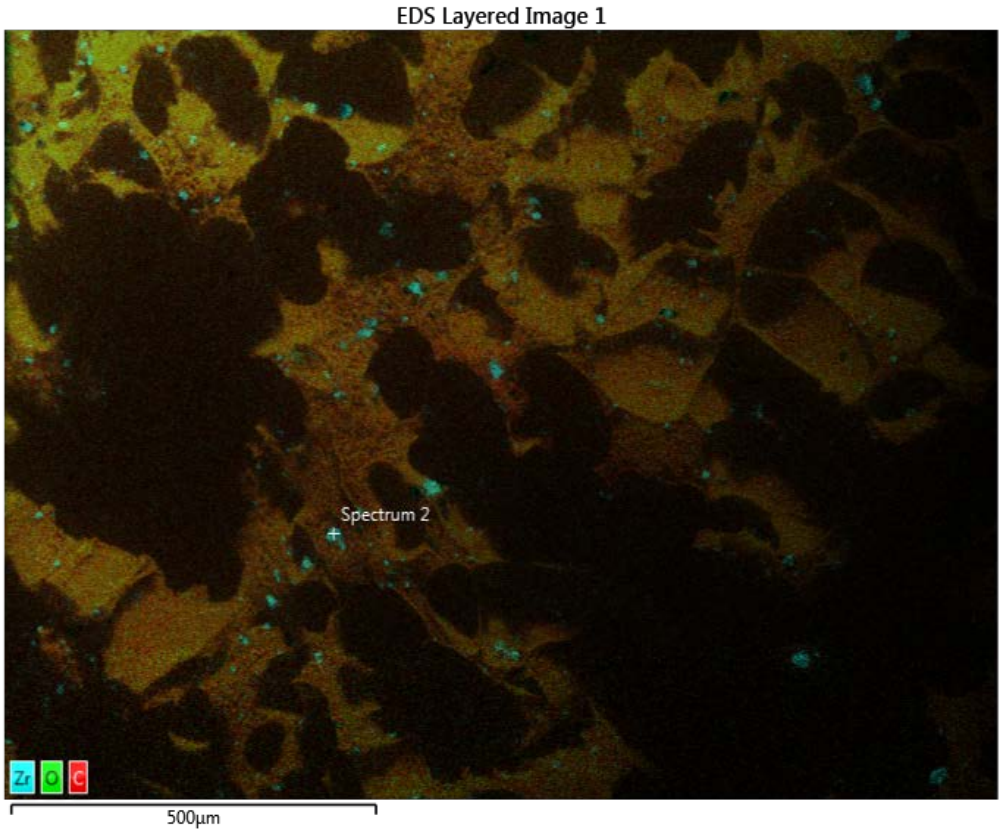

Figure 2: Overall composition map showing zirconium, oxygen, and carbon.

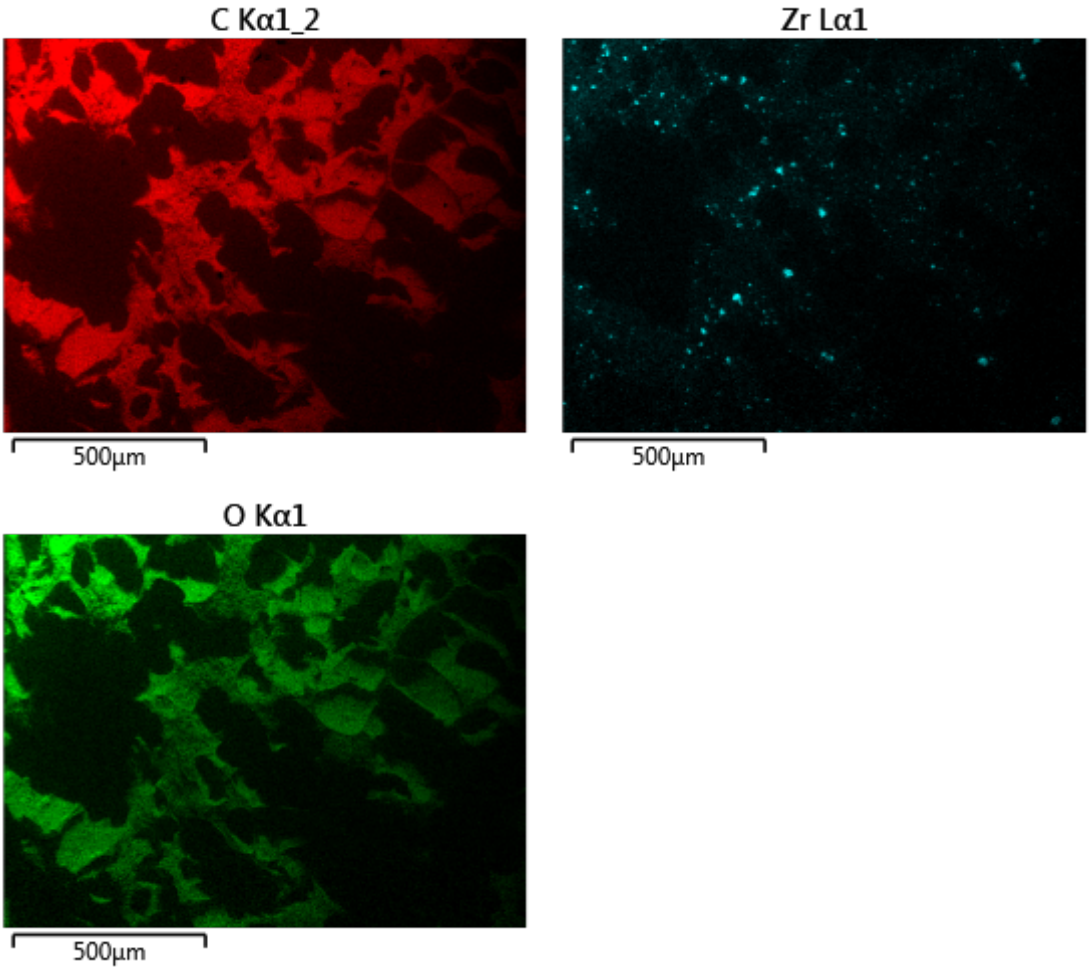

Figure 3: Individual compositional maps for carbon, zirconium, and oxygen.

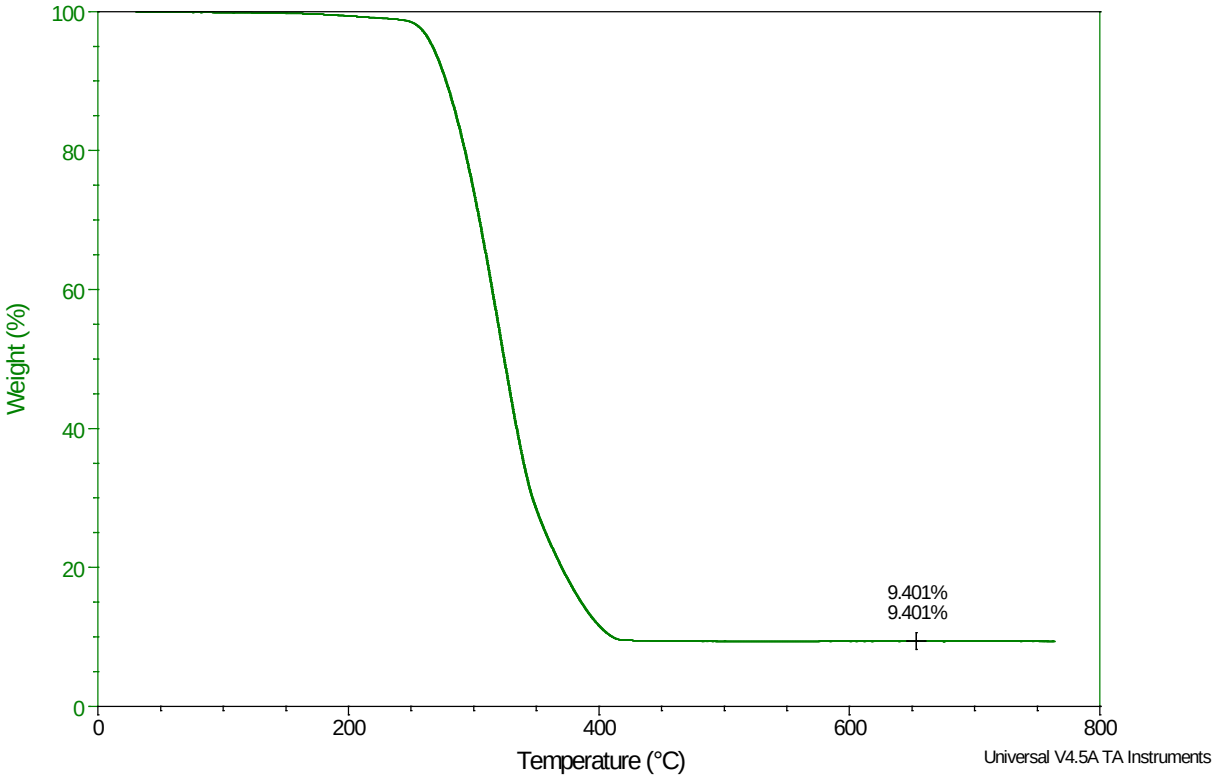

Figure 4: Thermogravimetric analysis of specimen showing a filler content of 9.4 wt. %.