



## B217 Vibrational Spectroscopic Analysis of 3D-Printed Polymers Pre- and Post- Manufacturing

Ryan G. Zdenek\*, West Babylon, NY 11704; April Bowen, BS, University of New Haven, West Haven, CT 06516; John A. Reffner, PhD, John Jay College of Criminal Justice, New York, NY 10019; Maria-Isabel Carnasciali, PhD, University of New Haven, West Haven, CT 06516; Brooke W. Kammrath, PhD, University of New Haven, West Haven, CT 06516

**Learning Overview:** After attending this presentation, attendees will understand the value of vibrational spectroscopy for the analysis of polymers used in the manufacturing of 3D-printed objects.

**Impact on the Forensic Science Community:** This presentation will impact the forensic science community by providing information about the chemistry of polymers used in 3D printing, pre- and post-manufacturing, and how that information can be obtained through vibrational spectroscopy, thus informing criminalists about the significance of vibrational spectra of 3D-printed objects.

Additive manufacturing, commonly known as 3D printing, is becoming increasingly common in today's society. The ease of use and decreasing cost make this technology accessible to a wide range of individuals. 3D printing has been used to manufacture a range of legal items, including airplane and automobile parts, footwear, medical prosthetics, and even models for forensic reconstructions and court presentations. Unfortunately, it is also readily available for individuals to manufacture items that can be used in criminal activity, such as firearm components, knuckle dusters, pipe bomb components and ATM skimmers. In an investigation in which 3D-printed parts are recovered and a 3D printer is found, it would be valuable to be able to associate the printed object with an unused spool of polymer. Thus, there is a need for forensic-focused research to evaluate whether an association can be made between 3D-printed objects and their raw material (i.e., the polymer filament) as well as the discrimination potential of polymers produced from different batches and different manufacturers. It is the focus of this research to be able to understand the chemical nature of the polymers used in 3D printing, including changes in their crystallinity via the manufacturing process, in addition to methods for their classification and discrimination.

Polymer crystallinity refers to the degree of structural order or alignment of the molecular chains in a solid composed of repeating structural units. Different polymers have various ranges of degrees of crystallinity, which refers to the percentage of order within the solid. Polymers can crystallize upon cooling from the melt; thus, it is possible for there to be a change in polymer crystallinity as a result of the 3D manufacturing process. In order to associate a 3D-printed object with its polymer filament, it is imperative to understand any changes to the crystallinity of a polymer as a result of the 3D-printing process.

Infrared (IR) and Raman spectroscopy are common instruments used in forensic laboratories and are well known and validated analytical methods for polymer characterization and analysis. In addition to identifying the components of the polymer, such as the main chemical, additives, and pigments, vibrational spectroscopy has been used for analyzing polymer crystallinity. Changes in polymer crystallinity can result in peak splitting and changes in peak shape, which may result in a shift in the computer-selected peak position.

This research focused on the vibrational spectroscopic analysis of two common polymers used in 3D printing: Polylactic Acid (PLA) and Acrylonitrile Butadiene Styrene (ABS). For each polymer type, filament spools of different colors within the same brand and also different brands were analyzed. Pre-manufactured samples were analyzed from each spool at increments of 24in for a total of five pre-manufactured measurements per spool. Additionally, for all polymer filament spools, three items were manufactured at three different temperatures for a total of nine 3D-printed objects per spool.

IR and Raman spectral analysis resulted in the identification of the major and minor components (e.g., additives and pigment) of the polymers for classification as well as lot and brand comparisons. It was concluded that different brands and colors of polymers were able to be discriminated based on their vibrational spectra. Within a spool of polymer, there were no meaningful detectable differences, indicating that the polymers within a spool are homogeneous. Last, statistical comparisons of the peak positions, splitting and Full Width Half Max (FWHM) values of the pre- and post-manufactured polymers indicated that there were no consistent differences over the range of melting temperatures to indicate a measurable change in crystallinity via the 3D-printing process. Overall, vibrational spectroscopy was shown to be a valuable tool for 3D-printed polymer identification, which can be used to associate a 3D-printed object with a specific manufacturer's polymer filament.

### 3D-Printed Polymers, Infrared Spectroscopy, Raman Spectroscopy