

Raman Metrology: Towards Traceable and Quantitative Measurements

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Introduction

Raman spectroscopy is a powerful surface analytical technique for rapid, non-destructive characterization of materials. It operates under ambient conditions, often without the need for sample preparation. Its applications span biomedical, microelectronics, pharmaceutical, security sectors, and include fundamental research on quantum and nano-materials. Miniaturized handheld Raman instruments have broadened in-field measurement capabilities to include environmental monitoring, hazardous chemical identification, and illicit drug analysis. Despite nearly a century of development, Raman spectroscopy remains predominantly a qualitative analytical technique. A major obstacle to using Raman analysis in regulatory applications is the lack of traceable quantification and the absence of certified reference and documentary standards. This poster will present the ongoing effort within the Raman Task Group of the Surface-Analysis Working Group (SAWG-CCQM) on the development of mixed polymer blend samples to enable traceable and quantitative Raman measurement of weight fraction in mixed polymers.

Method

- The intensity of a Raman spectrum is directly proportional to the concentration of the molecules in the probe volume
- However, it is very difficult to determine the Raman excitation probe volume (confocal volume) and most measurements are associated with large uncertainty
- For Raman spectra of mixtures, the relative peak intensities is directly related to the relative concentration of the components
- Goal of the Pilot study: Traceable quantitative measurements of weight fraction of a two component mixture
 - Reference samples with a range of mole fraction is used to establish Raman intensity calibration curve
 - Measure an unknown sample to test the procedure
- Traceable mixture samples (e.g. polymers) prepared through traceable gravimetric weighing which is calibrated and traceable to kg
- A set of reference samples with varying weight fraction is prepared for Raman intensity ratio calibration
- An unknown sample is then measured and weight fraction determined using the calibration curve
- Polymer exhibits strong and sharp Raman spectrum which is ideal for quantitative study
- However, most polymers are not miscible which will results in phase separation during casting process. (Fig. 1)

Sample Fabrication and Measurements

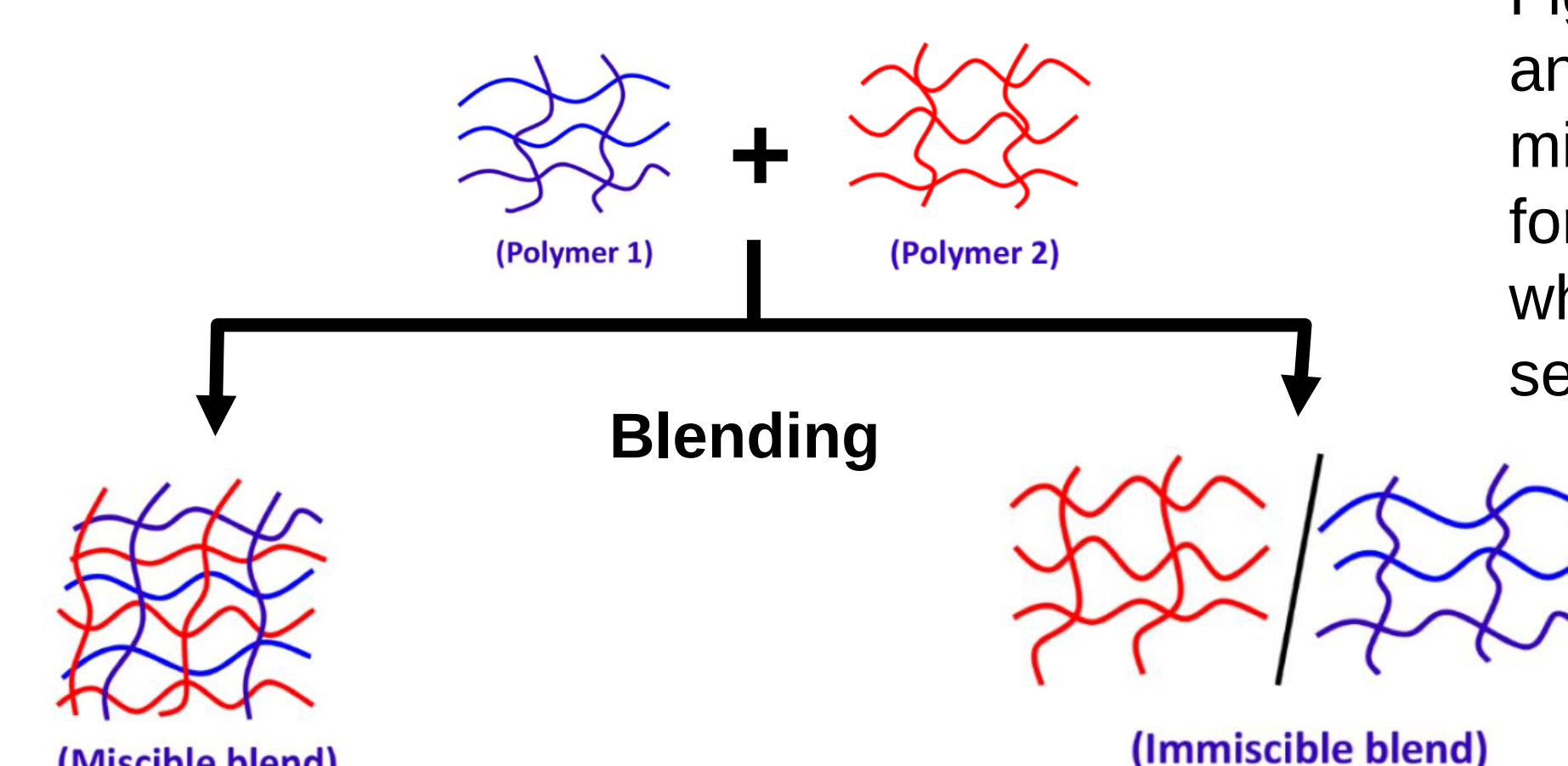


Figure 1. Graphic depiction of miscible and immiscible blend of polymer mixtures. Miscible blend polymers forms homogenous interlinked chain where as the immiscible blend phase separate

- There are a few sets of known polymer pairs that are perfectly miscible
- Polystyrene (PS) and polyphenylene oxide (PPO) are miscible polymer sets which form homogenous and uniform mixture samples which is selected for this study

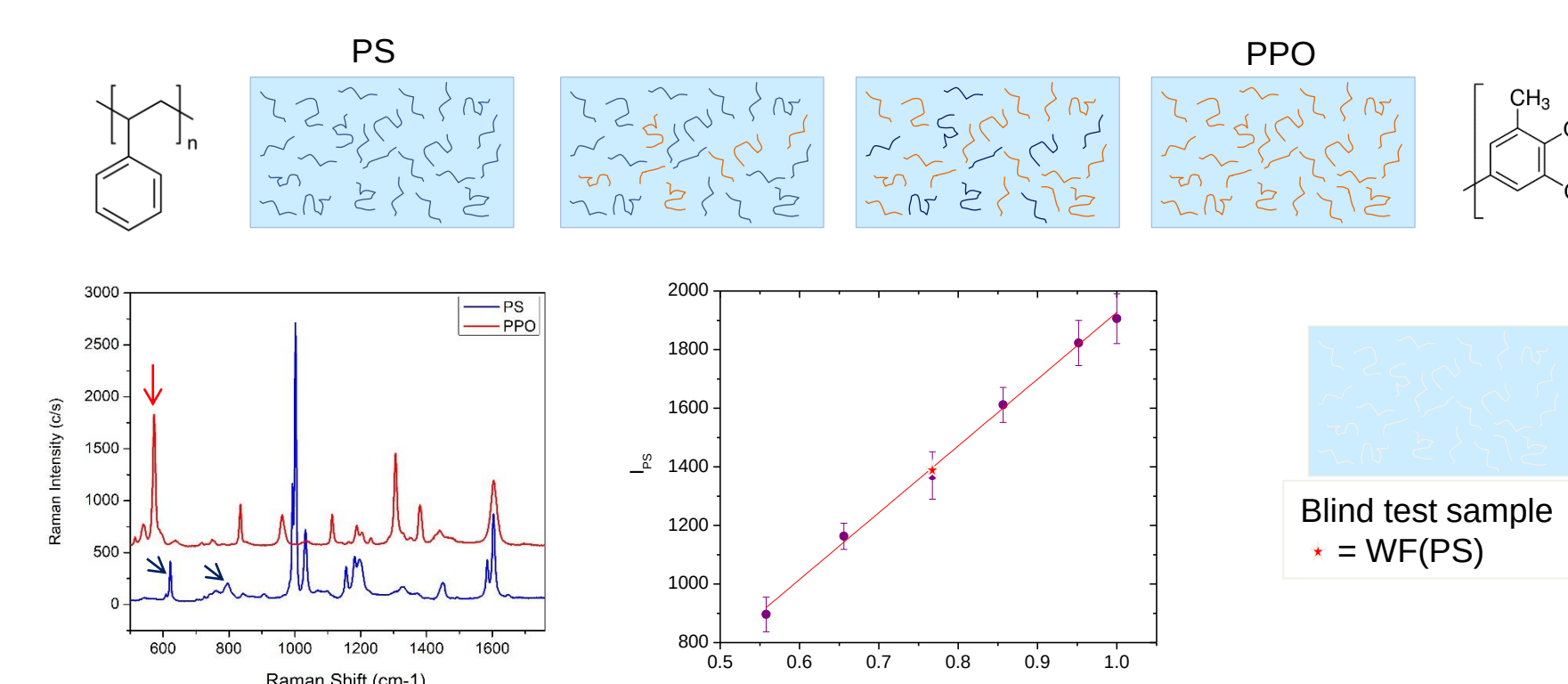


Figure 2. Schematic depiction of mixed polymer films (top); Raman spectra of PS and PPO (bottom left) and calibration curve (bottom middle) is used to determine the weight fraction of a blind test sample

- Different weight fractions of PS and PPO prepared with traceable weighing. The mixtures are dissolved in benzene 10% w/v (for the total weight in benzene)
- Different weight fraction of mixed polymer film is casted on wellled glass slide



Figure 3. Photograph of the PS-PPO mixed polymer samples

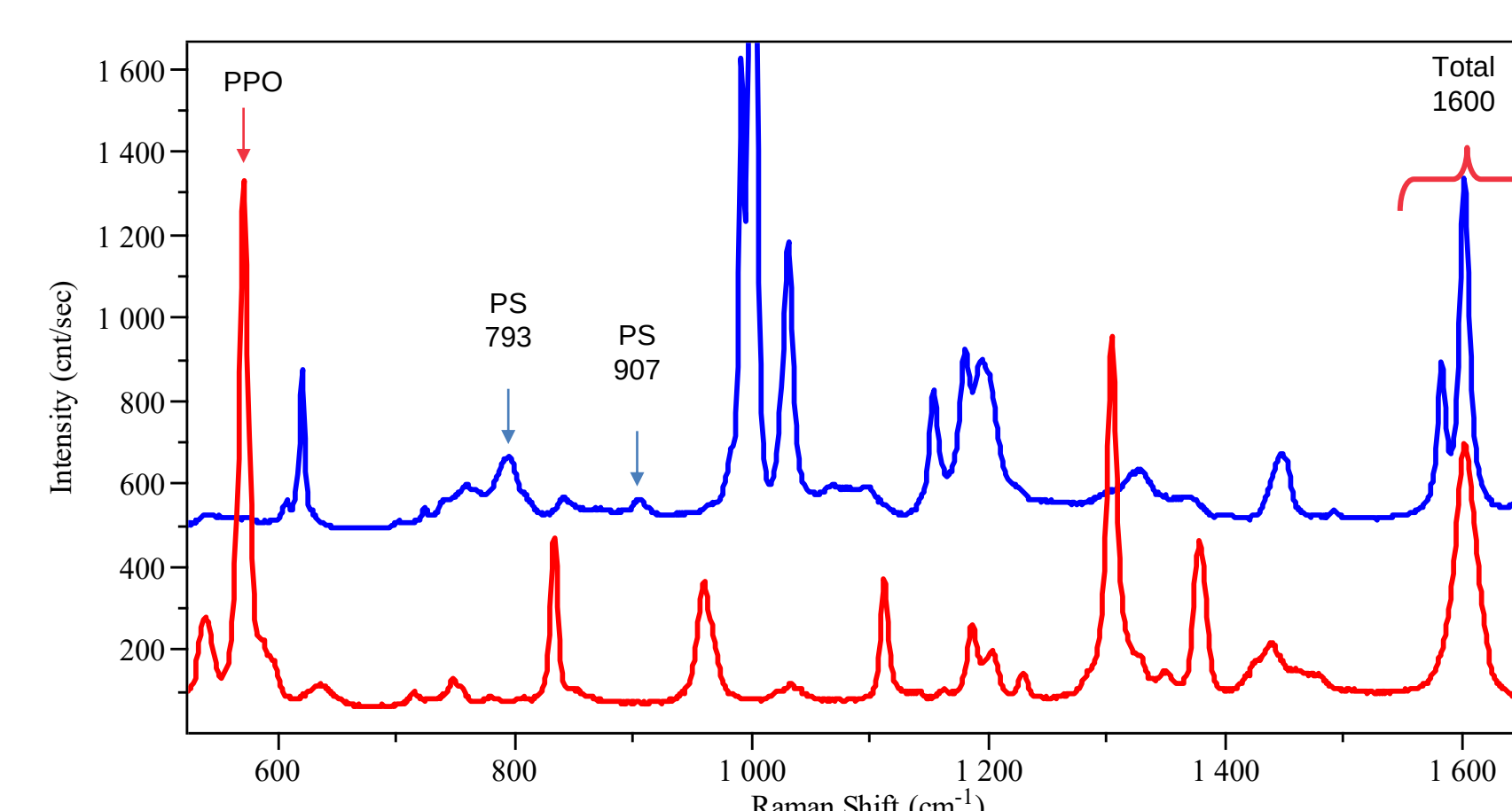


Figure 4. Raman spectra of PS (blue) and PPO (red). Arrows shows the distinct peaks

Results and Discussion

- There is a clear distinct and non-overlapping band at 572 cm⁻¹ (for PPO)
- There appears to be a few distinct PS peaks at 615, 793 and 907 cm⁻¹. However, only the 907 cm⁻¹ peak does not have any significant overlap with PPO spectrum and is suitable for the weight fraction analysis.
- There are also a number of strongly overlapping peaks (e.g. ring vibrations centered at 1600 cm⁻¹) which can be used as the “total” quantity
- As probe volume can vary from each acquisition, the calibration curve is established by ratioing the intensity of polystyrene peak to the CH peaks

$$\omega_i = \frac{m_i}{m_{tot}} = \frac{I(PS: 907 \text{ cm}^{-1})}{I(tot: 1600 \text{ cm}^{-1})} \quad \text{Weight fraction of PS} \quad (1)$$

$$\omega_j = \frac{m_j}{m_{tot}} = \frac{I(PPO: 572 \text{ cm}^{-1})}{I(tot: 1600 \text{ cm}^{-1})} \quad \text{Weight fraction of PPO} \quad (2)$$

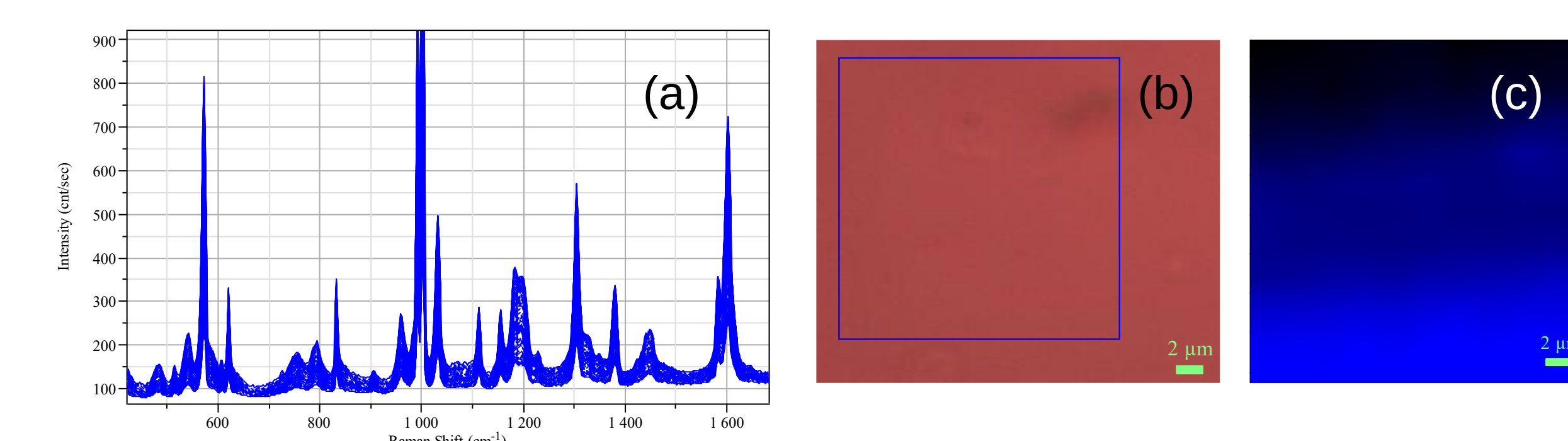


Figure 5. (a). Raman spectra of 0.5459 PS weight fraction sample acquired from 121 spots on the PS-PPO sample. (b) Optical image and (c) Raman hyperspectral map of the 907 cm⁻¹ peak.

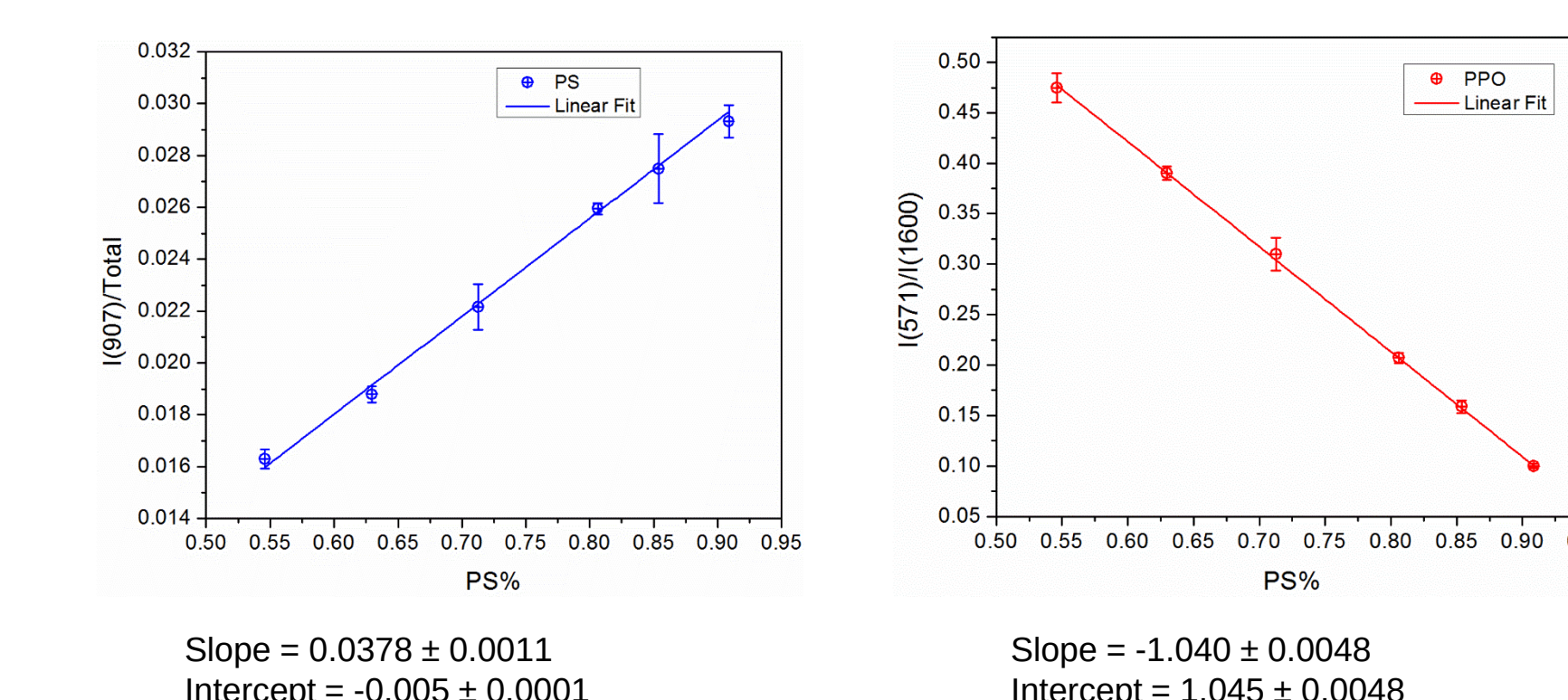


Figure 6. Calibration curve of PS and PPO as determined from the ratio of peak intensities as shown in eq. (1) and (2) above

Conclusion

Mixed polymer blend samples made of PS and PPO have been evaluated with Raman spectral measurements. From the intensity peak ratio, PS or PPO calibration curves are established. These calibration curves can then be used to determine weight fraction of a test sample with unknown composition. Stability of the polymer blends are currently under evaluation before launching the pilot study under the Surface Analysis Working Group (SAWG-CCQM).