

Reverse engineering of multi-layer films

This contribution introduces the combined application of Raman microscopy and band-target entropy minimization (BTEM) in order to successfully reverse-engineer a multi-layer packaging material. Three layers are identified, namely, polyethylene, a paper and talc layer (with two distinct cellulose forms), and a poly-styrene co-polymer composite containing anatase and calcite. This rapid and non-destructive approach provides a unique opportunity for the assessment of multi-layer composites, including the constitution of the additives present.

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Multi-layer thin films are widely used in a variety of industries ranging from packaging, printing, electronics, healthcare, medicine, etc.¹. This interest is largely driven by the possibility of obtaining a combination of two or more specific characteristics, such as particular thermal, electrical, or mechanical properties, hydrophobicity, hydrophilicity, printability, corrosion resistance, selectivity, etc. in a single multi-layer material¹.

Characterization of such multi-layer films is often carried out in order to examine the quality and the composition of the films. Common analytical methods used to analyze these materials presently include differential scanning calorimetry (DSC)², nuclear magnetic resonance (NMR)³, secondary ion mass spectrometry (SIMS)⁴, infrared spectroscopic ellipsometry (IRSE)⁵, and high performance liquid chromatography (HPLC)⁶. Although they are not so commonly used in thin film analysis, vibrational spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy, can provide some unique opportunities and possible advantages. FTIR and Raman spectroscopic methods are able to provide very detailed structural and chemical

information on polyatomic constituents, thus they can be directly utilized to identify many organic and inorganic components present in films. Also, vibrational spectroscopies frequently require little or no sample preparation and are in most cases non-destructive. Although FTIR and Raman spectroscopy are complementary to each other, Raman spectroscopy can offer some advantages over FTIR, due to the higher spatial resolution of up to circa 250 nm.

In vibrational spectroscopy, identification of the components present in the system is commonly achieved by simple inspection of the primary spectral bands appearing in the measured spectrum, since they can often be associated with particular functional groups. However, in many experimental situations, the true identity of the constituents is difficult to confirm. This is particularly true for more complex systems with many constituents. These complications are often due to the considerable spectral overlap between components, as well as the low signal-to-noise ratio for some of the minor components present. In addition, many real-world experimental problems such as baseline changes and fluorescence can further complicate analysis⁷.

In recent years, various multivariate statistical analysis techniques have been developed to treat collected sets of vibrational spectra simultaneously. One class of techniques is collectively called self-modeling curve resolution (SMCR), where the basic idea is to recover the pure component spectra from a set of mixture spectra without relying on any spectral library or any *a priori* information⁸. Among the widely used SMCR techniques, band-target entropy minimization (BTEM) has some unique capabilities, which are not found in other algorithms. In particular, BTEM is suitable for recovering the pure component spectra of minor components. For example, accurate pure component spectra of trace components possessing weak spectroscopic signals, i.e. considerably less than 1 % of the total measured signals can be readily recovered in many cases⁹. Consequently, the BTEM technique has found considerable utility in the areas of organometallic and catalytic chemistry, biomedical and pharmaceutical sciences, as well as archaeology and authentication¹⁰⁻¹⁵.

In the present contribution, the combined use of Raman microscopy mapping and BTEM analysis is applied to multi-layer thin films. The Raman mapping spectra from the cross-section of a multi-layer thin film are first collected, subsequently the pure component spectra of the underlying constituents are reconstructed using BTEM and the thickness and composition of each layer are determined.

Experimental section

The multi-layer thin film sample used in the present study was obtained from a commercial packaging material. More specifically, the packaging material was an envelope used for hydroscopic optical windows. The thickness of the film was *circa* 120 μm . The sample, with a size of 2 $\times$ 2 mm, was mounted in self-closing stainless steel tweezers. This prevented contamination and/or the appearance of signals from the holder/mount.

The Raman microscopic measurements were performed on the cross-section of the multi-layer film using a InVia Reflex instrument (Renishaw) equipped with a near-infrared enhanced deep-depleted thermoelectrically Peltier-cooled CCD array detector (576 $\times$ 384 pixels) and a high grade Leica microscope. The Raman scattering was excited with a 785 nm near-infrared diode laser and a 50 $\times$ objective lens was used to collect the backscattered light. The beam size was *circa* 1 – 2 microns and the power level was 30 mW. Measurement scans were collected using a static 1800 groove per mm dispersive grating in an extended spectral window from 100 to 1800 cm^{-1} . The acquisition time for each Raman spectrum was around 35 s. Raman mapping measurements in an area of 120 μm by 120 μm with a step size of 3 μm in both the x and y directions were performed. This resulted in *ca.* 1681 Raman spectra.

BTEM analysis

Some of the collected Raman spectra were preprocessed in order to remove the contributions due to cosmic ray spikes. Subsequently,

the preprocessed data were subjected to BTEM analysis in order to reconstruct the pure component spectrum of the underlying constituents, one at a time, without using any spectral libraries or any *a priori* knowledge. In other words, BTEM is an advanced blind deconvolution technique. When all normalized pure component spectra of all underlying constituents have been reconstructed, the spatial distribution for all constituents can be obtained by projecting them back onto the baseline-corrected and normalized Raman data set. A detailed description of combining Raman microscopy measurements and BTEM analysis for other types of applications, i.e. authentication and pharmaceutical tablets, appears elsewhere. For a more in-depth discussion of the mathematics of the BTEM algorithm, readers can refer to references¹⁰⁻¹⁵.

Results

Fig. 1a shows the 20 $\times$ magnification of the visible microscope image of the cross-section of a multi-layer thin film. Closer inspection on the visible image reveals that there are at least two visible layers with very distinctive shades, i.e. darker and brighter regions. Raman mapping measurements were then performed at a designated area covering both observed regions (and the full width of the film). The collected spectra were pre-processed to remove the spike signals recorded from the cosmic rays. The stacked plot of 300 of the 1681 acquired Raman spectra from this cross-section area is shown in Fig. 1b. As can be seen, the obtained Raman spectra show that a relatively good signal-to-noise ratio is obtained and there is considerable pixel-to-pixel variation in the spectra.

The preprocessed Raman mapping spectra were subsequently subjected to BTEM analysis. This numerical analysis revealed a total of seven underlying patterns in the set of 1681 Raman spectra. These seven underlying patterns correspond to the normalized pure component spectra of the constituents present in the multi-layer film. These are shown in Fig. 2. It is worth repeating that these spectral estimates were obtained without any *a priori* information or spectral libraries.

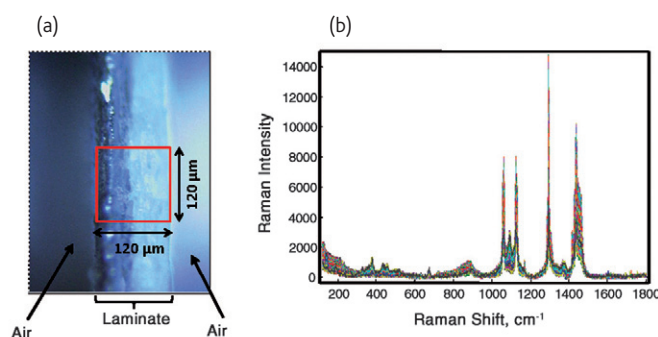


Fig. 1 (a) 20 $\times$ visible microscope image of the laminate cross section mounted in self-closing tweezers. (b) A selected subset of the despiked Raman mapping spectra collected from the cross-sectional area.

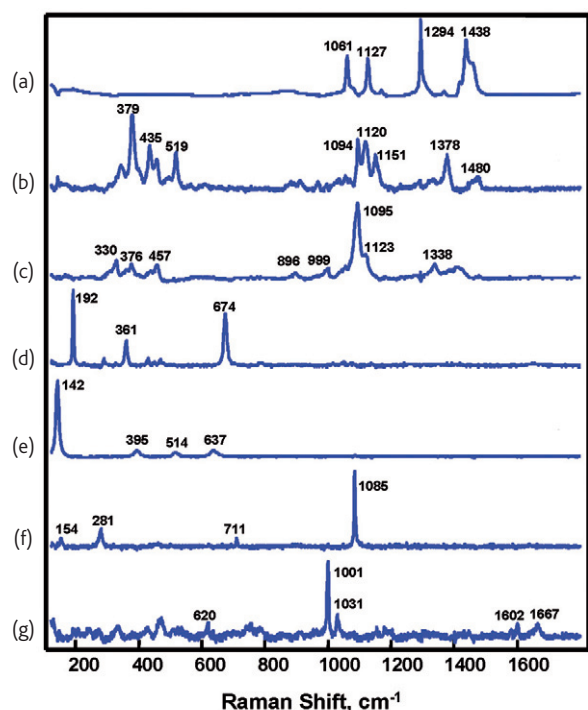


Fig. 2 The reconstructed pure component spectral estimates via BTEM analysis: (a) polyethylene; (b) paper fiber form I; (c) paper fiber form II; (d) talc; (e) anatase TiO_2 ; (f) calcite; (g) polystyrene co-polymer.

The reconstructed pure component spectral estimates were then compared to known spectral libraries associated with polymers and fibers. It was found that spectral estimate (a) is consistent with the Raman spectrum of polyethylene¹⁶. The relatively strong Raman bands observed at 1061, 1127, 1294, and 1438 cm^{-1} correspond to the antisymmetric C-C stretching, symmetric skeletal C-C stretching, CH_2 wagging, and CH_2 bending respectively.

The reconstructed BTEM estimates (b) and (c) have spectral patterns which closely resemble the pure component Raman spectra of cellulose form I and cellulose form II¹⁷. Accordingly, these two estimates are assigned as the Raman spectra of paper fiber form I and form II. The presence of two different forms of paper fiber is certainly not too surprising, as it had been previously shown that natural paper fiber, i.e. metastable cellulose form I will partly undergo polymorphic transformation to another more stable cellulose form II during mercerization or sodium hydroxide treatment¹⁸. The crystal structures of cellulose form I^{19,20} and form II²¹ are known to be different. These differences are primarily associated with changes in hydrogen bonding and hence changes in the conformations and packing of the cellulose chains. As shown in Fig. 2, these changes appear to effect both the low-wavenumber (below 700 cm^{-1}), as well as higher-wavenumber vibrations. Peak shifting and relative intensity changes are also observed.

The spectral estimate in Fig. 2d, and particularly the vibrations at 192, 361, and 674 cm^{-1} , is consistent with $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$,

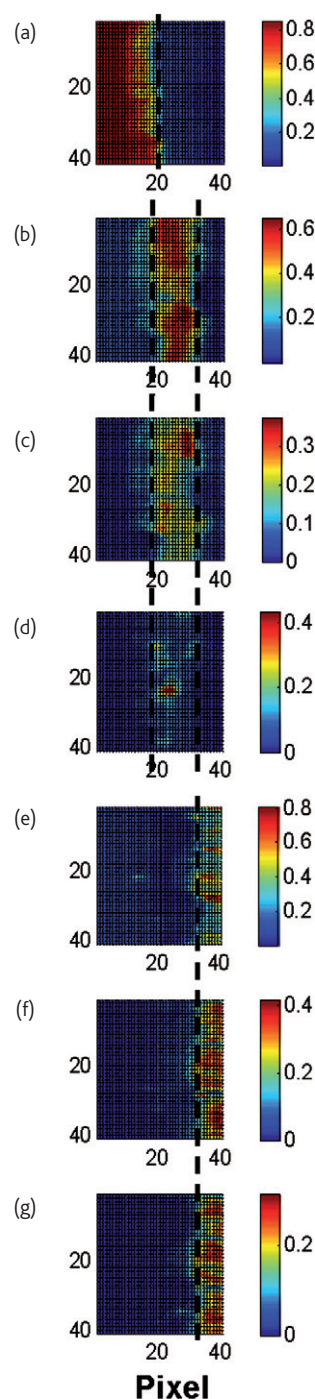


Fig. 3. The spatial distributions of each component in the Raman mapping: (a) polyethylene; (b) paper fiber form I; (c) paper fiber form II; (d) talc; (e) anatase TiO_2 ; (f) calcite; (g) polystyrene co-polymer. The three layers of the laminate are easily distinguished as comprising component (a) in the left layer, components (b) – (d) in the center layer and components (e) – (g) in the right layer.

Instrument citation

In Via Reflex Renishaw Raman Microscope

the mineral talc²². The BTEM estimate (e) shows significant Raman peaks at 142, 395, 514, and 637 cm^{-1} . These peak positions and peak relative intensities are very consistent with the Raman spectrum of anatase reported in previous work²³. The BTEM estimate (f) shows significant Raman peaks at 154, 281, 711, and 1085 cm^{-1} , which are in good agreement with the Raman spectrum of calcite¹⁶. The BTEM estimate (g) shows significant Raman peaks at 620, 1001, 1031, and 1602, and 1667 cm^{-1} . The first four Raman peaks are quite consistent with the Raman spectrum of polystyrene, which correspond to C-C ring twisting, benzene trigonal ring deformation²⁴, in-plane ring deformation, and in-plane ring stretching respectively²⁵. However, the additional peak at 1667 cm^{-1} found in this estimate may indicate that this is not pure polystyrene. More specifically, the spectrum (g) appears to correspond to a polystyrene co-polymer. The Raman peak at 1667 cm^{-1} is perhaps due to a C=C vibration i.e. blocks of polybutadiene²⁶, and hence, the co-polymer may be a block co-polymer of polystyrene-polybutadiene.

Subsequently, the spatial distribution of each component was obtained by projecting the BTEM spectral estimates back onto the preprocessed Raman mapping spectra (preprocessing involves despiking, baseline correction, and normalization to maximum height). The spatial distributions of components (a) – (g), in the 120 × 120 micron Raman mapping area, are shown in Fig. 3. The maps clearly show that the multi-layer film is composed of three layers, where polyethylene (a) is on one side, the components (b) – (d) are in the middle layer, and the components (e) – (g) are in the third layer. It is worth noting that the axes for spatial distribution are in pixel number, which can be directly converted to distance by multiplying by 3 μm for each pixel. Accordingly, the approximately layer thicknesses of the laminate are circa 60 μm , 40 μm , and 20 μm respectively. Combined altogether, the seven reconstructed pure component spectra accounted for more than 99 % of the measured Raman mapping signals.

In the context of reverse-engineering the original packaging material, the polyethylene film probably provides vapor-barrier protection (i.e. preventing moisture penetration to the enclosed optical components), the talc impregnated paper layer provides opaqueness for the packaging and the polystyrene copolymer/anatase/calcite layer probably provides a rather durable layer that is also opaque. Indeed, it is well known that talc is a common component in some types of paper²⁷ and anatase and calcite are used in composite polystyrenes²⁸.

Conclusion

A combination of Raman microscopy measurements and BTEM analysis has been successfully applied to a multi-layer packaging material in order to reverse-engineer the layers present. The analysis of the set of Raman microscopy measurements provided excellent pure component spectra of the constituents present without the use of any *a priori* information or libraries. Subsequently, the pure component spectra were matched to known reference materials in order to confirm the identity of the packaging materials. In addition, the BTEM spectral estimates were mapped back onto the original data in order to assess the spatial distributions of the materials present and hence the thickness and compositions of the layers. Such an approach is non-destructive, rapid, and general. Consequently, it appears applicable to a wide range of thin-layer problems, including verification of authenticity (in other words, counterfeit detection). Much more complex multi-layer films should not present any practical problems to reverse-engineering using this method. 

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