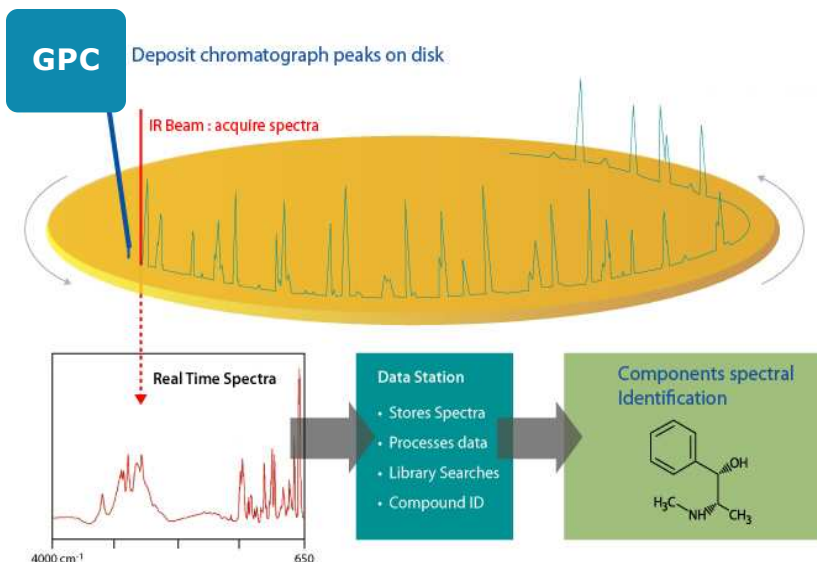
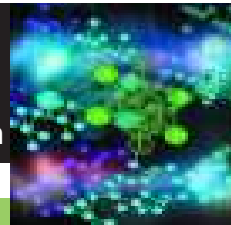


DiscovIR-GPC™

Deposition and Detection System

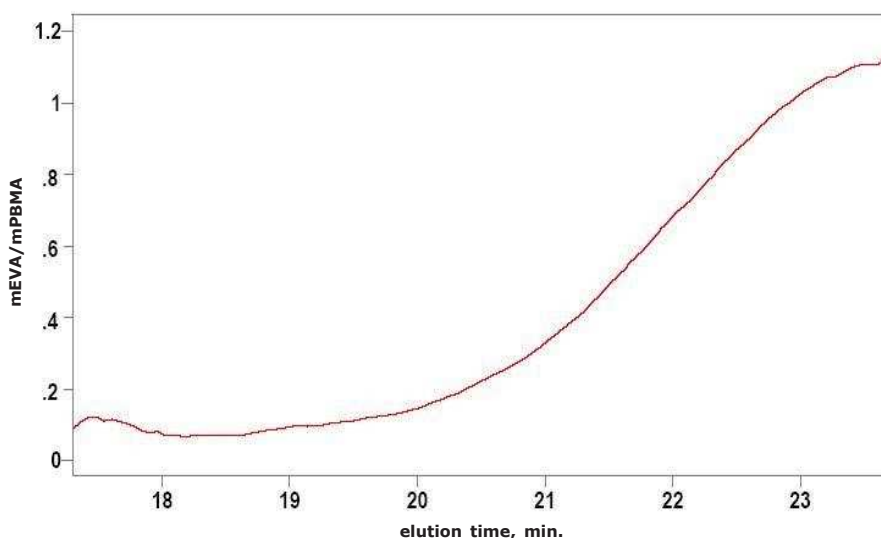


The DiscovIR-GPC is a powerful new tool for materials analysis. When connected to the outlet of a GPC column, the DiscovIR deposits GPC eluants as a continuous track on an infrared transparent substrate. The built-in interferometer simultaneously captures a set of time-ordered infrared spectra from the deposited track. The result is a map of molecular structure of all sample components.

ANALYSIS OF POLYMER BLENDS BY GPC-FTIR

SUMMARY

A polymer blend sample of Polybutylmethacrylate (homopolymer) / Ethylene-Vinyl Acetate (copolymer) was analyzed using combined GPC-FTIR to characterize molecular weight distribution of components. Molecular weight distributions of the two polymer components completely overlapped. It was nonetheless possible to map the elution distribution of the three functional groups present in the prepared samples. Shown below is the mass distribution ratio of the two polymeric components across the molecular weight elution profile.



The EVA copolymer utilized was shown to exhibit uniform composition throughout its molecular weight range. This example demonstrates the ability of the equipment utilized to rapidly and simply map components' molecular weight distributions despite overlapping elution profiles and superimposed infrared absorption bands.

INTRODUCTION

Polymer blends comprise 30 - 40% of plastics products, and are increasingly employed in the design of novel materials. Among the reasons for the popularity of polymer blends are:

- Versatility in tailoring end products' properties
- Synergistic combinations of blend ingredients to optimize orthogonal properties, such as high modulus with toughness, effective diffusional barriers with good mechanical properties, improved biodegradability and recycling characteristics
- Low investment costs in new materials design, and lower costs than copolymer solutions

Most commercial blends consist of two polymers combined with small amounts of a third compatibilizing polymer, typically a block or graft copolymer. Composition analysis of these materials can prove challenging, inasmuch as component compatibilities tend to counteract ready separation of components. Polymer blends are thus populations of independent molecular distributions, each of which can vary in MW and composition of functional groups. This application note describes deformation of a polymer blend of two polymer components with similar molecular weight distributions, hence no GPC chromatographic separation of the two components. The sample was a blend of PBMA (homopolymer-polybutyl methacrylate) and EVA (copolymer of ethylene and vinyl acetate). The two polymers used also had mostly common IR bands. One can nonetheless obtain composition distribution data from generation of specific IR chromatograms of various bands.

EXPERIMENTAL

A representative polymer blend was made up from materials obtained from Scientific Polymer Products, Inc.:

- Ethylene/Vinyl Acetate, CAT #246; vinyl acetate content 33%; molecular weight average: 150K Daltons
- Poly(n-Butyl Methacrylate), CAT #111; molecular weight average: 180K Daltons

Samples were prepared in tetrahydrofuran (THF). Chromatography was performed on a Jordi mixed bed GPC 50-cm x 10-mm OD column, using THF as the mobile phase. Column eluants were collected/scanned as solid phase deposits on a DiscovIR LC zinc selenide sample collection disk.

RESULTS

Figures 1 (below) and 2 (next page) show the spectra obtained of the two polymers.

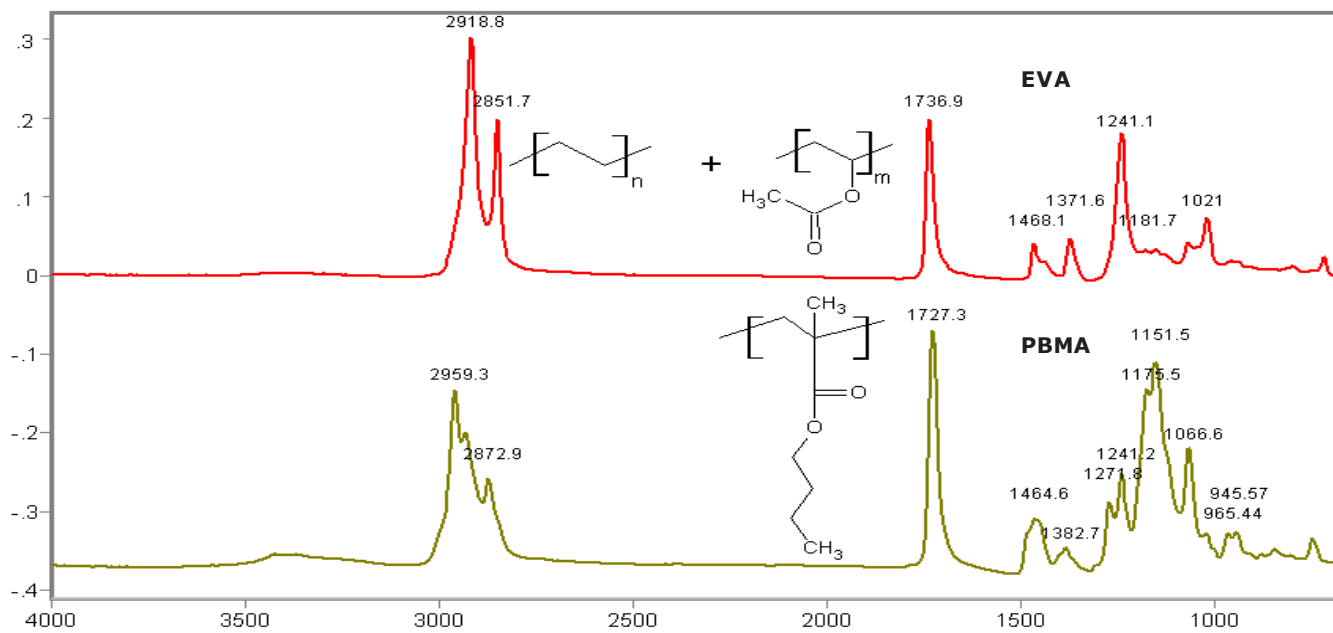


Figure 1 - Spectra of EVA (red) and PBMA (green)

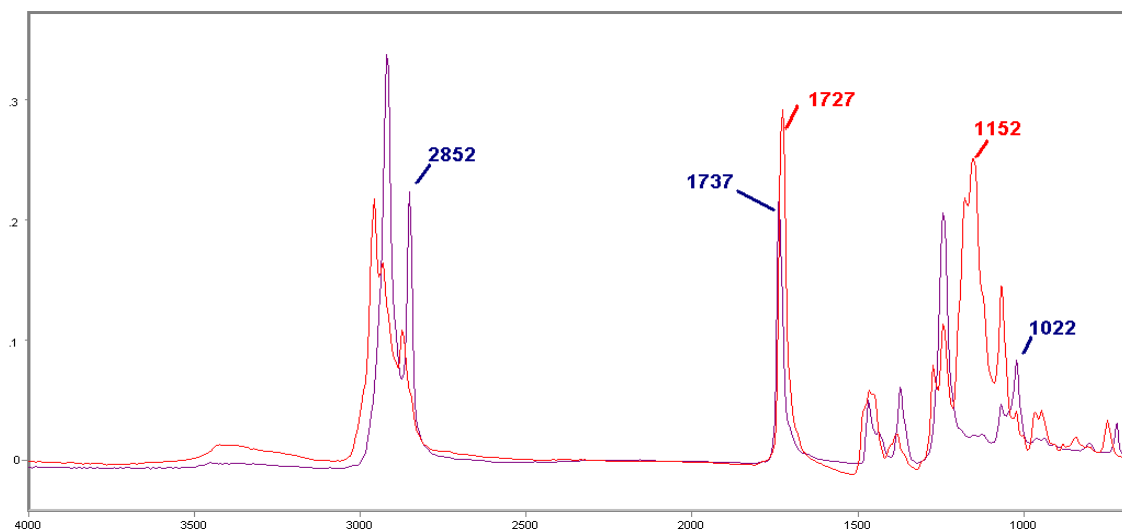


Figure 2 - EVA and PBMA overlaid spectra

The 1152 cm^{-1} (acrylate) doublet band was strong in the PBMA spectrum, and absent from the EVA. There is virtually no band in the EVA spectrum that does not have a proximate band in the PBMA spectrum. The methylene C-H stretch (EVA) bands are sharp and strong; with the symmetric stretch lying on the shoulder of the PBMA C-H stretch group. The C-O stretch (1022 cm^{-1} band) of EVA is also coincident with a weak PBMA band.

Note: The PBMA spectrum shown in the above figures includes a broad band in the 3100-3500 cm^{-1} region, typical of -OH stretching. This is not a functional group present in PBMA, and it is not evident in the chromatographically separated samples of PBMA. It is believed to be a (low MW) additive present in the PBMA sample we obtained. Given the chromatographic and spectral overlaps, it is quite challenging to extract composition mapping of this particular polymer blend.

A sample of the blend of the two polymers was injected onto a GPC column, and the eluate deposit collected in the DiscovIR-GPC.

Figure 3 displays a set of infrared chromatograms generated from this experiment (Run: EVA-PBMA).



Figure 3 - Spectral chromatograms of the EVA/PBMA sample

The PBMA and EVA have very similar overlapping molecular weight distributions. The top trace shows the elution chromatogram of the EVA-PBMA blend sample. This is the "peaks" chromatogram, generated by the DiscovIR software during data collection. The values of the peak chromatogram represent the most intense mid-IR spectral level of each subfile collected during the column elution / sample deposition. The middle trace is a band chromatogram of the 1152 cm^{-1} band (unique to the PBMA), and the bottom band chromatogram is the 2852 cm^{-1} band generated by the EVA. Note the somewhat earlier initiation of a PBMA sample as compared to EVA.

Use of Peak Ratios to Determine Compositional Drift

The spectral band intensities of samples deposited by the DiscovIR-GPC are a product of the band extinction coefficient, the relative composition of co-deposited species, and the deposit thickness from the column eluant. When the time-ordered spectral data set is processed as the ratio of two spectral bands, the deposit thickness is cancelled out, and the ratio value reflects solely the relative mass contributions of a multi-component sample. The sample described here is a blend of two polymers, one of which is a copolymer; so the analysis has to address three functional groups' composition variation.

Calibration

A set of direct injection deposits (no chromatography) was made, their purpose being to serve as calibrants. Solutions of 0.8 mg/ml PBMA (A) and 0.9 mg/ml EVA (B) were prepared. Three mixtures of these solutions in proportions listed below were made, and 10- μl aliquots were direct-injected to the DiscovIR sample collection disk. Replicate direct injections were made of the following composition samples.

Mixtures A and B	μg PBMA	μg EVA
PBMA (A)	8	0
PBMA (A)	8	0
EVA (B)	0	9
EVA (B)	0	9
75%A / 25%B	6	2.25
75%A / 25%B	6	2.25
50%A / 50%B	4	4.5
50%A / 50%B	4	4.5
25%A / 75%B	2	6.75
25%A / 75%B	2	6.75

EVA Composition Drift

A sample of 100% EVA was chromatographed, and the sample was examined for composition changes in the ethylene-vinyl acetate ratio. The 2852 cm^{-1} band was used to represent the ethylene content, and 1732 cm^{-1} to represent the carbonyl content (see Figure 4 below).

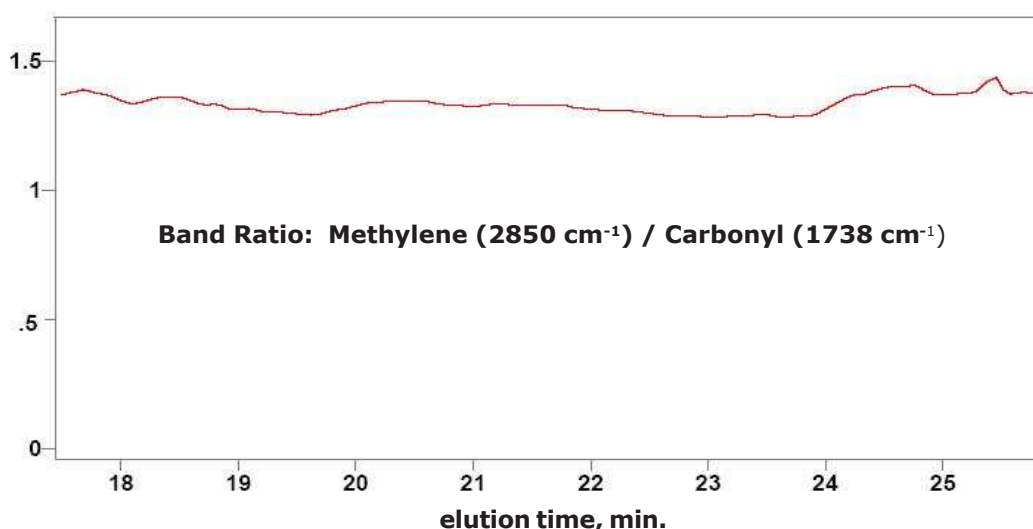


Figure 4 - EVA band ratio plot showing no variation in comonomer content.

The band ratio is basically flat across the elution profile, and indicates that this EVA material exhibits no composition drift of comonomers.

Band Ratio Analysis of the Polymer Blend

Figure 5 shows the relationship of polymer mass amounts to their absorbances at the selected frequencies of 1022 cm^{-1} (EVA) and 1152 cm^{-1} (PBMA). The data points are fit to a linear best line, whose equation is shown below.

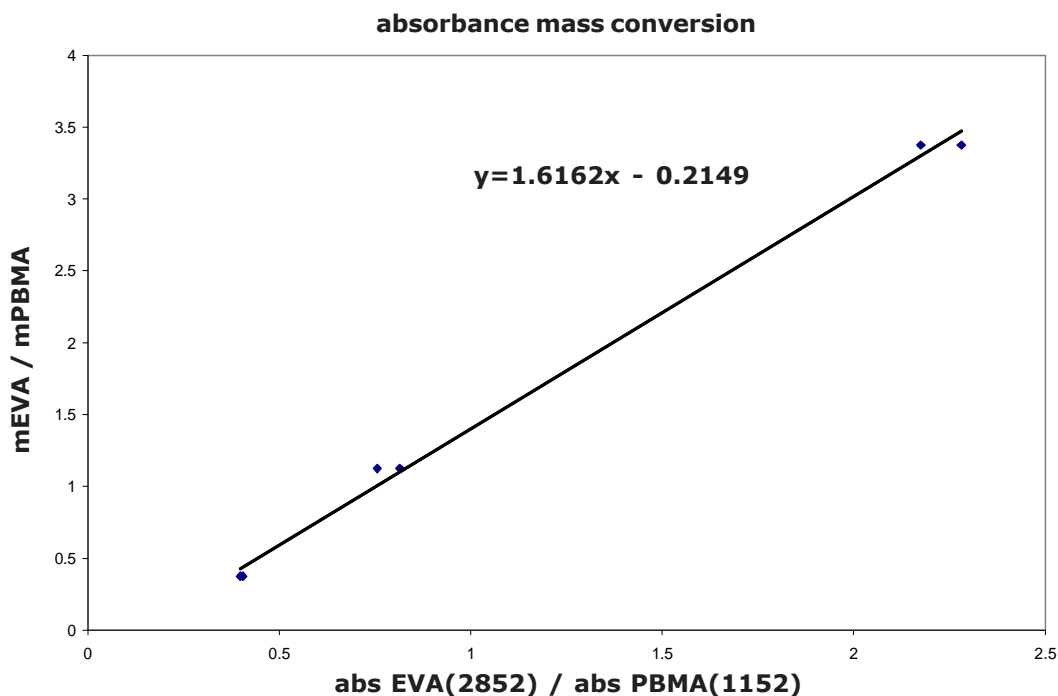


Figure 5 - Correlation of mass ratios of the two polymers to absorbance ratios

DiscovIR data collected from the prepared sample was used to generate spectral chromatograms of various specific peaks. The technique of generating peak ratio chromatograms was used, to cancel out the effects of the varying mass amounts across the elution profile. The 1022 cm^{-1} and 1152 cm^{-1} bands were selected to form an absorbance ratio chromatogram of the EVA and PBMA across the elution profile. Using the equation generated by the correlation plot in Figure 5, the absorbance ratio chromatogram was transformed to the mass ratio chromatogram of the blended polymers. Data are presented in elution times, but it is a simple matter to use column calibration data to turn the x-axis to a log-linear molecular weight axis.

The resulting GPC distribution of the two polymers is shown below in Figure 6:

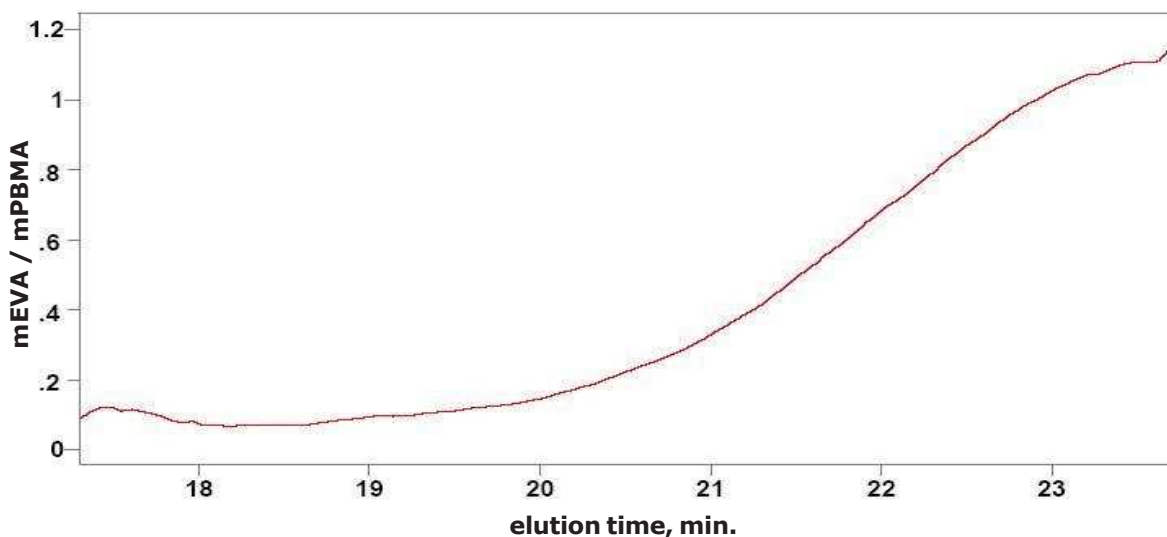


Figure 6 - EVA/PBMA composition determined by spectral peak ratios

In the initial elution phase, the EVA/PBMA ratio is $\sim 1/20$ and rises during the elution profile to approximately a 1.1/1 ratio.. This is consistent with the suppliers molecular weight values for the EVA and PBMA - 150K and 180K respectively. The PBMA elution starts slightly before the EVA. The data gets quite noisy at the tails of polymer distributions, due to forming a ratio two very small numbers, but reflects the composition trend through most of the distribution envelope. Similar results are obtained when using the 2852 cm^{-1} band rather than the 1022 cm^{-1} band for the EVA.

Band Frequency Analysis of the Polymer Blend

The carbonyl bands of the two materials largely overlap as seen in Figure 2. The EVA ester carbonyl band has a maximum intensity at 1737 cm^{-1} , and the PBMA acrylate carbonyl maximum intensity is found at 1727 cm^{-1} . Since these bands are so closely spaced, a mixture of PBMA and EVA exhibits a carbonyl peak shift, rather than two separate peaks. The position of the peak maximum is a function of the relative amounts of the two carbonyl bands in the blend sample as highlighted in Figure 7 below:

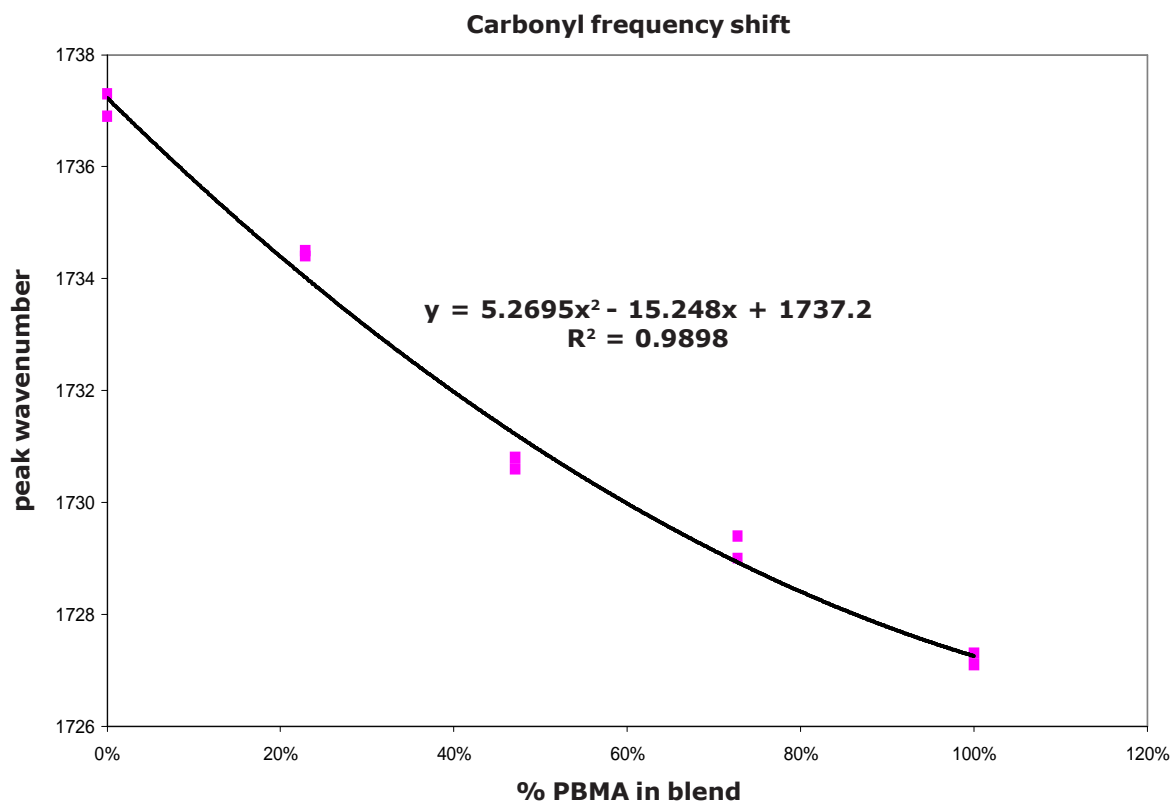


Figure 7 - Carbonyl frequency as a function of composition.

When the carbonyl frequency is plotted against composition, the result is a well correlated data set, indicating that compositional drift of this blend of polymers can also be determined directly from carbonyl frequency measurements.

Figure 8 (below) shows this peak frequency shift applied to the polymer blend elution data. Peak frequencies were determined at one-minute intervals of the elution data, and plotted against elution time. The increase in peak frequency maximum with elution time reflects the increasing proportion of EVA in the eluant. In a GPC run of a blend sample, a chromatographic plot of peak frequency vs. elution time could be generated, and then transformed to a composition vs. elution time via the fitting equation shown on the frequency shift plot. This could be advantageous especially in the tails of the polymer components distributions, where the low intensities of peak height ratio measurements become quite noisy. This is not a general solution for all polymer blends, but is attractive as a confirmatory technique. Where two bands give rise to peak splitting, it is expected that determining the first moment of the band doublet can serve to provide repeatable values similar to the data presented here.

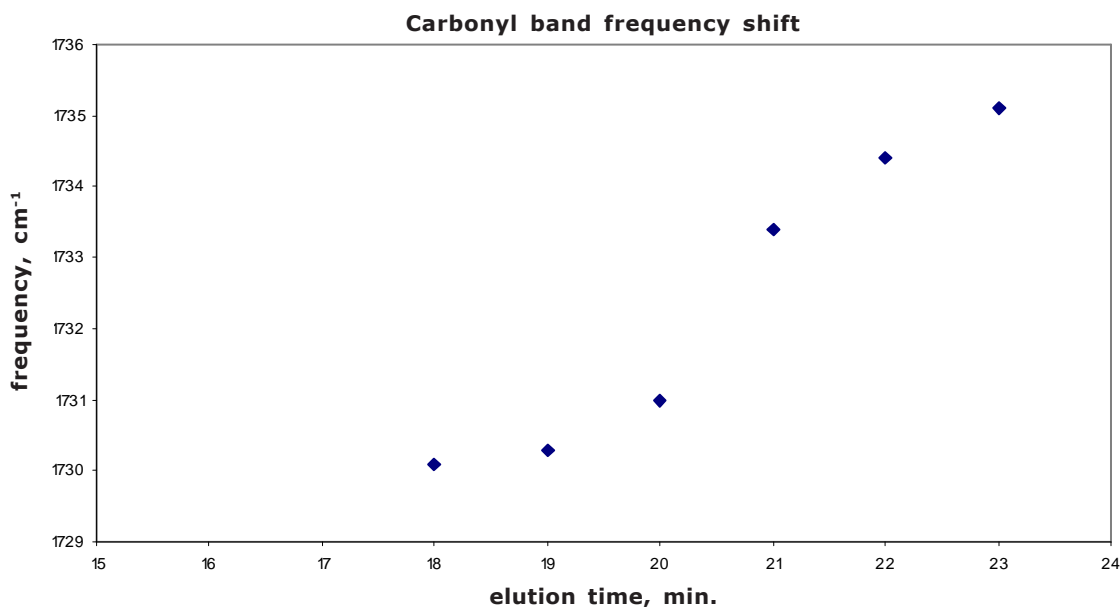


Figure 8 - Carbonyl peak frequency shift indicates changing amount of the two carbonyls

CONCLUSIONS

Characterization/deformulation of polymer blends is a time intensive process when performed by traditional fractionation methods. Fractionation of these multi-component samples is an analytical challenge.

The linking of chromatography and infrared spectroscopy provides a powerful, fast tool for this task. Spectral data processing of GPC-IR data sets allows one to identify components and map their composition, despite overlaps in chromatographic separation and infrared spectral bands.