Rapid Identification of Bulk Mixture Components of an Ethylene/Vinyl Acetate Copolymer Blend Using Pre-computed ATR-FTIR Mixture Spectra

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Purpose: Rapid identification of polymer mixtures and additives

Introduction

Using libraries of pre-computed ATR-FTIR mixture spectra and a conventional library of ATR-FTIR polymer spectra, we have identified three major components from a single ATR-FTIR spectrum of a sample labelled "EVA".

Experimental

Spectra were run on an ATR with a monolithic diamond crystal. No baseline correction was performed. Optical resolution was 2 cm^{-1}.

Search Method

The full range of the sample spectra were searched against the libraries, except where noted. The search algorithms were correlation coefficient (CC) or correlation coefficient derivative (CCD). The libraries used were the

- **FDM ATR Polymers Diamond**, [resins, polymers, copolymers, terpolymers, monomers, plasticizers and polymer additives]

- **FDM ATR Plastics Kit**, which consists of these four libraries:
    - (i) FDM ATR Resins Two Components
    - (ii) FDM ATR Resins and Fillers
    - (iii) FDM ATR Resins and Plasticizers
    - (iv) FDM ATR Resins and Polymer Additives

In this work (i) and (iv) were searched.

Discussion:

Initial inspection immediately suggested that the "EVA" spectrum was too complex to be simply EVA (Ethylene/vinyl acetate). Direct comparison with an EVA spectrum from the **FDM ATR Polymers Diamond** showed dozens of extra peaks. See Figure 1.

Searching the "EVA" spectrum against **FDM ATR Polymers Diamond** confirmed the essential EVA character but suggested a variety of polymer additives.

To see if another resin was present the sample was searched against the **FDM ATR Resins Two Components** library. See Figure 2.
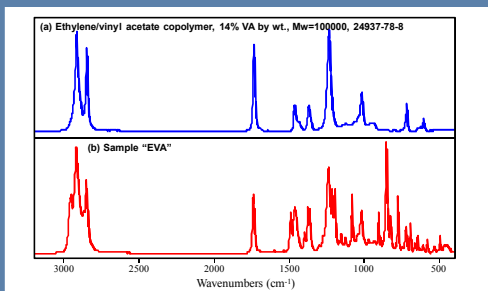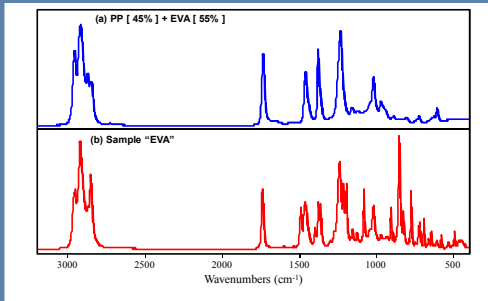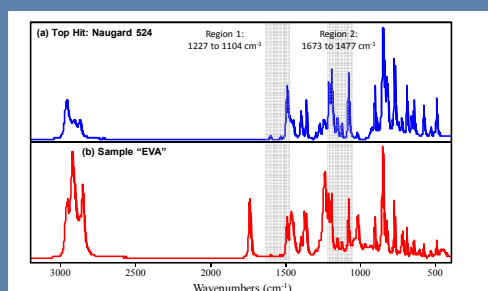

FIGURE 1: Sample is too complex to be simply EVA.

(a) Ethylene/vinyl acetate copolymer, 14% VA by wt., Mw=100000, 24937-78-8

(b) Sample "EVA"

Wavenumbers (cm^{-1})

FIGURE 2: Polypropylene is found by searching the FDM ATR Resins Two Components.

(a) PP [45%] + EVA [55%]

(b) Sample "EVA"

Wavenumbers (cm^{-1})

Noticing there were still peaks unaccounted for, we searched the regions of 1220-1062 cm^{-1} and 1673-1407 cm^{-1}. Both results produced strong hits for the polymer additive Naugard 524. See Figure 3. Thus, we have a strong case for the "EVA" sample being largely composed of EVA, PP and Naugard 524. Note the distinctiveness in the scores between the top two hits and the third hit in both hit lists.

**FIGURE 3: The polymer additive Naugard 524 is identified.**

(a) Top Hit: Naugard 524

Region 1: 1227 to 1104 cm^{-1}

Region 2: 1673 to 1477 cm^{-1}

(b) Sample "EVA"

Wavenumbers (cm^{-1})

FDM ATR Polymers Search Results 1227-1104 cm^{-1}

Score	Name
0.9375	Naugard 524; Tris(2,4-di-t-butylphenyl)phosphite, 31570-04-4
0.9367	Irgafos 168; Tris(2,4-ditert-butylphenyl)phosphite, 31570-04-4
0.5483	Tetrakis(2,4-di-tert-butylphenyl)-1,1-biphenyl-4,4'-diylbisphosphonite…
0.5388	Sandostab P-EPQ, 119345-01-6
0.4757	Polystyrene, 90% isotactic, Mw=400000, 9003-53-6

FDM ATR Polymers Search Results 1673-1477 cm^{-1}

Score	Name
0.9727	Naugard 524; Tris(2,4-di-t-butylphenyl)phosphite, 31570-04-4
0.9714	Irgafos 168; Tris(2,4-ditert-butylphenyl)phosphite, 31570-04-4
0.8783	Poly(4-chlorostyrene), Tg=110, 24991-47-7
0.8266	PEEK Rod, Polyether ether ketone, Ge xtal
0.7972	Isodecyl diphenyl phosphate, 29761-21-5

To confirm the analysis, a three component mixture library was created (by digitally combining ATR-FTIR spectra to model varying relative concentrations of EVA, PP and Naugard 524) and appended to the **FDM ATR Resins and Polymer Additives**. The "EVA" spectrum was searched against the updated library. Figure 4 shows a score of 0.9567 for the first hit and visual inspection confirms that essentially all peaks have been accounted for.

FIGURE 4: The sample labelled "EVA" is EVA and PP and Naugard 524; (Tris(2,4-di-t-butylphenyl)phosphite).

(a) Top Hit: PP [30%] + EVA [35%] + Tris(2,4-di-t-butylphenyl)phosphite [35%]

(b) Sample "EVA"

Wavenumbers (cm^{-1})
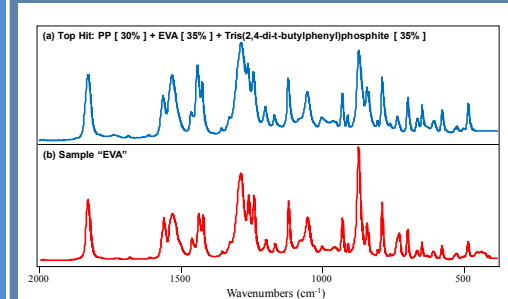
Three Component Mixtures Search Results

Score	Name
0.9567	PP [30%] + EVA [35%] + Tris(2,4-di-t-butylphenyl)phosphite [35%]
0.9538	PP [25%] + EVA [40%] + Tris(2,4-di-t-butylphenyl)phosphite [35%]
0.9538	PP [25%] + EVA [35%] + Tris(2,4-di-t-butylphenyl)phosphite [40%]
0.9537	PP [30%] + EVA [40%] + Tris(2,4-di-t-butylphenyl)phosphite [30%]

Conclusions

Searching a single spectrum against the **FDM ATR Polymers Diamond** and the **FDM ATR Plastics Kit** is shown to be effective for identifying bulk components in a plastic material.

The concept of libraries of pre-computed mixture spectra was validated by generating additional pre-computed mixture spectra and finding they are extremely similar to the original sample spectrum.

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