Characterization of inorganic fillers in complex matrices using mid-IR and far-IR Spectroscopy

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Overview

Purpose: To study the effects of spectral range on the identification and quantification of inorganic fillers in polymer composites.

Methods: A multi-range Fourier transform infrared spectrometer (FTIR) capable of both mid-infrared (mid-IR) and far-infrared (far-IR) measurements was used to spectroscopically examine inorganic fillers and polymers. An integral Diamond Attenuated Total Reflectance (ATR) accessory was used for all reported measurements.

Results: The minimum detectable amount of inorganic filler in a polymer matrix is dependent on the filler/polymer pairing studied and the spectral range selected for analysis. In general, the far-IR spectral range had lower detection limits for the filler/polymer pairs examined in this study .

Introduction

Inorganic powders are often added to polymers to alter the mechanical and optical properties of the composite material. Spectroscopically characterizing these composite materials improves with the use of a multi-range FTIR system. The mid-infrared spectral range is used to identify the components of composite materials including the polymers, fillers and additives. The far-infrared range is needed in to study filled-polymers because some inorganic fillers absorb only in the far-IR region or have mid-infrared bands that overlap with other components of the composite material. These measurements were made using a purged FTIR system, a single infrared source and one infrared detector, obviating the need for a costly vacuum FTIR system. The successful identification of filler material in the different polymer matrices is shown and the minimum detectable amount of filler determined for the filler/polymer pairings studied in both the mid-IR and far-IR spectral ranges.

Methods

Sample Selection

Three polymers: polypropylene (PP), polyethylene (PE) and polyethylene terephthalate (PET) and four inorganic fillers: talc, titanium (IV) oxide (anatase), calcium carbonate and fused silica where chosen for this study due to their extensive use in composite materials.

Sample Preparation

Samples were analyzed "as is" for both far-IR and mid-IR analyses. For the inorganic fillers, enough powder was placed onto the Diamond surface to cover it (~1-3 milligrams) and the pressure device used to force the sample into contact with the Diamond crystal. The slip clutch feature of the pressure tower enables consistent pressure to be applied to each sample. The polymer films were placed over the Diamond surface and pressure applied in the same manner as the powder samples. Isopropanol was used to clean the Diamond crystal and pressure tower tip after each sample spectrum was obtained.

FTIR Analysis Methods

Samples were analyzed using the Thermo Scientific™ Nicolet™ iS™50 FTIR spectrometer system. Far-IR Attenuated Total Reflection (ATR) measurements were made using a built-in Diamond ATR accessory, solid substrate beamsplitter and standard IR source. Mid-IR ATR measurements were made using a built-in Diamond ATR accessory, potassium bromide (KBr) beamsplitter and standard IR source. All spectra were obtained using 64 scans at 4 cm^{-1} resolution; total analysis time was three minutes per sample. The data were collected and processed using Thermo Scientific™ OMNIC™ software.

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FIGURE 1. Thermo Scientific™ Nicolet™ iS™50 FTIR FTIR System with integral Diamond ATR

Results

FTIR Analyses

Four inorganic fillers and three polymers were analyzed using both mid-IR and far-IR spectral ranges to evaluate the impact of spectral range on identifying inorganic fillers in composite polymers. A Diamond ATR accessory was used for all spectroscopic measurements. The minimum amount of filler material expressed in weight percent was determined for each filler/polymer pairing. In general, the minimum detectable amount of inorganic filler varied with the spectral range used and the filler/polymer pairing.

FIGURE 2. Mid-IR spectra of inorganic fillers obtained using a Diamond ATR

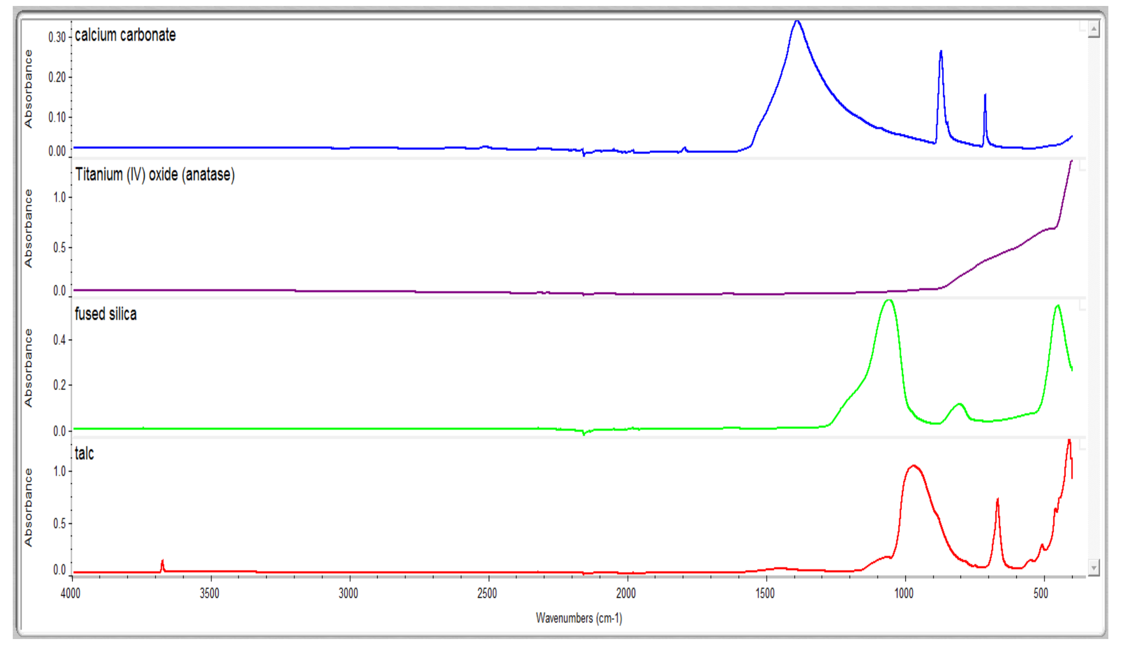
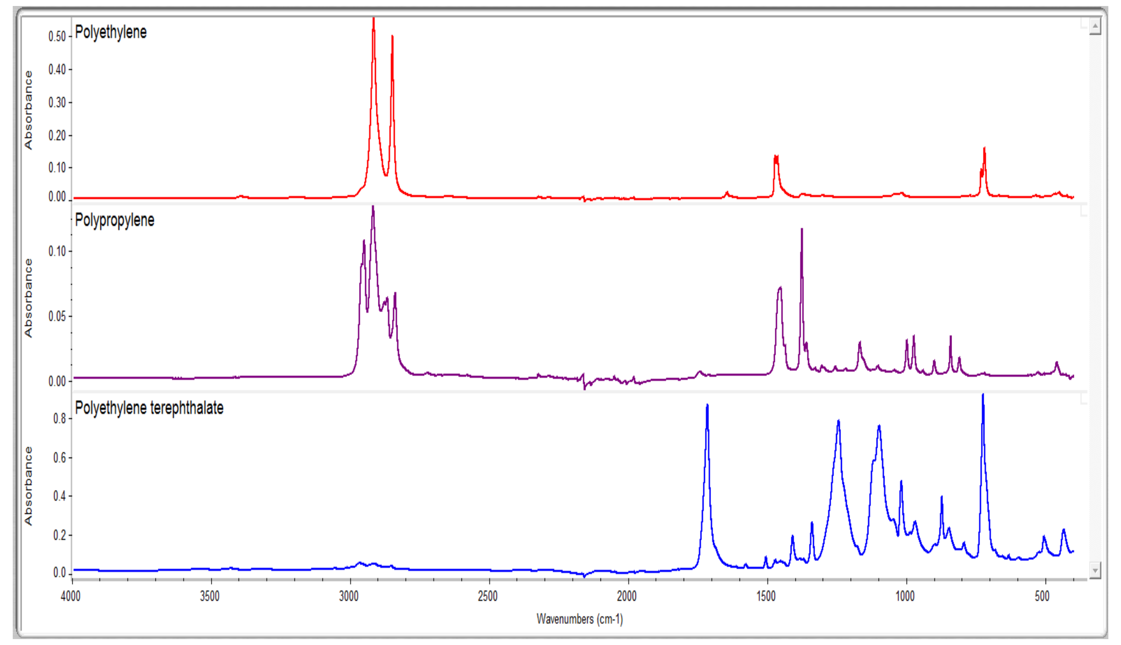


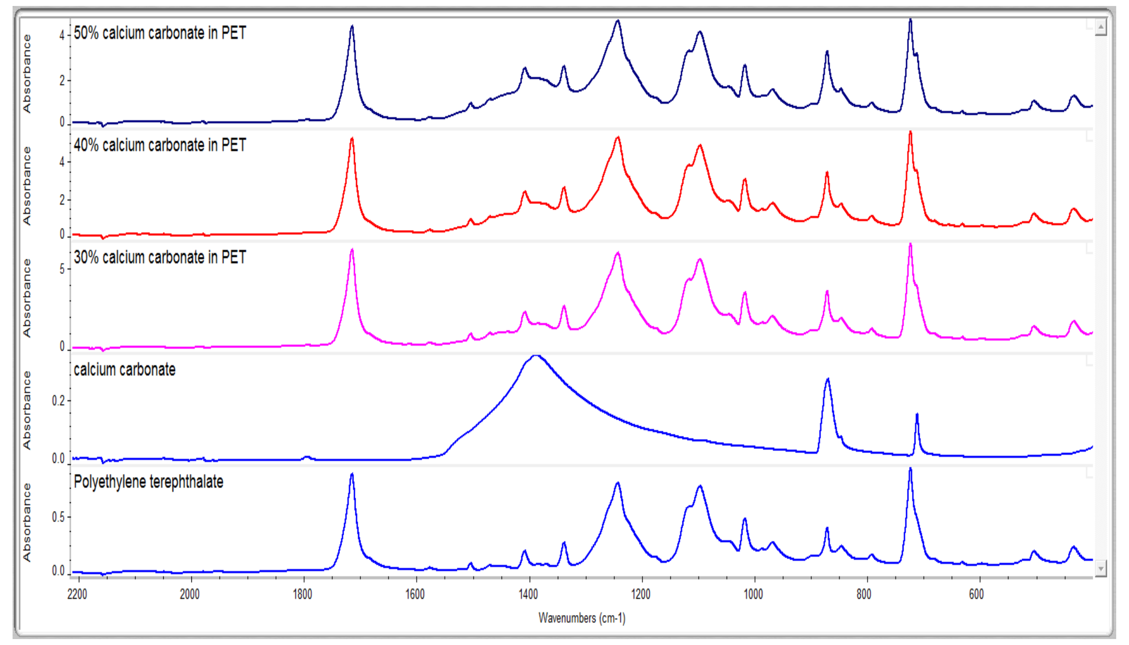
FIGURE 3. Mid-IR spectra of common polymers obtained using a Diamond ATR



Presence testing for calcium carbonate in PET composites using Mid-IR ATR

Mid-IR ATR spectra of a PET polymer and calcium carbonate filler were obtained. Linear combinations of the polymer and filler spectra were then used to create composite spectra in the 10% to 50% filler in polymer range. The calculated spectra were used to determine if the presence of the filler material could be established with high confidence. In figure 4, the presence of calcium carbonate is not easily discerned from the mid-IR spectrum until a concentration of ~40% because the calcium carbonate spectral peaks at 1838, 870 and 712 cm^{-1} are masked by the PET peaks.

FIGURE 4. Calculated spectra of 30%, 40% and 50% calcium carbonate filler in PET shown with mid-IR spectra of PET and calcium carbonate



Presence testing for calcium carbonate in PP composites using Mid-IR ATR

Linear combinations of PP polymer and calcium carbonate filler spectra were calculated in the 10% to 30% filler range to determine if the presence of the calcium carbonate filler material could be established with high confidence. In figure 5, the presence of calcium carbonate is readily seen even at the lowest concentration of calcium carbonate studied (10%). The calcium carbonate absorbance peaks at 712 and 870 cm^{-1} are easily seen at all concentrations studied. Figure 6 summarizes the minimum amount of filler needed to detect its presence in a given polymer matrix and lists the mid-IR spectroscopic peaks used for each filler.

FIGURE 5. Calculated spectra of 10% and 20% calcium carbonate in PP shown with mid-IR spectra of PP and calcium carbonate

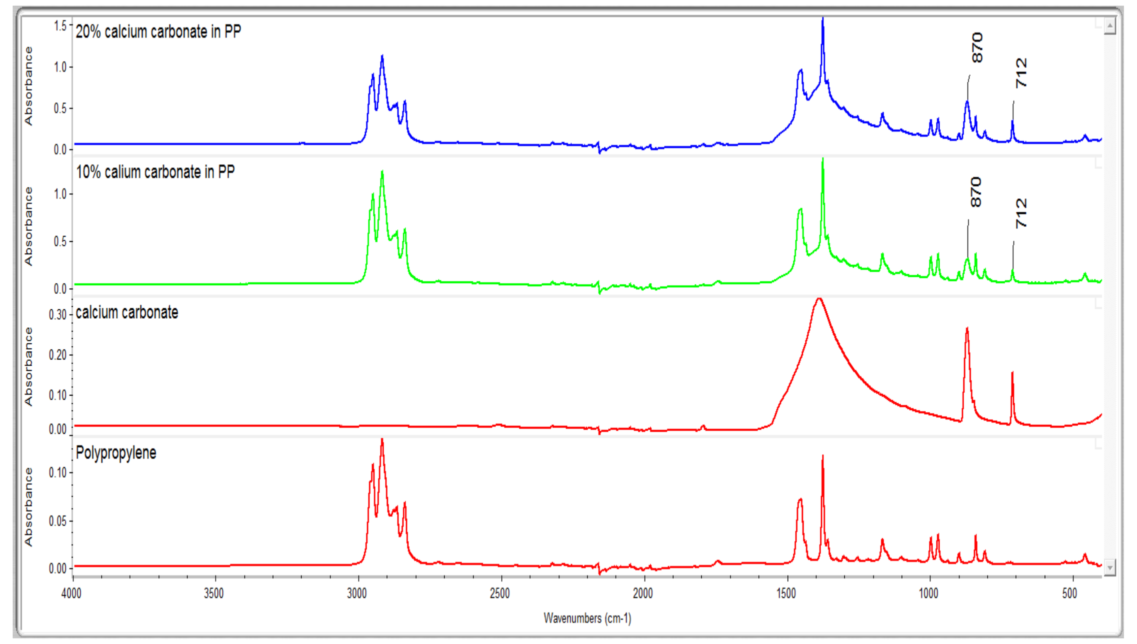


FIGURE 6. Mid-IR detection limits for each filler/polymer pairing

Minimum wt% of filler detected in polymer matrix for Mid-IR ATR

	Calcium carbonate	Titanium (IV) oxide	Fused Silica	Talc
	1839, 870, 712 cm-1	no defined peak	1062, 807, 452 cm-1	3674, 971, 667 cm-1
PET	40%	n/a	40%	10%
PP	10%	n/a	10%	10%
PE	10%	n/a	10%	10%

Far-IR ATR Analyses

The integral Diamond ATR accessory with solid substrate beamsplitter was used to obtain far-IR spectra of four inorganic filler and three common polymers to evaluate the usefulness of the far-IR ATR technique in identifying the presence of inorganic fillers in polymer composites. The far-IR spectral range used is 1800 to 100 cm^{-1}.

FIGURE 7. Far-IR spectra of inorganic fillers obtained using a Diamond ATR

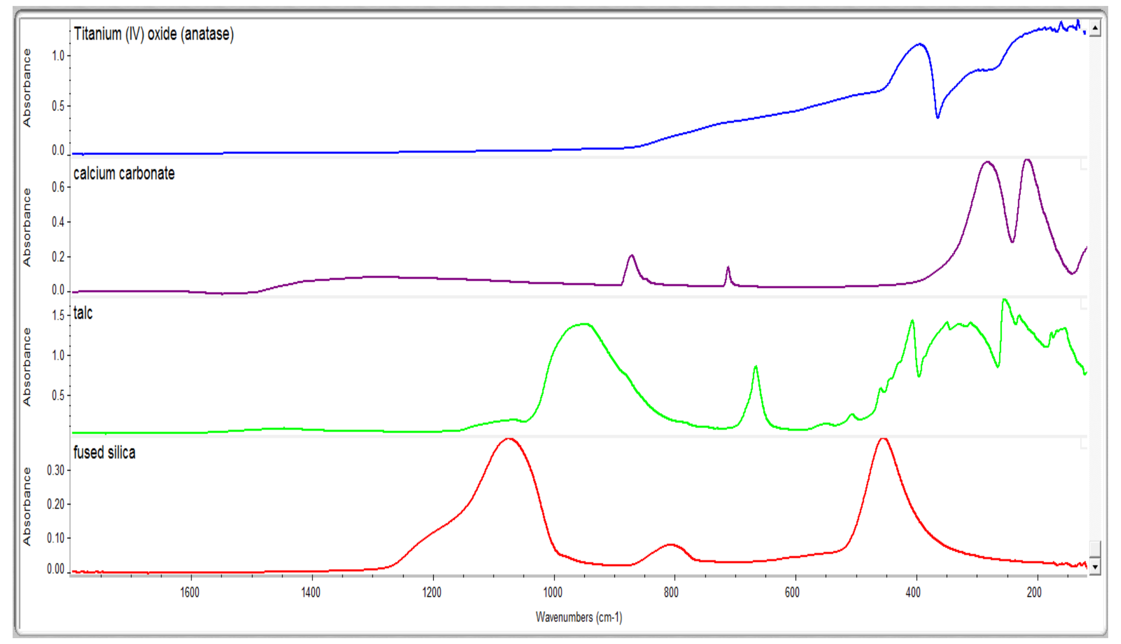
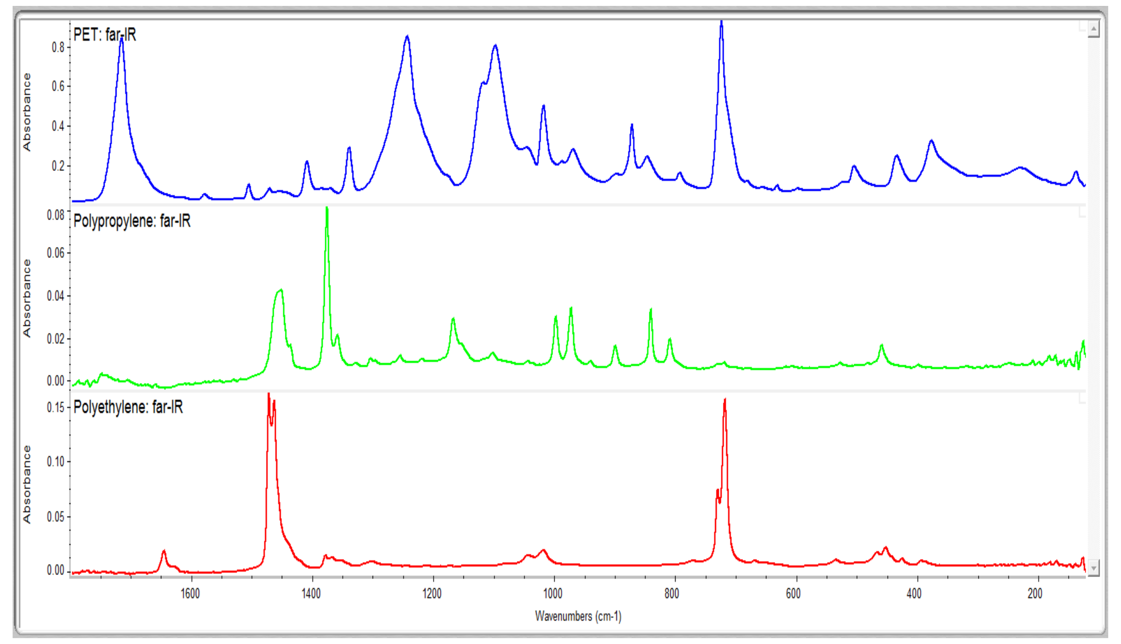


FIGURE 8. Far-IR spectra of common polymers obtained using a Diamond ATR



Presence testing for calcium carbonate in PET composites using Far-IR ATR

Far-IR ATR spectra of PET and calcium carbonate were obtained. Linear combinations of the pure polymer and pure filler spectra were used to calculate the composite spectra in the range of 10% to 50% filler to polymer. The calculated spectra were then used to determine if the presence of the calcium carbonate filler material in the composite spectra could be established with high confidence. In figure 8, the presence of calcium carbonate is readily seen even at the lowest concentration of calcium carbonate studied (10%). The calcium carbonate absorbance peak at 281 cm^{-1} is readily observed at all concentrations studied. Figure 10 summarizes the minimum amount of filler needed to detect its presence in a given polymer matrix and the peak positions used for each inorganic filler.

FIGURE 9. Calculated far-IR spectra of 10% and 20% calcium carbonate in PET shown with spectra of PET and calcium carbonate standards for comparison

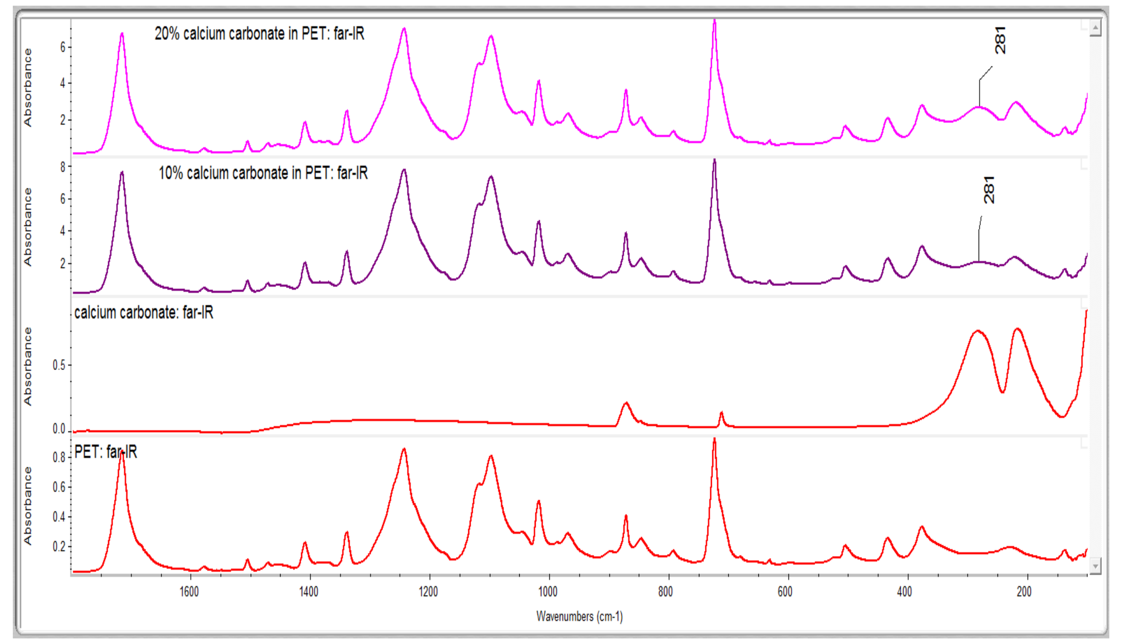


FIGURE 10. Mid-IR detection limits for each filler/polymer pairing

Minimum wt% of filler detected in polymer matrix for Far-IR ATR

	Calcium carbonate	Titanium (IV) oxide	Fused Silica	Talc
	281, 218 cm-1	395, 298 shoulder cm-1	452 cm-1	406, 350, 327 cm-1
PET	10%	50%	40%	10%
PP	10%	10%	10%	10%
PE	10%	10%	10%	10%

Conclusion

- **A multi-range FTIR system configured with an integral Diamond ATR accessory was used to analyze common inorganic fillers and common polymers. Detection limits for twelve filler/polymer pairs were estimated for both the mid-IR and far-IR spectral ranges.**
- **The presence of Titanium (IV) oxide filler in polymer matrices is best studied using the far-IR spectral range.**
- **PET was the most challenging polymer matrix to detect the presence of the inorganic fillers studied. The far-IR ATR approach gave lower detection limits for the fillers in the PET matrix than the mid-IR ATR approach.**