

Using FT-Raman Spectroscopy for Quantitative Determination of High Filler Content in Particulated Composites

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ABSTRACT: FT-Raman spectroscopy was used as an alternative to typical thermogravimetric techniques in order to determine the filler content in calcium carbonate/high-density polyethylene composites. As predicted, the selected band ratio had good linearity with the volume fraction ratio of filler and matrix even at a high filler content, up to 75% of the weight fraction. FT-Raman spectroscopy provided comparable results compared to values obtained from thermogravimetric analysis. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1947–1954, 2000

Key words: FT-Raman; quantitative analysis; thermogravimetry; particulate-filled composites; filler content

INTRODUCTION

The use of particulated composites in engineering applications has grown rapidly as an alternative to using costly engineering plastics. The combination of commodity polymers—for example, polyethylene and polypropylene—and rigid fillers has modified properties of the materials to a certain extent, depending on various parameters, namely, type of matrix, type of filler, the ratio of matrix/filler, interface integrity, and so forth.^{1–4} Among these, the actual content of the fillers in the composites is a crucial factor in determining the properties of composites. Although the amount and ratio of raw materials, fillers, and matrix can be calculated and weighted prior to processing, it is not certain that the resulting composite pellets contain a filler content similar to the nominally calculated values. The loss of filler from the composites can occur as a result of

problems from various sources—for example, loss at the feed-in section or hopper, or fillers not being commingled in the matrix during mixing because processing conditions are not well defined, especially at a high filler fraction.

Therefore, the determination of filler content present in the composite or in the end product is important in order to ascertain that such materials possess the properties as initially designed. Various techniques have been employed as tools to measure the filler content. A simple burning test, which employs high temperature to burn out the volatile organic matrix, leaving only the non-volatile inorganic fillers as an ash, is one popular method.⁵ Thermogravimetric analysis is an instrumented version of the burning test in which the weight change while heating the sample at a controlled heating rate is monitored and precisely measured by an instrument.⁶ Also reported on have been other quantitative techniques that could possibly be used, including Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR).^{7–10} Indirect method such as image analysis of the polished section of

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the sample coupled with mathematical computation was also employed in some cases.^{11–12}

Although these methods can be used to determine the filler content in the composites, they are destructive, difficult, and sometimes complicated to implement. In recent years Raman spectroscopy has received greater interest as a tool for identifying the unknown substance and for studying several properties of the materials.^{13–15} Raman spectroscopy's advantage is the virtually absence of sample preparation because the shift in scattered frequency is detected instead of absorption, as would happen with its counterpart, infrared spectroscopy. Thus this technique is nondestructive and can be rapidly carried out. Although Raman spectroscopy is mainly utilized as a qualitative identification tool, it can also be employed as an alternative method of quantitative analysis. In the past the limitations of its laser and low-resolution detector of this instrument have restricted the use of Raman technique as a quantitative tool. However, in recent years the development of a new, reliable laser and advances in optical tools such as grating and filter and a high-resolution detector have permitted the use of Raman spectroscopy as a quantitative analyzing tool. Thus, Raman has become a common alternative to the IR technique in determining the composition of a sample. When using Raman as a quantitative tool, absolute intensities are difficult to determine because they depend on several factors, including the instrumental profile, incident laser power, absorptivity of the material, and concentration of the materials. Therefore, an internal or external standard is required to achieve a quantitative result. However, the study of Raman spectroscopy as a quantitative tool has been confined to liquid mixtures in low-concentration ranges.^{16–19} A solid mixture is less attractive probably because the Raman intensity of a powder mixture depends not only on the concentration of each component in the mixture but also on particle size, density of packing, and homogeneity of the mixtures.¹⁷ This article reports on quantitative analysis using FT-Raman spectroscopy on calcium carbonate-filled polyethylene solids in a range from low to very high filler content, up to approximately 75% weight fraction. Results obtained using the FT-Raman technique were compared to results acquired from typical thermogravimetric analysis in order to validate the relationship between the Raman intensities ratio and the filler concentration in the composites.

EXPERIMENTAL

Materials and Methods

Materials

Used in this study were high-density polyethylene-grade (HDPE) 7000F (melt flow index 0.04 g/10 min), in the form of pellets (obtained from Bangkok Polyethylene Co., Ltd., Thailand), and calcium carbonate powder-grade Omega (average particle size 5.53 μm), supplied by Lime Quality Co., Ltd., Thailand. The densities of the polyethylene and calcium carbonate were 0.956 and 2.70 mg m^{-3} , respectively.

Sample Preparation

CaCO_3 powder and HDPE pellets were first pre-mixed mechanically at various fractions, and the mixtures were then fed into a corotating twin screw extruder (Betol BTS40L), producing composites with filler volume fractions ranging from 0.10 to 0.60. Unfilled polyethylene was processed in a similar manner as a control. The composite pellets were then powderized by a centrifugal mill through a screen mesh 0.5 mm with the help of liquid nitrogen to prevent oxidation. Compression molding was used to prepare 4-mm-thick isotropic sheets of these composites.

Thermogravimetric Analysis (TGA)

After processing, measurement of the filler content in the composites was performed by a thermogravimetric analyzer (Perkin-Elmer TGA System 7). Small pieces of the composites were cut from the compression-molded plates and then scanned in the instrument at temperatures ranging from room temperature to 600°C at the rate of 20°C/minute. Changes in weight of the samples were monitored and then analyzed by the TGA analysis program.

FT-Raman

All spectra were obtained with a Perkin-Elmer FT-Raman spectrometer system 2000R supplied with radiation of 1064 nm from a Nd^{3+} :YAG laser and a InGaAs detector. The power was set at 400 mW, and the scanning number was 150 with a resolution of 4 cm^{-1} . The laser spot size was approximately 300 μm . Back-scattered light from all polarization directions was collected by the lenses and went to the Michelson-Mosley interferometer. The sample was in the form of 4-mm-thick

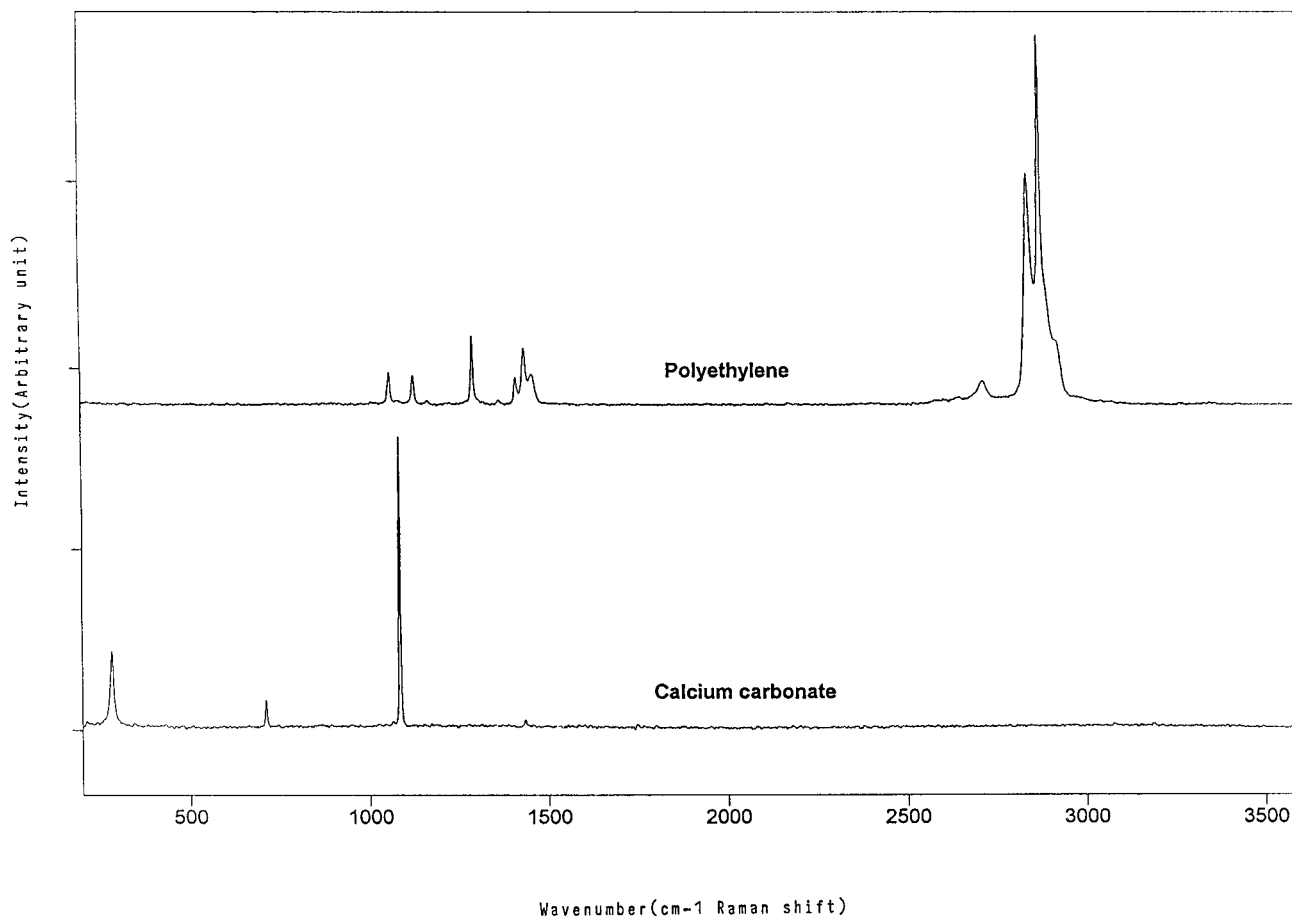


Figure 1 Raman spectra of HDPE and calcium carbonate.

compression-molded plaque. For each volume fraction, duplicate runs were carried out according to the procedure indicated.

RESULTS AND DISCUSSION

The Raman spectra of two raw materials—namely, high-density polyethylene (HDPE) and calcium carbonate—are shown in Figure 1. For HDPE, the characteristic Raman bands from C—H stretching were observed at 2881 and 2847 cm^{-1} . Other bands that appeared were C—C stretching vibrations at 1129 and 1062 cm^{-1} , a C—H twisting vibration at 1295 cm^{-1} , and C—H bending vibrations at 1416 and 1439 cm^{-1} .²⁰ Calcium carbonate showed only one prominent characteristic carbonate band, at 1086 cm^{-1} . Other less prominent bands were seen at 712 and 282 cm^{-1} . From the appearance of these spectra, it was observed that the Raman bands of two raw materials in this composite were clearly sepa-

rated from one another, with no overlapped bands.

Typical Raman spectra of the composites produced at various filler volume fractions ranging from 0.10 to 0.40 are illustrated in Figure 2. It can be seen that the spectra contain the bands characteristic of both calcium carbonate and HDPE. As the filler loading was increased, the intensity of the calcium carbonate-assigned band (1086 cm^{-1}) was increased, while the intensity of the bands that belonged to HDPE was decreased. Therefore, it was concluded that it is possible to use the intensity of calcium carbonate and HDPE as a determinant of the concentration, or volume fraction, of the calcium carbonate in the composites.

Theoretically, the intensity of Raman bands depends on a complex expression involving the scattering-light parameter and the polarizability tensor of a molecule. In the case of quantitative analysis, a less rigorous relationship can be used, which is analogous to the Beer-Lambert law in

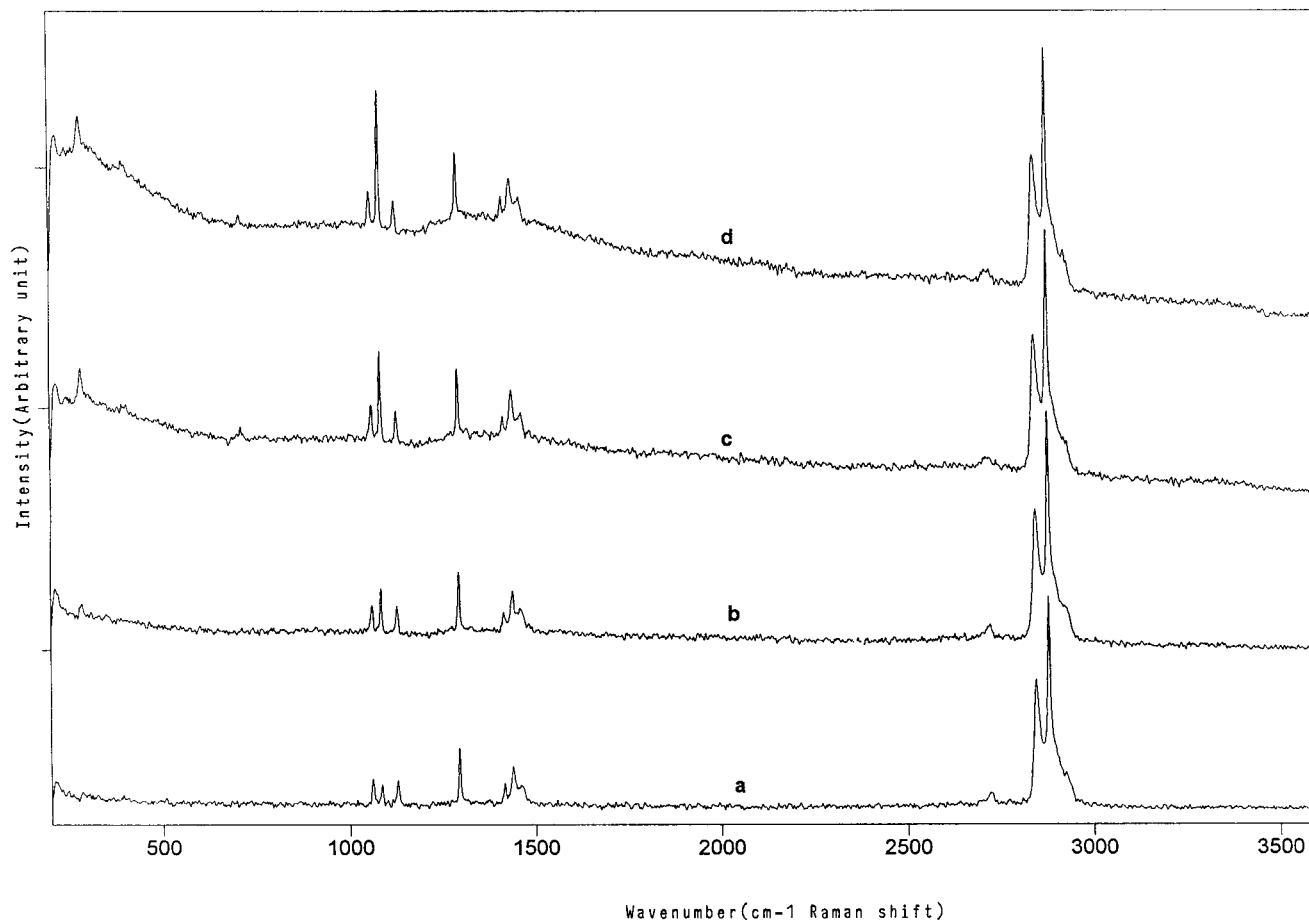


Figure 2 Raman spectra of various composites: (a) 0.1 v/v; (b) 0.2 v/v; (c) 0.3 v/v; (d) 0.4 v/v.

the case of infrared intensities. The scattering intensity of the Raman band (I) can be expressed as

$$I = K \cdot S \cdot C \cdot I_0 \quad (1)$$

where I_0 is the intensity of the exciting radiation, S is the volume of the sample illuminated by the laser source and viewed by the spectrometer, C is the concentration of the sample, and K is the constant for each band. Therefore, the scattering intensity is proportional to the concentration of the scattering species. The concentration can be found if the absolute values of S and K can be determined, which are rather difficult to achieve.

However, for a system of binary mixture, where the spectra of both components are measured under the same experimental conditions, as in this experiment, the problem can be simplified. According to eq. (1), the Raman intensity of calcium carbonate in the composite can be stated as

$$I_{ca} = K_1 \cdot S \cdot V_{ca} \cdot I_0 \quad (2)$$

where I_{ca} is the intensity of calcium carbonate, V_{ca} is the filler volume fraction that represents the filler content, and K_1 is the constant for the calcium carbonate band.

This is also true for HDPE, which is

$$I_{pe} = K_2 \cdot S \cdot V_{pe} \cdot I_0 \quad (3)$$

where I_{pe} is the intensity of HDPE, V_{pe} is the volume fraction of the matrix, and K_2 is the constant for each HDPE band.

Dividing eq. (2) by eq. (3) gives

$$\frac{I_{ca}}{I_{pe}} = \frac{K_1 S V_{ca} I_0}{K_2 S V_{pe} I_0} \quad (4)$$

Provided that the spectra were recorded at the same laser power and other conditions were the same, eq. (4) can be reduced to

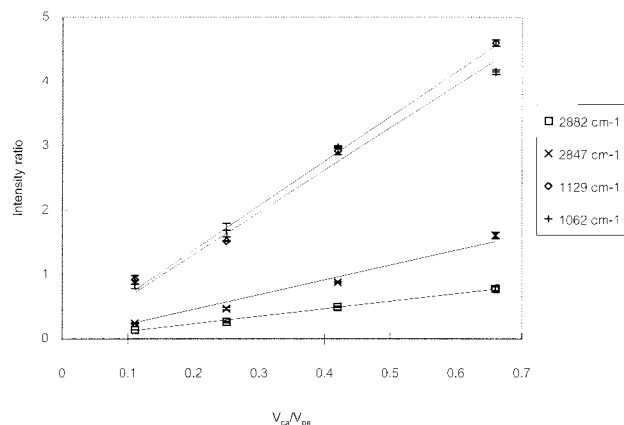


Figure 3 Raman intensity ratio versus volume fraction ratio for selected bands.

$$\frac{I_{ca}}{I_{pe}} = A \frac{V_{ca}}{V_{pe}} \quad (5)$$

where A is a constant.

From this relationship it is obvious that the plot between $\frac{I_{ca}}{I_{pe}}$ and $\frac{V_{ca}}{V_{pe}}$ should yield a linear line with a slope equaling the value of A , depending on the selected band, and that it intercepts the y axis at zero. One calcium-carbonated band, 1086 cm^{-1} , and four HDPE-assigned bands, 2861 , 2847 , 1129 , and 1062 cm^{-1} , were selected for analysis because of the strong and isolated characteristic. Figure 3 shows the plots of the intensity ratio of these Raman bands, $\frac{I_{1086}}{I_{2861}}$, $\frac{I_{1086}}{I_{2847}}$, $\frac{I_{1086}}{I_{1129}}$ and $\frac{I_{1086}}{I_{1062}}$, versus the volume ratio between the theoretical filler content of composites produced and the polyethylene fraction. The intensity of each band was then calculated by locating the start and the end of the band using the first-derivative method. A linear line was drawn connecting these two points, and then the height from this baseline up to the peak was determined.

From the curves it can be seen that all are linear and approach zero interception at zero filler volume fraction, as eq. (5) predicted. From a linear regression analysis of the curves, for which the y intercept in the fitting equation was fixed to zero, it was found that the correlation coefficient was greater than 0.98 for all cases (Table I). Thus, filler volume fraction (V_f) may be calculated from the intensity ratio as

For 2882 cm^{-1} Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{1.17} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (6a)$$

For 2847 cm^{-1} Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{2.29} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (6b)$$

For 1129 cm^{-1} Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{6.91} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (6c)$$

For 1062 cm^{-1} Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{6.56} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (6d)$$

In order to investigate the accuracy of this technique compared to the typical thermogravimetric technique, the filler content for each composition determined using FT-Raman technique was calculated from the intensity ratio as described previously, using eqs. (6a)–(6d). It can clearly be seen in Table II, which tabulates the results of the comparison, that both techniques produce comparable results. The values determined by the FT-Raman technique are generally close to (the average of the percentage difference for all bands is approximately 9%) but slightly greater than the ones found from TGA analysis. This is thought to be a result of using the theoretical, not the actual values of the composites for the filler volume frac-

Table I Linear Regression Results of Relationship Between Intensity Ratio and Filler Volume Ratio. The Y Interception was Fixed at Zero in the Fitting Equation for All Cases

Intensity Ratio	Slope	R^2
$\frac{I_{1086}}{I_{2882}}$	1.17	0.99
$\frac{I_{1086}}{I_{2847}}$	2.29	0.98
$\frac{I_{1086}}{I_{1129}}$	6.91	0.99
$\frac{I_{1086}}{I_{1062}}$	6.56	0.98

Table II Comparison of Filler Content in Composites Determined by Different Methods. Values from FT-Raman were Based on the Theoretical Volume Fraction Ratio

Volume Fraction of CaCO ₃	Theoretical Filler Weight Fraction (%)	Experimental Filler Weight Fraction from TGA Method (%)	Experimental Filler Weight Fraction from Raman Method (%) [eq. (6a)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (6b)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (6c)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (6d)]
0.10	24	22	26	28	28	22
0.20	41	36	38	40	38	40
0.30	55	54	55	52	55	56
0.40	65	63	65	65	65	64

tion, from which the equations were derived, as can be seen by comparing the TGA results with the theoretical values (Table II). All the actual filler contents found from TGA were lower than the theoretical values and could thus cause the error in the prediction. If the filler content in the relationship is replaced by the actual filler content obtained from TGA analysis, the relationship will be more accurate and becomes:

For 2882 cm⁻¹ Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{1.26} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (7a)$$

For 2847 cm⁻¹ Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{2.48} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (7b)$$

For 1129 cm⁻¹ Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{7.45} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (7c)$$

For 1062 cm⁻¹ Raman shift

$$\frac{V_f}{(1 - V_f)} = \frac{1}{7.08} \left(\frac{I_{ca}}{I_{pe}} \right) \quad (7d)$$

A similar comparison—between the values found from the newly derived equations by FT-Raman with those using TGA techniques—is tabulated in Table III. It can be clearly seen that the results from both techniques are very close to each other. Compared to the results from eqs. (6a)–(6d), the relationship shows filler-content values even closer to each other (the average of the percentage difference for all bands is approximately 4%). Therefore, if the relationship is calibrated beforehand using samples for which the filler content is

Table III Comparison of Filler Content in Composites Determined by Different Methods. Values from FT-Raman were Based on Actual Volume Fraction Ratio

Volume Fraction of CaCO ₃	Experimental Filler Weight Fraction from TGA Method (%)	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7a)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7b)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7c)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7d)]
0.10	22	24	22	24	24
0.20	36	36	35	36	40
0.30	54	52	50	52	54
0.40	63	63	64	63	62

Table IV Comparison of Filler Content of 0.50 and 0.60 v/v Composites Determined by Different Methods

Volume Fraction of CaCO ₃	Experimental Filler Weight Fraction from TGA Method (%)	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7a)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7b)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7c)]	Experimental Filler Weight Fraction from Raman Method (%) [eq. (7d)]
0.50	68	70	68	72	71
0.60	75	75	75	78	77

known, the determination of filler amount by FT-Raman can yield accurate results.

To provide even stronger data validating the relationship, greater loading composites using the initially calculated filler volume fractions, of 0.50 and 0.60, were prepared. By employing the relationship derived from the initial experiment, [eqs. (7a)–(7d)], the filler content of the newly produced composites was determined and compared to the TGA results, as shown in Table IV. It can be seen that the FT-Raman technique still yields results comparable to the TGA technique, even when the data were not included in deriving the equations (the average of the percentage difference for all bands is approximately 3%).

Therefore, by obtaining the Raman spectrum of the calcium carbonate–HDPE sample, the filler content may be calculated rapidly using the above relationship. As the range of filler volume fraction in this study is equal to the maximum weight fraction of 75%, which is very high indeed, it is supposed that this technique is practical for all ranges of filler volume fraction. Not only can liquid mixtures be quantified by Raman spectroscopy, but, as was done in this study, the solid mixtures and composite solids can also be analyzed quantitatively by such a technique. However, it should be noted that this technique is applicable only when the experimental conditions for all materials are identical, and without the proper known filler content in the sample with which to calibrate the regression curve, the filler content calculated will be only a relative figure. It should also be noted that the signal-to-noise ratio is another factor that can affect the accuracy and the repeatability of the results. A high signal-to-noise ratio is preferable in all cases. In addition, the distribution of the filler in the matrix is assumed to be good; therefore, the small sampling area illuminated by the laser is sufficient to rep-

resent the whole sample. In a case when the homogeneity of the filler distribution is uncertain, the results should be cautiously interpreted; a statistical analysis could be done to ascertain the validity of the results.

CONCLUSIONS

The use of FT-Raman as an alternative quantitative technique in determining the filler content in calcium carbonate–polyethylene composites was demonstrated. It was shown that this technique could determine the filler amount in the HDPE–CaCO₃ composites with values comparable to those found using typical thermogravimetry. As the theory predicted, a range of application from low to high filler content was observed. The advantage of this technique is that it is nondestructive and rapid to carry out. However, the technique's limitation is its applicability only when experimental conditions for all materials are identical and when calibration of the regression curve is needed. Otherwise, the calculated filler content will be only a relative figure.

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