Determination of Filler Content in Thermoplastic Composites by FTIR Analysis

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SYNOPSIS

FTIR quantitative analytical method is described as an alternative technique for computation of the filler content in polypropylene composites. White rice husk ash (WRHA) was incorporated as a filler material into polypropylene homopolymer. Absorption peaks at 480, 621, and 790 cm^{-1} chosen for the quantitative analysis work have been shown to give good linearity with increasing filler contents. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Filler content of polymer composite is commonly determined using the thermogravimetric analysis. In our previous publications, we have described the computation of filler contents of several types of polypropylene composites based on simple expressions derived from thermogravimetric analyses.[1,2] The technique has shown that there was a good agreement and consistency between the analyzed and the incorporated fillers, and that a uniform filler distribution prevails within the polypropylene composites.

In this study, quantitative analysis of Fourier Transform Infrared (FTIR) spectroscopy will be described as a means of quantifying the filler loading of polypropylene composites. Though more popular as a tool for qualitative analysis of polymers,[3-5] the infrared spectroscopy technique may also be used as a method for the quantitative analysis of those materials.[6] The technique may be less sensitive than ultraviolet spectroscopy, but it has the advantage of being more specific and is suited to the analysis of mixtures. Although numerous absorption bands of various compounds may appear, it is usually possible to select the bands specific to the components of interest in the mixture.

The choice of correct absorption bands is of great importance for quantitative analysis work. Among the criteria of a suitable band are: strong or large absorption coefficient, isolated from other bands to avoid interferences and outside regions of compensated absorption (away from the CO_2 and H_2O absorption regions).

The application of rice husk ash (RHA) as a filler material in polypropylene has been reported in our earlier publications, and the effects of some coupling agents were also described.[7,8] As the name implies, the RHA used in this experimental work is derived from rice husks, which is usually regarded as agricultural waste and an environmental hazard. Rice husk, when burnt in open air outside the rice mill, yields white ash that consists predominantly of silica and has a good potential to serve as filler in polypropylene.

EXPERIMENTAL

The white rice husk ash (WRHA) was collected from open air burning sites outside a rice mill. The polypropylene used was Propelinas 600G (homopolymer) from Polypropylene (M) Sdn. Bhd. with density and melt index specified as 0.90 g/cm^3 and 12 g/10 min, respectively. No coupling agent was used in the composites.

The fillers were compounded into polypropylene by means of a Brabender DSK 42/7 twin screw

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Journal of Applied Polymer Science, Vol. 56, 1557-1560 (1995)
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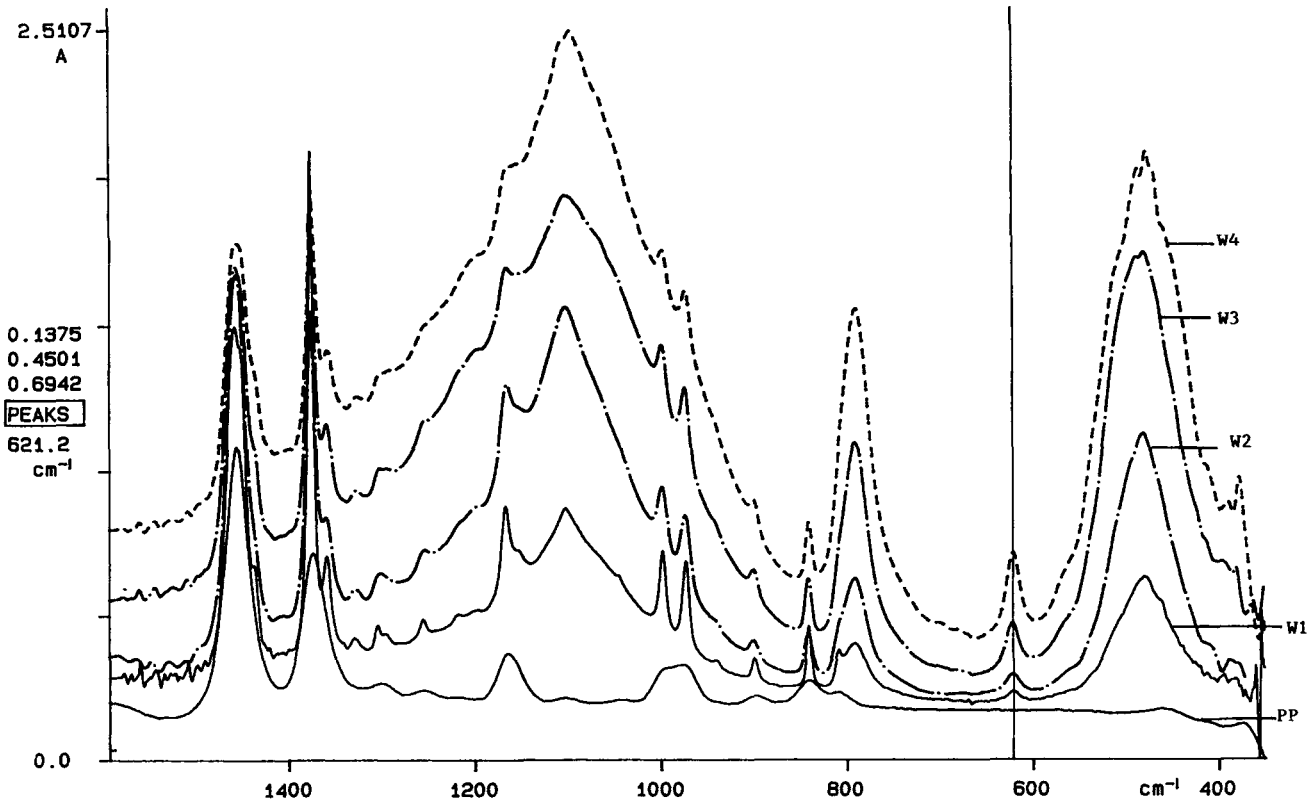

Figure 1 Effect of WRHA filler content on the infrared absorption spectra. W1, W2, W3, and W4 indicate filler content of 10, 20, 30, and 40 wt %, respectively.

compounder, having barrel temperatures of 170 to 190°C from feeding zone to the die zone, respectively. Four levels of loadings were prepared for all composites. The incorporated filler contents for the white RHA composites were 10, 20, 30, and 40% (by weight). The compounds were extruded through a twin 4 mm rod die into a water bath, pulled and pelletized. The compounded samples were injection molded into test specimens using a Battenfeld BA 200 CD Plus machine and a test specimen mold from Mastermold Inc.

The white RHA filler was subjected to the FTIR analysis to characterize the silica-related groups present in the filler material. A Perkin–Elmer 1610 FTIR spectrophotometer with a single-beam scanning Michelson interferometer, configured with a lithium tantalate detector and an optical system that provides 4 cm^{-1} resolution, was employed for this investigation. Because the WRHA is in powder form, it cannot be analyzed directly by the common transmission method, and an alternative method technique was useed, i.e., the diffuse reflectance technique. The RHA powder was placed in a sample cup of a diffuse reflectance accessory (DRIFT of Spectra Tech) and scanned for 16 times to reduce the noise-to-signal ratio within the range of 4,000 to 400 cm^{-1}. The spectrum was converted to the approximate normal transmission mode using the Kubelka–Munk function available directly in the system software.

In order to qualify for quantitative analysis work, all the RHA composite samples were prepared into uniform thin films of 15 μm thickness by means of a constant thickness film maker apparatus (Model: Specac 15620). A small amount of the injected sample was cut off and allowed to melt between two heated platens at 190°C for about 5 min. Pressure was applied to the platens by means of a 15-ton hydraulic press, using a force of about 3 tons and maintained for a period of 3 min. The platens were allowed to cool before the thin films were peeled off and mounted in a card mount. All samples were scanned for 16 times and the spectra were subjected to the smooth and flat functions accordingly for optimization.

RESULTS AND DISCUSSION

The effect of filler loading on the FTIR spectra may be observed from the spectra of WRHA composites at 10, 20, 30, and 40% filler content in Figure 1.

Three major peaks may be attributed to the WRHA, viz. peaks at 480, 621, and 790 cm^{-1}. These peaks may probably be assigned to the following respective silica-related bonds: Si—O_2, SiH_3, and Si—$(CH_3)_x$.[9] Similar peaks are not present in the spectrum of the unfilled polypropylene. As the filler loading is increased, it may clearly be seen that the absorbance of the three peaks of interest increases proportionally with the filler content.

It is of interest to find out if these absorbance peaks may be used to quantify the filler content of the WRHA composite. The absorbances of each peak at various filler loadings (including the polypropylene peak) were measured using the instrument software and are given in Table I. Multiple linear regression analysis was performed on each peak to obtain the absorbance–filler content relationship. The regression curves for the absorption peaks are shown in Figure 2. Interestingly, the curves show that (in accordance to the Beer's law) there exists a linear relationship between the infrared absorbance and the concentration of WRHA filler in the composite.

Beer–Lambert–Borguer law states that for monochromatic light:

$$A = ecl \tag{1}$$

where A is the absorbance and, e, c, and l refer to the extinction coefficient, concentration, and pathlength, respectively. Because e and l are constants (l = 15 μm), the equation may be simplified further,

$$A = Kc \tag{2}$$

where K is a constant related to the WRHA material.

If ϕ_f is the filler volume fraction that represents the filler content, the filler concentration may be related to the infrared absorbance at the 480 cm^{-1} peak [Fig. 2(a)] as:

$$A = 9.03\phi_f + 0.22 \tag{3}$$

Thus, filler content may be calculated from the absorption peak as:

$$\phi_f = \frac{A - 0.22}{9.03} \tag{4}$$

Likewise, if similar statistical treatment was performed on the other two peaks, similar relationship will be obtained. For the 621 cm^{-1} peak, from Figure 2(b),

$$A = 2.52\phi_f + 0.09 \tag{5}$$

and for the 790 cm^{-1} absorption peak (Figure 2c),

$$A = 6.41\phi_f + 0.11 \tag{6}$$

Thus, by obtaining the infrared absorption of an 'unknown' WRHA sample, the filler content may be calculated using the above equations for a particular peak. The constants at the end of eqs. (3), (5), and (6) are related to the absorbance of the polypropylene, which acts as the 'carrier' material for the WRHA filler. Among the three peaks, 790 cm^{-1} absorption peak give the least standard error

Table I Linear Regression Analysis on the Absorbance Values of the FTIR Peaks

	Peak 480 cm^{-1}		Peak 621 cm^{-1}		Peak 790 cm^{-1}	
Filler Volume Fraction ϕ_r	Absorbance A	Regressed Point, A'	Absorbance A	Regressed Point, A'	Absorbance A	Regressed Point, A'
0.00	0.13	0.22	0.14	0.09	0.17	0.11
0.04	0.61	0.62	0.20	0.20	0.38	0.39
0.09	1.12	1.06	0.27	0.32	0.60	0.71
0.15	1.75	1.57	0.45	0.47	1.09	1.07
0.22	2.06	2.21	0.69	0.64	1.55	1.52
Regression Output:						
Constant		**0.22**		**0.09**		**0.11**
Standard error of A estimate		0.15		0.05		0.07
R squared		0.97		0.96		0.99
No. of observations		5		5		5
Degrees of freedom		3		3		3
ϕ_f Coefficient		**9.04**		**2.52**		**6.41**
Standard error of ϕ_f coefficient		0.84 (+/−9.3%)		0.29 (+/−11.5%)		0.42 (+/−6.5%)

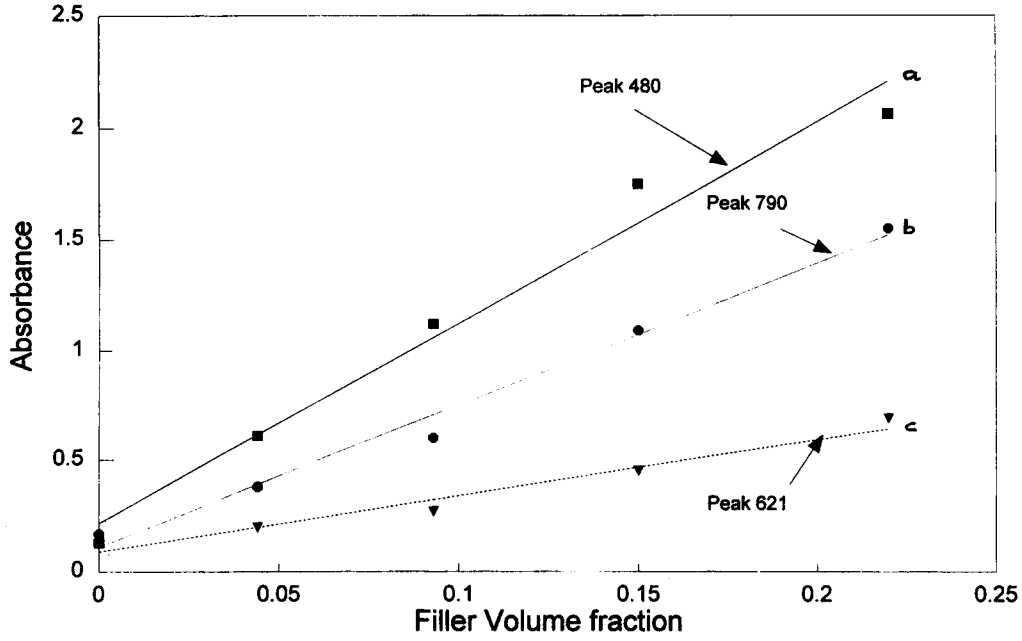

Figure 2 Infrared absorption vs. filler content curves (linearly regressed) for the selected peaks.

of ϕ_f coefficient and it is also the most prominent peak, thus making it the ideal peak for quantitative analysis work for the WRHA composites.

It should be borne in mind, however, that without proper standard samples to calibrate the regression curves, the ϕ_f value obtained for the 'unknown' is only a relative figure and not absolute as in the case determined by the thermogravimetric analysis. Of course, no such standards exist for the WRHA composites, but should there be a composite system with a reliable 'standard' sample, then the true filler content may be measured through the described technique.

CONCLUSION

The FTIR technique has been shown as a viable alternative for the determination of filler content for the WRHA composites. Three absorption peaks that were analyzed quantitatively give good linear absorption–volume fraction relationship and may be used for such quantitative work. Unlike the thermogravimetric technique, however, the FTIR method yields relative value due to unavailability of true WRHA standard sample for calibrating the absorption–volume fraction curves.

MPKSN of the government of Malaysia is acknowledged for the financial support.

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Received May 26, 1994
Accepted December 7, 1994