



## NRC Publications Archive Archives des publications du CNRC

### **New approach to quantitative analysis of two-component polymer systems by infrared spectroscopy**

Cole, K. C.; Thomas, Y.; Pellerin, E.; Dumoulin, M. M.; Paroli, R. M.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

#### **Publisher's version / Version de l'éditeur:**

*Applied Spectroscopy*, 50, 6, pp. 774-780, 1996

#### **NRC Publications Record / Notice d'Archives des publications de CNRC:**

<https://nrc-publications.canada.ca/eng/view/object/?id=c6274324-ce6c-429e-be59-f7e89f7c5246>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=c6274324-ce6c-429e-be59-f7e89f7c5246>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





<http://www.nrc-cnrc.gc.ca/irc>

## **New approach to quantitative analysis of two-component polymer systems by infrared spectroscopy**

---

**NRCC-38820**

Cole, K.C.; Thomas, Y.; Pellerin, E.; Dumoulin, M.M.; Paroli, R.M.

January 1996

A version of this document is published in / Une version de ce document se trouve dans:  
*Applied Spectroscopy*, 50, (6), pp. 774-780, 1996

The material in this document is covered by the provisions of the Copyright Act, by Canadian laws, policies, regulations and international agreements. Such provisions serve to identify the information source and, in specific instances, to prohibit reproduction of materials without written permission. For more information visit <http://laws.justice.gc.ca/en/showtdm/cs/C-42>

Les renseignements dans ce document sont protégés par la Loi sur le droit d'auteur, par les lois, les politiques et les règlements du Canada et des accords internationaux. Ces dispositions permettent d'identifier la source de l'information et, dans certains cas, d'interdire la copie de documents sans permission écrite. Pour obtenir de plus amples renseignements : <http://lois.justice.gc.ca/fr/showtdm/cs/C-42>



National Research  
Council Canada

Conseil national  
de recherches Canada

Canada



# New Approach to Quantitative Analysis of Two-Component Polymer Systems by Infrared Spectroscopy

K. C. COLE,\* Y. THOMAS, E. PELLERIN, M. M. DUMOULIN, and R. M. PAROLI

National Research Council Canada, Industrial Materials Institute, 75 De Mortagne Blvd., Boucherville, Québec J4B 6Y4, Canada (K.C.C., Y.T., E.P., M.M.D.); and Institute for Research in Construction, Ottawa, Ontario K1A 0R6, Canada (R.M.P.)

A new treatment is proposed for quantitative analysis of two-component polymer systems by infrared spectroscopy. Like much previous work, it is based on a ratio involving two peaks in the same spectrum. The relationship between such a ratio and the concentration of a given polymer is inherently nonlinear. It is shown that this nonlinearity can be well described by a simple equation derived from the laws of optical transmission. This equation has the form  $\chi_1 = m_1 + m_2R/(1 + m_3R)$ , where  $\chi_1$  is the weight fraction of polymer 1, the  $m_i$  are adjustable coefficients, and the ratio  $R$  is equal to  $A_a/(A_a + A_b)$ . The quantities  $A_a$  and  $A_b$  are the absorbances (peak heights or areas) at two frequencies  $a$  and  $b$  of which the first is associated mainly with polymer 1 and the second with polymer 2. This equation has been applied to various peak combinations in spectra of miscible blends of poly(phenylene ether) with polystyrene (both mid-IR and near-IR data) and immiscible blends of polypropylene with polyethylene (mid-IR data). It is shown that the equation is valid in all cases, covering the full concentration range from 0 to 100% even when the peaks used for the analysis involve absorption by both polymers. It is therefore believed to be of broad general usefulness for the analysis of polymer blends and copolymers.

Index Headings: Quantitative analysis; Polymer blends; Infrared spectroscopy; FT-IR; Polyethylene; Polypropylene; Poly(phenylene ether); Polystyrene.

## INTRODUCTION

In working with polymer blends or copolymers, it is often necessary to verify the composition of a two-component system. Infrared (IR) transmission spectroscopy has long been used for this purpose, sometimes in an on-line setting but generally as a laboratory technique. However, recent developments have opened up new possibilities for IR spectroscopy as an on-line technique, and we have undertaken work to study the application of near-infrared transmission spectroscopy to the extrusion of polymer blends.<sup>1</sup> In the course of this work, it became necessary to verify the composition of a number of samples by a more conventional technique, namely, transmission of thin cast films in the mid-infrared. This requirement prompted a re-examination of the method used to analyze the data and led to the development of a simple but nonlinear equation that has several advantages over those commonly used. The purpose of this paper is to describe this equation and demonstrate its successful application in different situations.

The basis of all quantitative analysis by transmission of infrared radiation is the relationship developed by Bouguer, Lambert, and Beer, which states that for a mixture of  $n$  components:

$$A(\bar{\nu}) = -\log T(\bar{\nu}) = \sum_{i=1}^n K_i(\bar{\nu}) \cdot C_i \cdot t \quad (1)$$

where  $\bar{\nu}$  is the frequency of the radiation;  $A(\bar{\nu})$  is the absorbance of the sample;  $T(\bar{\nu})$  is the transmittance of the sample (defined as the ratio of the transmitted energy with respect to the incident energy,  $I/I_0$ );  $K_i(\bar{\nu})$  is the intrinsic absorptivity of component  $i$ ;  $C_i$  is the concentration of component  $i$ ; and  $t$  is the sample thickness. The simple proportionality between absorbance and concentration is the cornerstone of infrared quantitative analysis. However, in its application it must be remembered that the concentration ought to be expressed in units that define the number of absorbing species (atomic groups) per unit volume. For simple compounds with a clearly defined molecular weight, it is convenient to express the concentration in moles per liter. For a material like a polymer, consisting of a mixture of molecules with varying weight and number of absorbing units, it is better to express the concentration in terms of mass per unit volume. This distinction is based on the reasonable assumption that the number of absorbing species per unit mass is a constant. For a pure polymer, the concentration would correspond to the density, which is the reciprocal of the specific volume,  $V_s$ .

For a two-component polymer mixture, the composition is usually expressed in terms of the weight fraction  $\chi_1$  of one of the polymers, the fraction of the other being  $\chi_2 = 1 - \chi_1$ . (The concentration of polymer 1 may also be expressed in weight percent, equal to  $100 \chi_1$ .) Consider a mixture of  $\chi_1$  g of polymer 1 and  $\chi_2$  g of polymer 2. The total weight is 1 g, and the total volume is therefore  $V_{sm}$ , the specific volume of the mixture in  $\text{cm}^3/\text{g}$ . The respective concentrations of polymers 1 and 2, in appropriate units of  $\text{g}/\text{cm}^3$ , are therefore  $\chi_1/V_{sm}$  and  $\chi_2/V_{sm}$ . Substituting into Eq. 1 gives:

$$A(\bar{\nu}) = \frac{K_1(\bar{\nu})\chi_1 + K_2(\bar{\nu})\chi_2}{V_{sm}} \cdot t \quad (2)$$

If there is no change of volume on mixing, the specific volume of the mixture will be given by  $V_{sm} = V_{s1}\chi_1 + V_{s2}\chi_2$ . In reality, however, interaction between the polymers will cause a change in volume, usually a reduction but in some cases an increase. For example, in the case of polystyrene and poly(phenylene ether), the volume of a 50:50 mixture is about 0.75% lower than that expected on a simple additive basis.<sup>2</sup> The effect of the interaction can be described to a first-order approximation in terms of a factor  $f$ :

$$V_{sm} = V_{s1}\chi_1 + V_{s2}\chi_2 + f\chi_1\chi_2 \quad (3)$$

Substituting in Eq. 2 and replacing  $\chi_2$  by  $1 - \chi_1$  leads to

Received 6 November 1995; accepted 10 February 1996.

\* Author to whom correspondence should be sent.

$$A(\bar{v}) = \frac{K_2(\bar{v}) + [K_1(\bar{v}) - K_2(\bar{v})]\chi_1}{V_{s2} + [V_{s1} - V_{s2} + f]\chi_1 - f\chi_1^2} \cdot t \quad (4)$$

An important point arising from this equation is that the absorbance is not normally a linear function of  $\chi_1$ . It will be linear only if the following two conditions are satisfied: (1) there is no specific interaction between the polymers ( $f = 0$ ), and (2) the two polymers have the same density ( $V_{s1} = V_{s2}$ ). It can be shown that if only the first condition is satisfied, then the absorbance is linear with respect to the volume fraction of polymer 1 rather than the weight fraction. However, this observation is of little use for practical purposes because often the density of the polymers is not known precisely and the importance of the interaction correction is not known. Furthermore, volume fraction is a rather nebulous concept in the case of copolymers. It is much simpler to express the blend or copolymer composition in terms of weight fraction or mole fraction.

This nonlinearity means that the classical relationship  $A \propto \chi$  cannot be applied, except as an approximation for which the validity must be tested. More sophisticated statistical methods like PLS (partial least-squares) can deal with the nonlinearity, but their application requires that the thickness of the samples used for calibration be precisely known. For polymer films, the thickness usually varies from one specimen to another and is difficult to measure accurately. A well-known way of overcoming this problem is to take the ratio of the absorbances of two peaks in the same spectrum, the first (at a frequency which we designate as  $a$ ) arising mainly from polymer 1, and the second (at frequency  $b$ ) arising mainly from polymer 2. When the ratio is taken, the thickness  $t$  and the specific volume  $V_{sm}$  in Eq. 2 cancel out because they are independent of frequency. The result is

$$\frac{A_a}{A_b} = \frac{K_{1a}\chi_1 + K_{2a}\chi_2}{K_{1b}\chi_1 + K_{2b}\chi_2} = \frac{K_{2a} + (K_{1a} - K_{2a})\chi_1}{K_{2b} + (K_{1b} - K_{2b})\chi_1} \quad (5)$$

where the subscripts  $a$  and  $b$  designate the two specific frequencies chosen. Unfortunately, this expression is still nonlinear with respect to  $\chi_1$  except for the fortuitous case where  $K_{1b} = K_{2b}$ . There have been different approaches to dealing with this problem. One is to find a peak  $b$  that arises only from polymer 2, in which case  $K_{1b} = 0$  and Eq. 5 becomes

$$\frac{A_a}{A_b} = \frac{K_{2a}}{K_{2b}} + \frac{K_{1a}}{K_{2b}} \frac{\chi_1}{\chi_2} \quad (6)$$

In this case the ratio  $A_a/A_b$  is a linear function of  $\chi_1/\chi_2 = \chi_1/(1 - \chi_1)$ . An example of the successful application of this approach is the use of the peaks at 691 and 1738  $\text{cm}^{-1}$  to analyze copolymers of vinyl chloride and vinyl acetate.<sup>3</sup> As a general method, however, it suffers from two main problems. First, it is often difficult to find "pure" peaks in the mixture spectrum. Second, if the mixtures analyzed include some with high values of  $\chi_1$ , the denominators become quite small with respect to the numerators, and this condition produces large values for the ratios along with large associated errors.

Some workers have found that although a plot of  $A_a/A_b$  against  $\chi_1$  is nonlinear, a plot of  $\log(A_a/A_b)$  against  $\chi_1$  is approximately linear, at least over a limited range of con-

centrations. Such is the case, for example, for the ratio  $A_{1493}/A_{1351}$  in styrene-isobutylene copolymer,<sup>4</sup> and for  $A_{1190}/A_{700}$  and  $A_{1030}/A_{700}$  in mixtures of poly(phenylene ether) and polystyrene.<sup>5</sup> While this approach works in certain cases, it has no theoretical basis, and taking the logarithm simply masks the nonlinearity.

The approach used in this work is based on the ratio of peaks but avoids the problems mentioned above. First, instead of the simple ratio  $A_a/A_b$ , we use the ratio  $R = A_a/(A_a + A_b)$ . This ratio has the advantage of being confined to the range of 0 to 1, the same range as  $\chi_1$ . Second, we consider the general case where the peaks  $a$  and  $b$  are not pure. This leads to the following equation:

$$R = \frac{A_a}{A_a + A_b} = \frac{K_{2a} + (K_{1a} - K_{2a})\chi_1}{K_{2a} + K_{2b} + (K_{1a} + K_{1b} - K_{2a} - K_{2b})\chi_1} \quad (7)$$

Although this relationship is nonlinear, it is relatively simple and does not involve the sample thickness, the volume mixing interaction, or the polymer densities. As a result of the current widespread availability of personal computers and software to perform nonlinear regression, the requirement of linearity is less critical than in the past.

Since the ultimate objective is to calculate  $\chi_1$  from the measured  $R$ , Eq. 7 is inverted and expressed in the convenient form

$$\chi_1 = m_1 + \frac{m_2 R}{1 + m_3 R} \quad (8)$$

where

$$m_1 = \frac{K_{2a}}{K_{2a} - K_{1a}}; \quad m_2 = \frac{K_{2b}K_{1a} - K_{2a}K_{1b}}{(K_{1a} - K_{2a})^2};$$

and

$$m_3 = \frac{K_{2b} - K_{1b}}{K_{1a} - K_{2a}} - 1. \quad (9)$$

The relationship is linear only for the fortuitous case where  $m_3 = 0$ . Otherwise, the coefficients  $m_1$ ,  $m_2$ , and  $m_3$  can be determined by nonlinear regression on data obtained from a set of calibration samples. The equation can then be used to determine the composition of any blend. If concentrations are expressed in percent,  $\chi_1$  is simply multiplied by 100. Also, if desired, the coefficients  $m_1$ ,  $m_2$ , and  $m_3$  can be used to calculate the ratios of absorptivities according to

$$\frac{K_{2b}}{K_{1a}} = \frac{m_2 + m_1(1 + m_3)}{1 - m_1}; \quad \frac{K_{2a}}{K_{1a}} = \frac{m_1}{m_1 - 1};$$

$$\frac{K_{1b}}{K_{2b}} = 1 - \frac{1 + m_3}{m_2 + m_1(1 + m_3)} \quad (10)$$

The rest of the paper is devoted to demonstrating the general application of Eq. 8 for the analysis of two-component polymer blends.

## EXPERIMENTAL

Data are reported for two different polymer blends: poly(phenylene ether) with polystyrene (PPE/PS) and

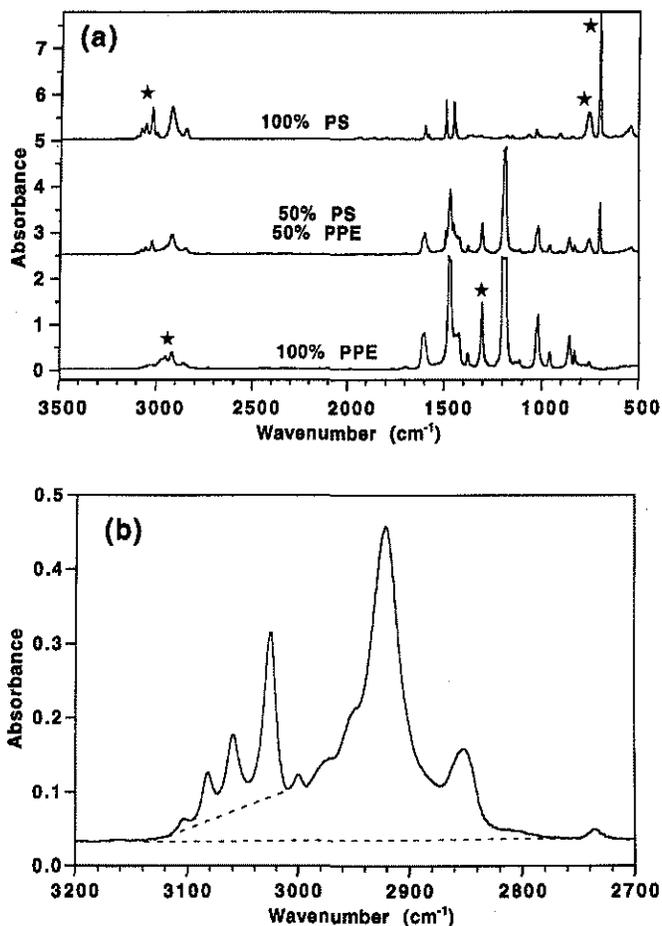


FIG. 1. (a) Typical spectra obtained for PS, PPE, and a 50:50 blend, with peaks used in the analysis indicated by a ★; (b) expanded view of the C-H stretching region for the 50:50 blend, showing the baselines used for peak integration.

polypropylene with polyethylene (PP/PE). The PP/PE data are from an earlier publication.<sup>6</sup> Both the PPE (from GE Plastics) and the PS (C-35 from Scott Polymer) were supplied as powders.

The PPE/PS mid-IR spectra were measured on a Nicolet 170SX FT-IR spectrometer (with MCT detector) at a resolution of  $1\text{ cm}^{-1}$ ; each spectrum corresponded to an accumulation of 64 scans. The samples used for analysis were obtained by dissolving precisely weighed amounts of PPE and PS in chloroform and casting thin films (typical thickness,  $15\text{ }\mu\text{m}$ ) on glass microscope slides. The solvent was allowed to evaporate overnight at room temperature, after which the films were heated under vacuum for 1 h at  $90\text{--}100\text{ }^\circ\text{C}$ . The films were separated from the slides by adding a drop of water at one corner and letting it penetrate between the film and the slide. They were then thoroughly dried before measurement. For each of the twenty-one different mixtures prepared, ranging from 0 to 100% PPE, two separate films were cast and analyzed.

The PPE/PS near-IR spectra were measured on molten material at the end of a twin-screw extruder. It was assumed that the blend composition at the extruder exit was the same as that of the dry mixture fed into the extruder. The probe was a single-immersion reflection-type fiberoptic probe from Sensotron, with an effective pathlength

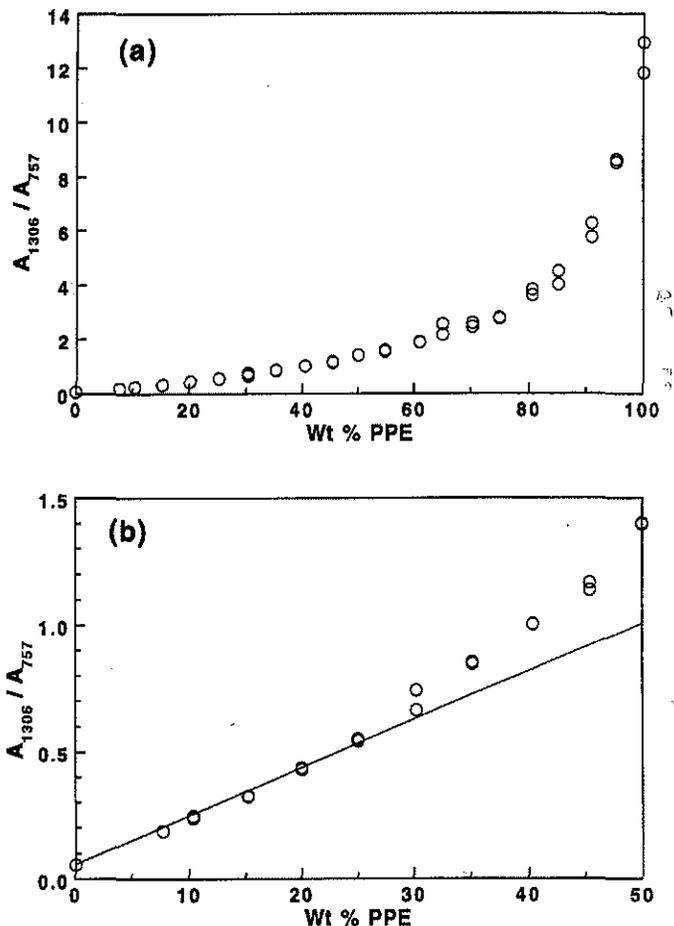


FIG. 2. The relationship between  $A_{1306}/A_{757}$  and the concentration of PPE in PPE/PS mixtures. (a) All data; (b) expanded view of lower-concentration data.

of about 6 mm. This was coupled to a Bomem Michelson MB155 FT-IR spectrometer (with quartz halogen source and InAs detector) by means of silica optical fibers of 1.5 m length. Each spectrum was an accumulation of 32 scans (measurement time about 40 s) at a resolution of  $4\text{ cm}^{-1}$ .

Data analysis and curve fitting were done on a Macintosh computer with the aid of the software Kaleidagraph V3.0 from Abelbeck Software.

## RESULTS AND DISCUSSION

**PPE/PS Mid-IR.** Figure 1a shows typical spectra recorded in the mid-IR region for the pure polymers and a 50:50 blend by weight. The different peaks used for quantitative analysis in this work are indicated by a ★. Their areas were calculated by means of the Nicolet software with a baseline drawn between the valleys on either side. In the C-H stretching region, combinations of peaks were analyzed as illustrated in Fig. 1b.

PPE and PS are generally considered to form highly compatible blends through intermolecular interactions. Koenig and co-workers<sup>7,8</sup> have reported that certain peaks in the PPE spectrum, notably those near  $1190$  and  $856\text{ cm}^{-1}$ , are particularly sensitive to these interactions and change shape on blending with PS. On the other hand, the peak at  $1306\text{ cm}^{-1}$  and all the peaks of PS are not

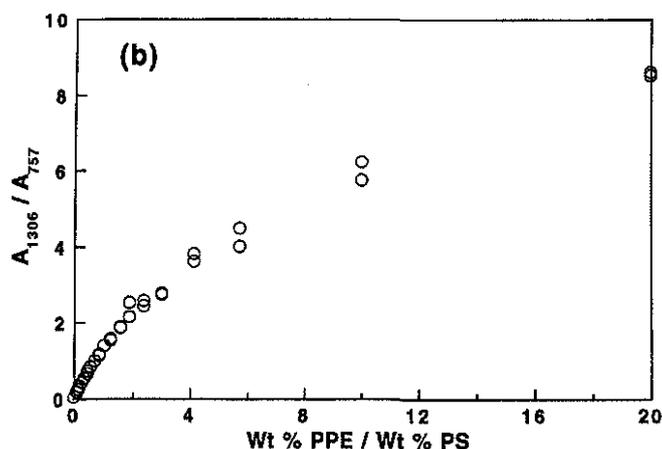
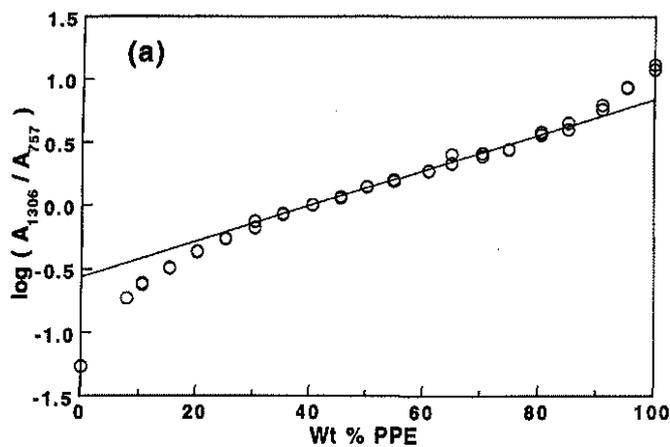


FIG. 3. Other representations of the data shown in Fig. 2. (a)  $\log(A_{1306}/A_{757})$  vs. wt % PPE; (b)  $A_{1306}/A_{757}$  vs. %PPE/%PS.

significantly affected by the blending. Mukherji et al. used for their quantitative analysis<sup>5</sup> the peaks at 1190 and 1030  $\text{cm}^{-1}$  for PPE and the peak at 700  $\text{cm}^{-1}$  for PS. In the present case, the peak at 1190  $\text{cm}^{-1}$  was saturated in many of the spectra, so the peak at 1306  $\text{cm}^{-1}$  was chosen instead. Apart from being less intense, the 1306- $\text{cm}^{-1}$  peak is free from polystyrene interference and insensitive to blend interactions. The choice of peaks for PS is more limited. The ones near 1600, 1500, and 1450  $\text{cm}^{-1}$  are subject to strong interference from PPE peaks; this leaves only those at 757 and 700  $\text{cm}^{-1}$  and the C-H stretching peaks above 3000  $\text{cm}^{-1}$ .

The first pair of peaks that we consider are the PPE peak at 1306  $\text{cm}^{-1}$  and the PS peak at 757  $\text{cm}^{-1}$ . Figures 2 and 3 illustrate the problems encountered when these are analyzed by traditional methods. As can be seen in Fig. 2a, a plot of the ratio of peak areas  $A_{1306}/A_{757}$  against

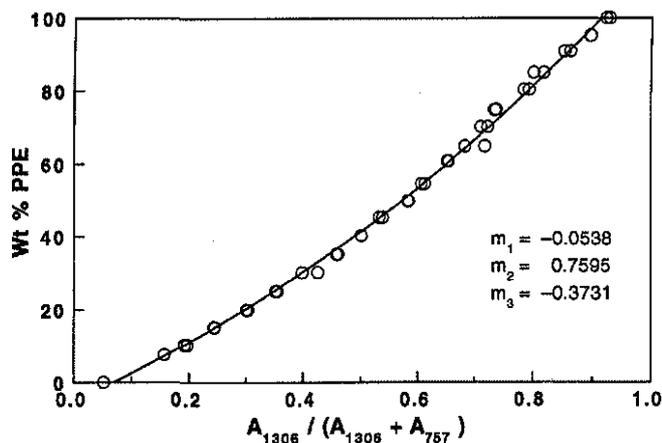


FIG. 4. The application of Eq. 8 to PPE/PS blends, based on the peaks at 1306 and 757  $\text{cm}^{-1}$ .

the weight percent of PPE is highly nonlinear, especially at high levels of PPE, where the ratio becomes very large. Even at lower levels of PPE (Fig. 2b), the relationship can be considered linear only up to about 25% PPE. Plotting the logarithm of the ratio (Fig. 3a) gives an S-shaped curve that can be considered linear over a limited range of about 35% to 65% PPE. This behavior is similar to that reported by Mukherji et al. for the 1190/700 pair. If the peaks being analyzed were "pure", then plotting the ratio  $A_{1306}/A_{757}$  against the ratio %PPE/%PS should give a straight line, but Fig. 3b shows that a curve is obtained. This happens because the 757- $\text{cm}^{-1}$  peak does not arise from PS alone; it also encompasses a weak PPE peak.

It is obvious that with the above approaches it is impossible to obtain a linear relationship that applies over a wide range of concentrations. Figure 4 shows the result obtained when the data are treated as described in the Introduction and fitted by means of Eq. 8. With the use of three coefficients, the slight curvature is well described and a good fit is obtained over the whole range of concentrations. The quality of this fit is compared in Table I, Column 2, with those obtained by means of other simple equations, namely, linear and polynomials of second, third, and fourth degree. It is seen that, in this particular case, while Eq. 8 is much better than a straight line, a second-degree polynomial (which also has three adjustable coefficients) works slightly better. However, it will be seen that this is not generally true.

The second pair of peaks that we consider are the PPE peak at 1306  $\text{cm}^{-1}$  and the PS peak at 700  $\text{cm}^{-1}$ . It should be noted that, because the latter is a very narrow peak, the spectral resolution of 1  $\text{cm}^{-1}$  used in this work was found to give more accurate integrated peak areas than

TABLE I. Regression results for PPE/PS (mid-IR).<sup>a</sup>

Peaks→ Fit↓	1306 and 757		1306 and 700		1306 and CH[arom]		CH[arom] and CH[total]	
	Corr.	SEE	Corr.	SEE	Corr.	SEE	Corr.	SEE
Eq. 8	0.99867	1.55	0.99993	0.27	0.99996	0.26	0.99984	0.54
Linear	0.99224	3.75	0.99992	0.28	0.98742	4.77	0.99666	2.46
Polynomial-2	0.99894	1.38	0.99993	0.27	0.99956	0.89	0.99983	0.55
Polynomial-3	0.99903	1.33	0.99993	0.26	0.99994	0.33	0.99984	0.53
Polynomial-4	0.99922	1.19	0.99994	0.26	0.99998	0.21	0.99987	0.48

<sup>a</sup> Note: Corr = correlation coefficient; SEE = standard error of estimate in wt %.

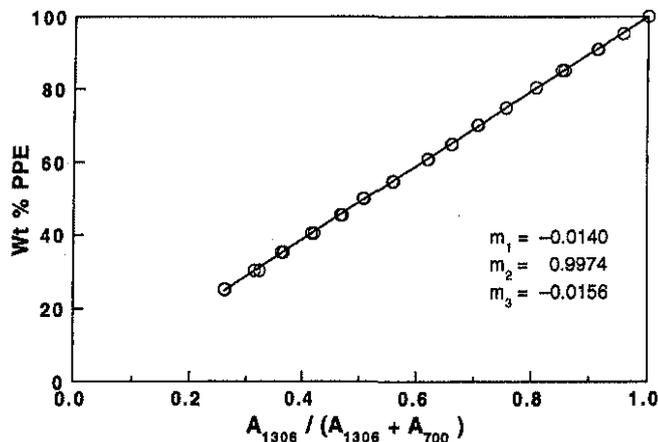


FIG. 5. The application of Eq. 8 to PPE/PS blends, based on the peaks at 1306 and 700  $\text{cm}^{-1}$ .

the more typical resolution of 4  $\text{cm}^{-1}$ . This peak is also rather strong and could not be measured accurately for mixtures containing 20% PPE or less. The analysis of the data by means of Eq. 8 is shown in Fig. 5. It was found that this case corresponds to the perfect scenario for analysis by means of peak ratios: the two peaks are almost perfectly "pure" and have almost the same intrinsic absorptivity. Hence  $m_1 \approx m_3 \approx 0$ , and  $m_2 \approx 1$ , so that % PPE  $\approx 100R$ , where  $R = A_{1306}/(A_{1306} + A_{700})$ . With such a good linear relationship, an excellent fit is obtained with any of the equations tested, as shown in Table I, Column 3. Again, this is by no means a common occurrence.

On comparing Figs. 4 and 5, it can be seen that there is much more scatter in Fig. 4 than in Fig. 5. The reason for this difference was investigated, and the cause was found to be traces of chloroform solvent remaining in the films. Chloroform has a very strong peak near 757  $\text{cm}^{-1}$ , and this interferes with the analysis in a randomly varying manner when the 757- $\text{cm}^{-1}$  PS peak is used. As mentioned above, PPE also has a weak peak in this region. Its presence gives rise to the curvature in Fig. 4, but this would not present a problem if the chloroform were absent.

Since neither of the two PS peaks tested so far is ideal, a third possibility was investigated. This consists of the aromatic C-H stretching peaks above 3000  $\text{cm}^{-1}$ , which arise mainly from PS. The integrated peak area, which we designate as  $A_{\text{CH[arom]}}$ , includes the peaks at 3025, 3059, 3082, and 3103  $\text{cm}^{-1}$ , as shown in Fig. 1b. Figure 6 shows the fit of these data by means of Eq. 8. There is much less scatter than with the 757- $\text{cm}^{-1}$  peak, and the whole range of concentrations is covered, unlike the case for the 700- $\text{cm}^{-1}$  peak. Furthermore, Eq. 8 gives an excellent fit, with a standard error of estimate (SEE) of 0.26 wt %. This is even better than that obtained with a third-degree polynomial, which has one more adjustable coefficient. The applicability of Eq. 8 is clearly demonstrated in this case.

A fourth approach was also tried. This consisted of taking the ratio of the aromatic C-H peaks against the total C-H absorption, from about 3140 to 2780  $\text{cm}^{-1}$  (Fig. 1b). The C-H peaks below 3000  $\text{cm}^{-1}$  arise mainly from PS, but PPE also contributes. The result from this analysis is shown in Fig. 7. Although the peak area ratio

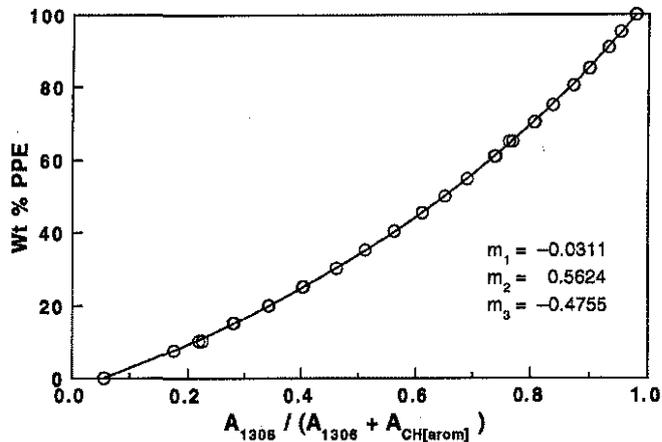


FIG. 6. The application of Eq. 8 to PPE/PS blends, based on the peak at 1306  $\text{cm}^{-1}$  and the aromatic C-H peaks.

covers a more limited range than in the previous cases, a good correlation is observed, and Eq. 8 fits it as well as a second- or third-degree polynomial (Table I). The SEE of 0.54 wt % is higher than in the previous case but is still quite acceptable. An advantage of this approach is that the peaks are all above 2500  $\text{cm}^{-1}$  in a region amenable to analysis by equipment using sapphire fiber optics or windows.

**PPE/PS Near-IR.** Figure 8 shows some typical spectra of PPE/PS blends in the near-infrared region corresponding to the second overtone of the C-H stretching vibration. Polystyrene shows a peak at 8741  $\text{cm}^{-1}$  corresponding to the aromatic C-H bonds and a weaker one near 8300  $\text{cm}^{-1}$  corresponding to the aliphatic C-H bonds. As PS is replaced by PPE, the aromatic C-H peak at 8741  $\text{cm}^{-1}$  decreases in intensity and a new methyl C-H peak grows at 8401  $\text{cm}^{-1}$ . Because of the peak overlap it is impossible to integrate individual peaks; therefore, in our analysis we have used instead the peak heights at the specific frequencies 8401 and 8741  $\text{cm}^{-1}$ , calculated with respect to a baseline drawn as shown in the figure. The results of the analysis are shown in Fig. 9, and the different curve fits are compared in Table II. Once again, Eq. 8 gives a good fit to the slightly curved relationship and is equivalent to a second-degree polynomial.

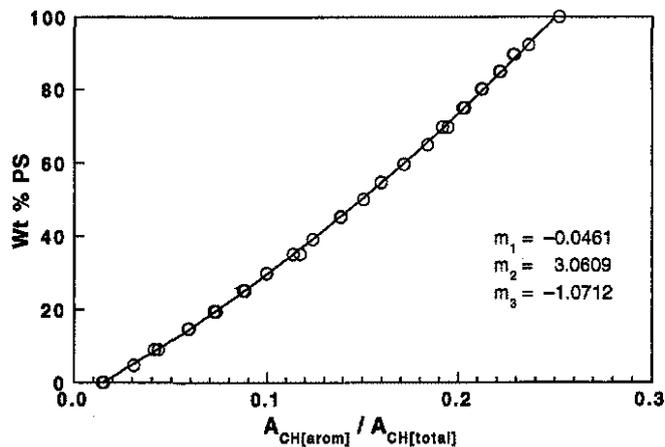


FIG. 7. The application of Eq. 8 to PPE/PS blends, based on the C-H aromatic peaks ratioed against the complete C-H absorption.

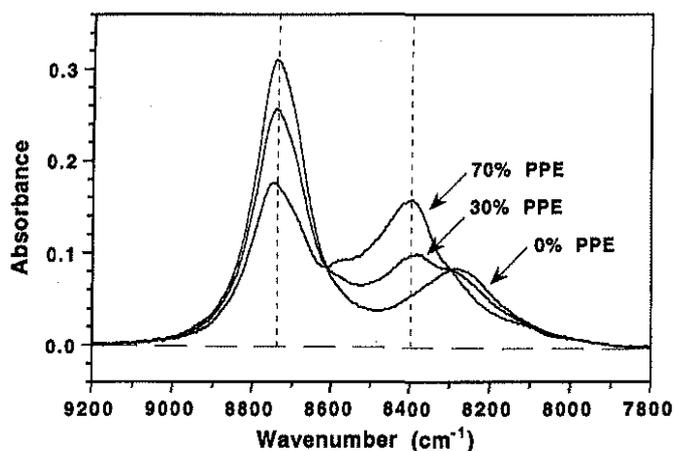


FIG. 8. Near-infrared spectra (second overtone bands) of molten mixtures of PPE and PS, showing the frequencies used for the analysis.

TABLE II. Regression results for PPE/PS (near-IR).<sup>a</sup>

Peaks→ Fit↓	8401 and 8741	
	Corr.	SEE
Eq. 8	0.99938	0.85
Linear	0.99862	1.26
Polynomial-2	0.99936	0.86
Polynomial-3	0.99940	0.83
Polynomial-4	0.99945	0.80

<sup>a</sup> Note: Corr. = correlation coefficient; SEE = standard error of estimate in wt %.

of PP, for films obtained by hot pressing. The curve was fitted with a fourth-degree polynomial. In Fig. 10 we have plotted the wt % PP against the same ratio and applied Eq. 8. In spite of the strong curvature, the fit with Eq. 8 is as good as with a second-degree polynomial (Table III). The slightly better fit obtained by using third- or fourth-degree polynomials is simply the result of better adjustment to experimental errors because of the extra coefficients, and does not contribute to better precision in the determination of the PP concentration. It is interesting to note that even though the two peaks used in this case are quite "pure" (the 1160-cm<sup>-1</sup> peak arises from methyl group wagging in PP and the 720-cm<sup>-1</sup> peak from methylene rocking in PE), there is still a strong nonlinearity. This is because the intrinsic absorptivity of the PE peak is about twice that of the PP peak. If they were the same, the relationship would be linear, as was found for the 1306/700 combination in the case of PPE and PS.

The spectra used for this analysis were also analyzed by means of the more sophisticated PLS method, which uses all the data points in the peaks under consideration. In the so-called cross-validation procedure, one spectrum at a time is removed from the calibration set, the calibration is done with the remaining spectra, and the result is used to predict the concentration for the removed spectrum. This is done for each spectrum in the set, and the root-mean-square value of the differences between true and predicted concentrations is known as the standard error of calibration (SEC). For the spectra analyzed here, the SEC for the PLS analysis was 0.43 wt % PPE. When a similar cross-validation was done for the method involving peak heights and Eq. 8, the SEC obtained was 0.97 wt % PPE. Obviously there is some loss of precision when only the peak heights are used rather than the entire spectrum. However, this approach could be applied with greater speed and simpler instrumentation, provided that the level of precision is acceptable.

**PP/PE Mid-IR.** The second polymer blend which we consider is the immiscible system polypropylene-polyethylene (PP/PE). Various peak combinations have been used to analyze blends and copolymers.<sup>9</sup> In an earlier publication,<sup>6</sup> we showed the relationship between the peak height ratio  $A_{1160}/(A_{1160} + A_{720})$  and the concentration

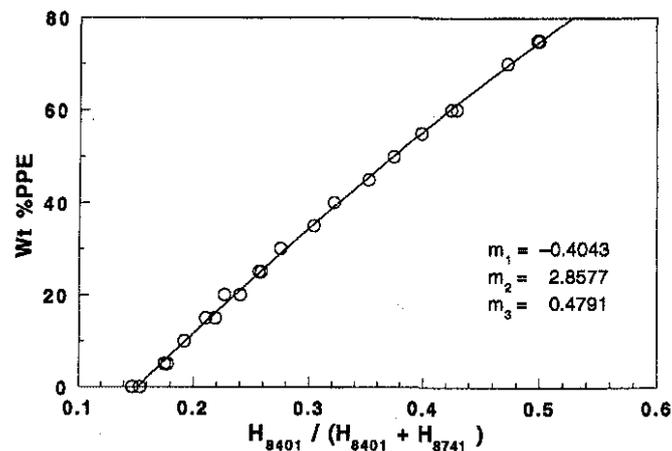


FIG. 9. The application of Eq. 8 to PPE/PS blends, based on the near-infrared absorptions at 8401 and 8741 cm<sup>-1</sup>.

Another set of peaks that has been used to analyze PP/PE blends involves the C-H deformation bands at 1378 and 1467 cm<sup>-1</sup>.<sup>9,10</sup> The two are present in both PP and PE, but the 1378-cm<sup>-1</sup> peak is stronger in PP because it arises from methyl groups. Figure 11 shows a plot of wt % PP against the ratio  $A_{1378}/(A_{1378} + A_{1467})$ . It is highly nonlinear, and the curvature is opposite to that observed in the previous case (Fig. 10). Nevertheless, Eq. 8 again provides a good fit, in this case considerably better than a second-degree polynomial (Table III). It would appear that, as a general rule, if the deviation from nonlinearity is small, then a second-degree polynomial works as well as Eq. 8, but if the deviation is large, then Eq. 8 is superior. This is to be expected because Eq. 8 is derived

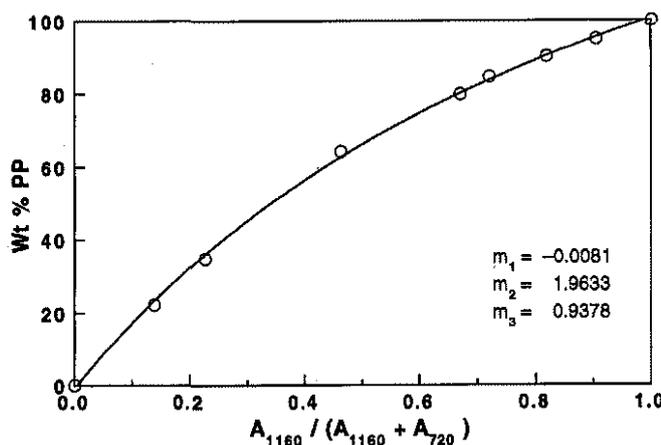


FIG. 10. The application of Eq. 8 to PP/PE blends, based on the peaks at 1160 and 720 cm<sup>-1</sup>.

TABLE III. Regression results for PP/PE (mid-IR).<sup>a</sup>

Peaks→ Fit↓	1160 and 720		1378 and 1467	
	Corr.	SEE	Corr.	SEE
Eq. 8	0.99967	0.87	0.99839	1.83
Linear	0.98564	5.72	0.95365	9.74
Polynomial-2	0.99967	0.87	0.99311	3.79
Polynomial-3	0.99984	0.59	0.99883	1.56
Polynomial-4	0.99991	0.45	0.99900	1.45

<sup>a</sup> Note: Corr. = correlation coefficient; SEE = standard error of estimate in wt %.

from fundamental principles, whereas a polynomial fit is empirical.

Table III shows that the 1378/1467 combination gives rise to a larger standard error of estimate than the 1160/720 combination. This may be because both the 1378 and 1467 peaks contain a significant contribution from PP, so that the ratio is not very sensitive to changes in the PP concentration. Other peak combinations have also been used for PP/PE blends, for example, the C-H stretching peaks around 3000 cm<sup>-1</sup> and combination or overtone peaks in the near-infrared.<sup>10,11</sup> Deviations from linearity are observed in almost all cases, and Eq. 8 would undoubtedly be capable of describing these relationships.

**Regression Analysis.** One disadvantage of the use of Eq. 8 is that nonlinear regression is required, but as already mentioned, this is no longer a serious problem. However, if nonlinear regression software is not available, the analysis can still be done by linear regression, although the procedure is more tedious. If a value is assumed for  $m_3$ ,  $\chi_1$  can be plotted against  $R/(1 + m_3R)$  and

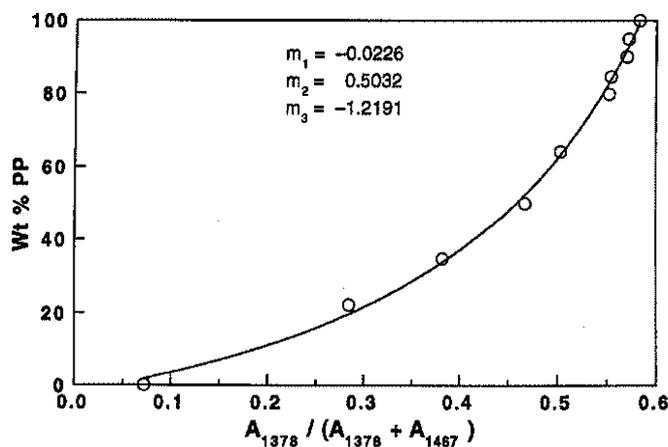


FIG. 11. The application of Eq. 8 to PP/PE blends, based on the peaks at 1378 and 1467 cm<sup>-1</sup>.

linear regression performed. The value of  $m_3$  is then changed and the process repeated until the value of  $m_3$  that gives the best linear fit is determined. If this approach is used, a starting value of  $m_3$  can be estimated from the experimental curve by using the equation

$$m_3 = \frac{\frac{2}{R_0 R_1} - \frac{1}{R_0 R_{0.5}} - \frac{1}{R_{0.5} R_1}}{\frac{2}{R_{0.5}} - \frac{1}{R_0} - \frac{1}{R_1}} \quad (11)$$

where  $R_0$ ,  $R_{0.5}$ , and  $R_1$  are the ratios corresponding to  $\chi_1 = 0, 0.5$ , and 1, respectively.

## CONCLUSION

The results presented demonstrate that the proposed approach for the quantitative analysis of two-component blends or copolymers through the use of peak ratios in the infrared spectrum has definite advantages over traditional methods. First, it is already well known that the use of a ratio involving two peaks from the same spectrum can eliminate the effects of film thickness, sampling depth, and the like. Second, Eq. 8, which is derived from the fundamental laws of optical transmission, has been shown herein to be capable of describing the inherent nonlinearity of calibration curves for a number of different cases. This equation is of broad general application because it covers the entire range of blend composition from 0 to 100%, and the two peaks or frequencies used for the analysis do not need to be "pure", i.e., associated exclusively with one or the other of the two polymers. However, as a general rule, the purer the peaks, the more sensitive the ratio will be to changes in composition.

1. Y. Thomas, K. C. Cole, E. Pellerin, and M. M. Dumoulin, *Polym. Mater. Sci. & Eng.* **72**, 19 (1995).
2. H. B. Hopfenberg, V. T. Stannett, and G. M. Folk, *Polym. Eng. & Sci.* **15**, 261 (1975).
3. E. G. Bartick, J. C. Corbett, and G. L. McClure, *ACS Symp. Ser.* **197**, 185 (1982).
4. J. E. Forrette and A. L. Rozek, *J. Appl. Polym. Sci.* **18**, 2973 (1974).
5. A. K. Mukherji, M. A. Butler, and D. L. Evans, *J. Appl. Polym. Sci.* **25**, 1145 (1980).
6. R. M. Paroli, J. Lara, J.-J. Hechler, K. C. Cole, and I. S. Butler, *Appl. Spectrosc.* **41**, 319 (1987).
7. S. T. Wellinghoff, J. L. Koenig, and E. Baer, *J. Polym. Sci., Polym. Phys. Ed.* **15**, 1913 (1977).
8. J. L. Koenig and J. M. Tovar Rodriguez, *Appl. Spectrosc.* **35**, 543 (1981).
9. H. V. Drushel, *CRC Crit. Rev. Anal. Chem.* **1**, 161 (1970).
10. C. Tosi and T. Simonazzi, *Angew. Makromol. Chem.* **32**, 153 (1973).
11. E. Nishio, M. Morimoto, and K. Nishikida, *Appl. Spectrosc.* **44**, 1639 (1990).