

Use of Mid- and Near-Infrared Techniques as Tools for Characterizing Blends of Copolymers of Styrene–Butadiene and Acrylonitrile–Butadiene

Stephanie R. Shield, Ghebrehiwet N. Ghebremeskel

Research and Development Center, Ameripol Synpol Corporation, 1215 Main Street, Port Neches, Texas 77651

Received 31 January 2002; accepted 12 April 2002

ABSTRACT: There is increased technological interest in using blends of various dissimilar elastomers in applications for which service, material availability, or cost of a single elastomer do not provide the necessary processing, vulcanizate, or economic properties. The properties of these polyblends are sensitive to small variations in the amounts of the individual polymers used. Accurately estimating the elastomer composition of blends is of vital importance to the elastomer industry. This study illustrates the feasibility of using mid-infrared (MIR) and near-infrared (NIR) spectroscopy to estimate the amount of styrene–butadiene and acrylonitrile–butadiene copolymers in blends composed of varying ratios of the two elastomers. Sometimes it is difficult to obtain a film of an elastomer amenable to IR analysis; to address this problem, several techniques were developed in this study [MIR transmission of a film, attenuated total internal reflection (ATR)-FTIR of a chunk, and NIR using a

fiber-optic probe]. A plot of the absorbance ratio (absorbance of the characteristic peak for styrene–butadiene rubber or acrylonitrile–butadiene rubber/absorbance of the C=C stretching vibration of polybutadiene) versus the amount of each elastomer in the blend was used to predict the blend composition. In addition, the blends were also characterized by ATR-FTIR using a plot of the characteristic peak absorbance versus the polymeric content for a series of standards. A partial least-squares algorithm was used to develop a calibration curve for the NIR region. Finally, the accuracy of the test methods developed in this work is compared to results obtained by pyrolysis-GC/MS and thermogravimetric analysis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1653–1658, 2003

Key words: infrared spectroscopy; blends; rubber; pyrolysis; thermogravimetric analysis (TGA)

INTRODUCTION

The use of polymer blends for industrial applications has become more prevalent over the past few decades. Today polymer blends are widely used in the tire, mechanical goods, and adhesive industries. The main reason for the wide acceptance of elastomer blends is the fact that it is possible to obtain the right compromise of finished product properties by blending two or three elastomers at a certain optimum composition. Many elastomers that are dissimilar in chemical structure are blended to improve processability, performance, durability, physical properties, and to achieve an economic advantage. Elastomers with similar polarities and solubility characteristics can be easily combined to produce a miscible polyblend.^{1–9}

In applications where excellent solvent resistance is not crucial, it is often desirable to replace a portion of the acrylonitrile–butadiene rubber (NBR) with styrene–butadiene rubber (SBR).¹⁰ SBR has an economic advantage over NBR. Unfortunately, NBR has limited

compatibility with nonpolar polymers such as SBR, polybutadiene (BR), and natural rubber (NR). However, the low acrylonitrile NBR grades can be blended with SBR over the full range of concentrations without significant deterioration in properties.^{1,11,12} In fact, a number of these blends are used in several critical applications. NBR/SBR blends are used to compensate the volume decrease in oil seal applications,¹³ whereas BR/NBR blends are used to improve performance in cold bending and flow behavior in injection molding and to reduce brittleness temperature and extrusion energy.^{13,14}

As stated above, in many instances small variations in the amount of elastomers that make up a blend can significantly affect the physical and mechanical properties. Therefore, there is a need in the elastomer industry for a variety of analytical tools to monitor blend compositions. Pyrolysis techniques have been employed extensively to characterize elastomers in the presence of nontransparent fillers. FTIR spectroscopy is also used to characterize the composition of elastoblends. The infrared (IR) method currently used (ASTM D3677¹⁵) for rubber identification requires a lengthy sample preparation that involves an extraction step followed by pyrolysis of the elastomeric portion. In a multilaboratory study, Frisone and cowork-

Correspondence to: G. N. Ghebremeskel.
Contract grant sponsor: Ameripol Synpol Corp.

ers¹⁶ demonstrated the use of FTIR to characterize polymer blends. Parker and Waddell¹⁷ used photoacoustic FTIR to determine the acrylonitrile content of NBR and the styrene content of SBR. In this study, mid-infrared (MIR) and near-infrared (NIR) methods were used to characterize blends of SBR and NBR.

EXPERIMENTAL

Sample preparation

The SBR (23.5 wt % styrene) was obtained from Ameripol Synpol (Port Neches, TX). The NBR (23.5 wt % acrylonitrile) was obtained from the Uniroyal Chemical Company.

SBR and NBR were dry-mixed at 60°C for 8 min in a Brabender with 0.25 phr antioxidant added. Samples were prepared at 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 SBR/NBR levels.

Procedures

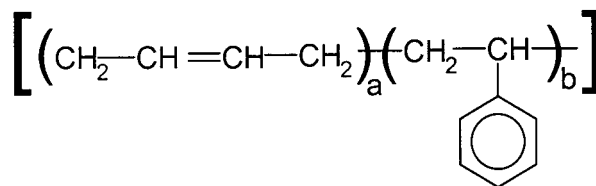
A Bruker Vector 33N FTIR/NIR (Bruker Instruments, Billerica, MA), equipped with a single bounce, horizontal attenuated total reflectance (ATR) element (ZnSe crystal) and a NIR fiber-optic probe (sheeted polyethylene fibers), was used to collect multiple (16) IR spectra, which were then signal-averaged. The sample preparation and specific experimental details are described below for each technique.

MIR spectroscopy

Thin films for MIR analysis were obtained by pressing approximately 0.2 g of sample for 3 min in a press (Pasadena Hydraulics, Pasadena, CA) held at 126°C and 35,000 psi. The film was then mounted onto a disposable adhesive IR card (Perkin-Elmer, Foster City, CA). Samples (small chunks) analyzed by ATR-FTIR were placed directly on the ZnSe (ATR) crystal and pressure was applied to mass the sample and obtain a uniform surface. Infrared spectra of the samples were collected from 400 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹. The resulting spectra (transmission and ATR) were normalized by setting the absorbance at 2100 cm⁻¹ (inactive region) to zero, and the absorbance was measured at specific wavenumbers characteristic to the elastomers.

NIR spectroscopy

NIR spectra were collected from 4000 to 12,000 cm⁻¹ (using a Peltier-cooled InAs diode detector) with 8-cm⁻¹ resolution using a fiber-optic diffuse reflectance probe. The resulting spectra were preprocessed using a vector normalization method. Three measurements of each standard were used to develop a NIR



Scheme 1 Styrene-butadiene rubber.

calibration and a partial least-squares (PLS) algorithm was used to cross-validate the model (Opus Quant 2 software).

RESULTS AND DISCUSSION

The mid-IR region in FTIR spectroscopy can be very useful for qualitatively identifying the individual elastomers that make up the polyblends. Each elastomer usually has one or more unique absorption bands that, if observed, may signify the presence of that particular polymer in the blend. Once the composition of the polyblend has been qualitatively determined, calibration curves can be established to determine the polymer blend ratio. In this study, the feasibility of using MIR and NIR spectroscopy to estimate polymer compositions of blends of SBR and NBR was investigated.

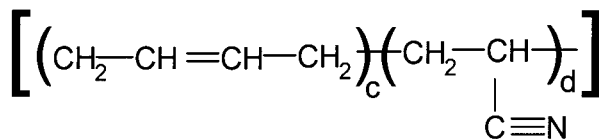
In the MIR method, the amount of incident radiation absorbed by a thin film was measured. As can easily be shown from Beer's law, the pathlength becomes less critical if one uses an absorbance ratio of two characteristic peaks of an elastomer, as shown in the following equation:

$$\frac{A_S}{A_B} = \frac{\epsilon_S b c_S}{\epsilon_B b c_B} = \frac{\epsilon_S c_S}{\epsilon_B c_B} \quad (1)$$

where A is the absorbance, ϵ is the extinction coefficient, b is the pathlength, and c is the concentration for styrene (S) and polybutadiene (B). The absorbance ratio of the blends was defined using a characteristic peak for each elastomer relative to the C=C stretching vibration of polybutadiene. The absorbance ratio was then plotted versus the amount of each component in the standards to develop a calibration curve.

Attenuated total internal reflectance FTIR (ATR-FTIR) can be employed for transmission measurements of elastomeric materials, which are often difficult to press into a smooth, thin film. The use of an ATR element eliminates scattering by the sample and maintains a constant pathlength, which allows direct analysis of the elastomer.

The frequencies selected for the characterization of the blends in this study are 1602, 1639, and 2237 cm⁻¹. The absorbance at 1602 cm⁻¹ is attributed to the carbon-carbon stretching vibration of the aromatic double bond (Scheme 1), ascribed to the styrene content of



Scheme 2 Acrylonitrile-butadiene rubber.

the elastomer. The absorbance at 1639 cm^{-1} is attributed to the stretching vibration of the olefinic portion of the elastomer (Schemes 1 and 2), ascribed to the butadiene in both SBR and NBR.

The absorbance at 2237 cm^{-1} is a weak stretching vibration assigned to $\text{C} \equiv \text{N}$ (Scheme 2), attributable to acrylonitrile.

Given that NIR provides information attributable to overtone and combination bands of the fundamental MIR stretching vibrational bands, it is more difficult to qualitatively identify blends; however, if the blend components are well known, a calibration model can be quickly and easily developed to quantitatively determine the blend composition.

Determination of the SBR content of SBR/NBR blends

MIR method

The FTIR spectra of the SBR/NBR blends clearly shows peaks that are characteristic of each elastomer, providing for relatively easy characterization. Figure 1 shows the FTIR spectrum of a 60/40 SBR/NBR blend, where the characteristic peaks are labeled as: styrene (1602 cm^{-1}), butadiene (1639 cm^{-1}), and acrylonitrile (2237 cm^{-1}).

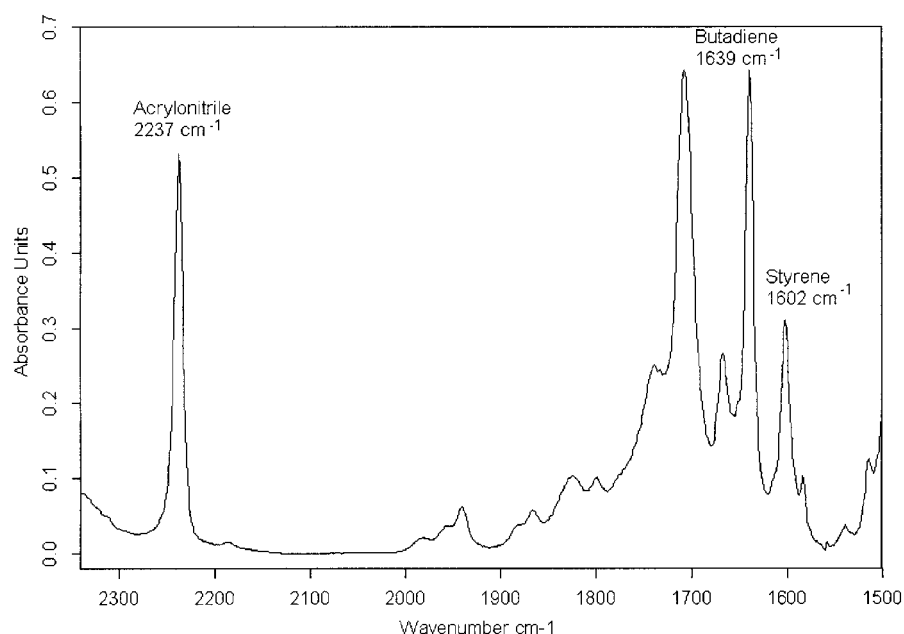


Figure 1 Characteristic peaks of styrene, polybutadiene, and acrylonitrile in an SBR/NBR (60/40) blend.

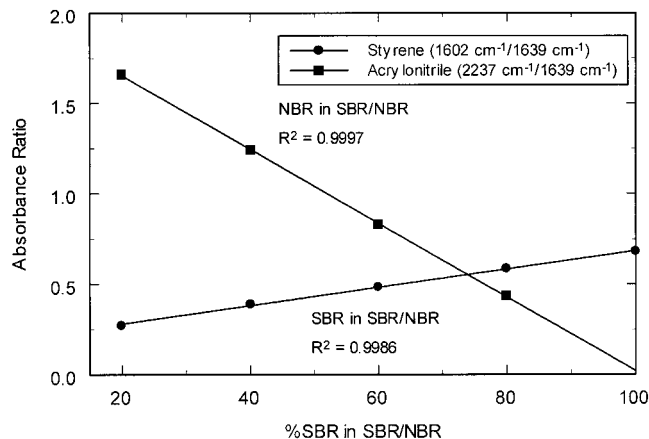


Figure 2 Plot of the absorbance ratio versus % SBR in SBR/NBR blends. Both absorbance ratios are plotted versus % SBR.

The SBR content of the SBR/NBR blends was determined from the ratio of peak heights of the absorbance peaks at 1602 and 1639 cm^{-1} , which correspond to styrene and butadiene, respectively. A plot of the absorbance ratio ($1602 \text{ cm}^{-1}/1639 \text{ cm}^{-1}$) versus the % SBR (Fig. 2) yielded a straight line with $R^2 = 0.9986$. The amount of SBR was then determined using the equation, $\% \text{ SBR} = (A_{1602 \text{ cm}^{-1}}/A_{1639 \text{ cm}^{-1}} - 0.1784)/0.0051$. The NBR content was determined from the ratio of peak heights for the absorbance peaks at 2237 and 1639 cm^{-1} , which correspond to acrylonitrile and polybutadiene respectively. The absorbance ratio of acrylonitrile/butadiene ($2237 \text{ cm}^{-1}/1639 \text{ cm}^{-1}$) versus % NBR was also plotted (Fig. 2) and yielded a straight line with $R^2 = 0.9997$. The amount of NBR

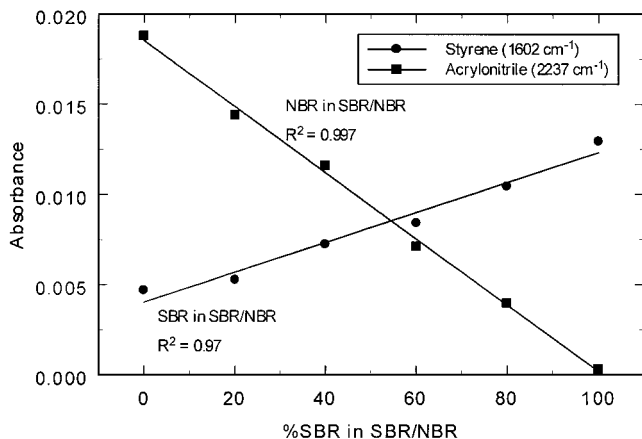


Figure 3 Plot of the ATR-FTIR absorbance versus % SBR in SBR/NBR blends. Both absorbances are plotted versus % SBR.

was then determined using the equation, % NBR = $(A_{2237 \text{ cm}^{-1}}/A_{1639 \text{ cm}^{-1}} - 0.0195)/0.0204$. The SBR and NBR content were determined independently from the two calibration curves and normalized to predict the blend composition.

The SBR and NBR contents in the blends were also determined by plotting the ATR absorbance peaks at 1602 cm^{-1} for styrene and 2237 cm^{-1} for acrylonitrile versus the SBR content of the blends (Fig. 3). The plot yielded a straight line with $R^2 = 0.97$ and $R^2 = 0.997$ for styrene and acrylonitrile, respectively. The technique assumes that the differences in the absorbance at 2100 cm^{-1} of the sample matrices used in this study

are not significant. The SBR and NBR contents were determined independently from the two calibration curves, using the equations % SBR = $(A_{1602 \text{ cm}^{-1}} - 0.0040)/8.27 \times 10^{-5}$ and % NBR = $(A_{2237 \text{ cm}^{-1}} - 0.0002)/0.0002$, and the results were normalized to predict the blend ratio.

NIR method

The raw NIR spectra of SBR and NBR over the data collection region are shown in Figure 4. Because NIR bands are overtones and combinations of fundamental bands, a factor analysis algorithm was used to interpret the data. A PLS model with cross-validation was employed in the region of 5443 to 6103 cm^{-1} , after vector normalization preprocessing of the data. Figure 5 shows the correlation between NIR predictions and the calculated % polymer in the SBR/NBR blends. The root mean squared error of cross-validation (RMSECV) and R^2 values were 0.6580 and 0.9996, respectively.

Technique accuracy

Several test samples of known SBR/NBR blend ratios were analyzed by FTIR, ATR, and NIR to verify and predict the error associated with the various methods of studying the blends. The SBR and NBR content were determined independently. On average, the deviation between the calculated and the determined blend ratios was less than 4% for the MIR methods and about 2% for the NIR method. The accuracy of the

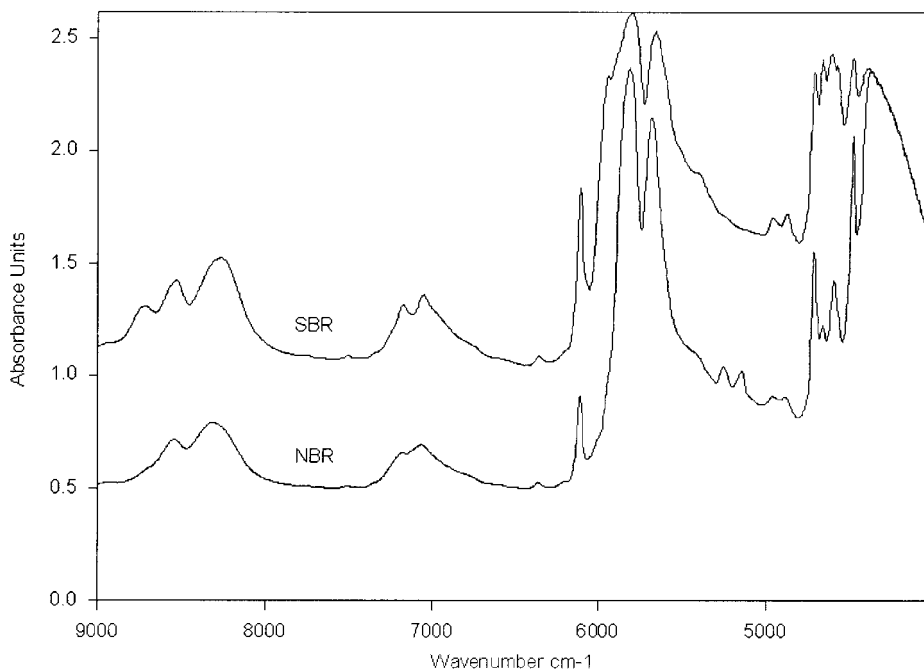


Figure 4 NIR spectra of SBR and NBR. The % SBR and % NBR of SBR/NBR blends was determined using a PLS model in the region of 5443 to 6103 cm^{-1} .

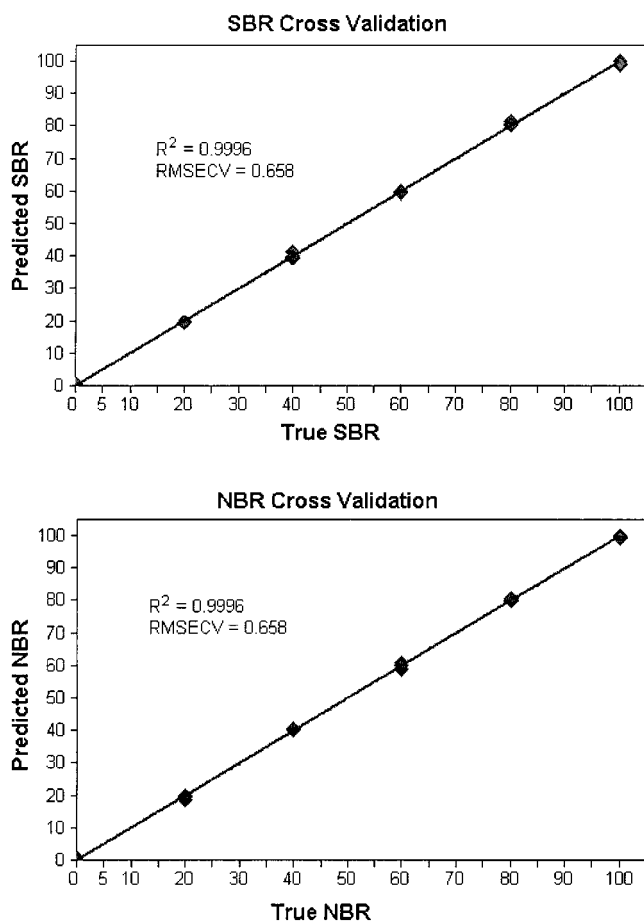


Figure 5 NIR predicted versus calculated % polymer in SBR/NBR Blends. Samples were analyzed in triplicate and a PLS algorithm with cross-validation was used to develop a calibration in the data region of 5443 to 6103 cm^{-1} .

predicted blend ratio obtained by FTIR, ATR, and NIR was also compared to the results obtained by thermogravimetric analysis (TGA) and pyrolysis-GC/MS (Py-GC/MS)¹⁸ (Table I).

Figure 6 shows the correlation between the absorbance ratio and the predicted SBR ($R^2 = 0.95$) and NBR ($R^2 = 0.98$) contents determined by pyrolysis-GC/MS. A plot of the ATR absorbance versus the calculated SBR ($R^2 = 0.95$) and NBR ($R^2 = 0.98$) con-

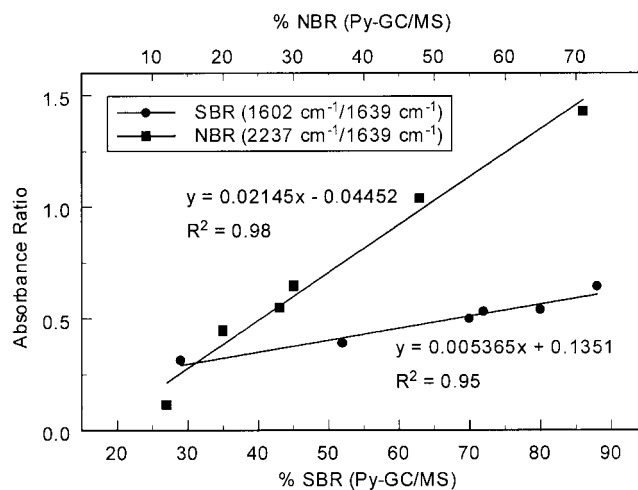


Figure 6 Absorbance ratio versus polymer content in SBR/NBR test samples as determined by pyrolysis-GC/MS. The absorbance ratio for SBR is plotted versus % SBR on the lower x -axis and the absorbance ratio for NBR is plotted versus % NBR on the upper x -axis.

tent by pyrolysis-GC/MS (Fig. 7) also showed a reasonably good correlation between the different methods. The FTIR-predicted blend ratios were comparable to those determined by other widely accepted techniques such as TGA and pyrolysis-GC/MS.¹⁸ Despite this high degree of correlation, one cannot assume that the techniques in question have been validated under all experimental conditions, given that high percentage errors are normally associated with the TGA and the pyrolysis-GC/MS techniques.

CONCLUSIONS

Elastomers are commonly blended to improve the processing, vulcanizate, or economic properties of the polymer. The physical, mechanical, and dynamic properties of these polyblends are sensitive to small variations in the amounts of the individual polymers. For this reason, there is a need in the elastomer industry for a variety of analytical tools to monitor blend compositions. In this study, methods for characterizing SBR/NBR blends were developed using FTIR

TABLE I
Predicted SBR/NBR Blend Ratios for Test Samples

Sample	SBR/NBR ^a	FTIR	ATR-FTIR	NIR	TGA ^b	Py-GC/MS ^b
1	89/11	95/5	91/9	86/14	73/27	88/12
2	79/21	77/23	82/18	78/22	67/33	80/20
3	70/30	73/27	66/34	73/27	63/37	72/28
4	67/33	67/33	65/35	67/33	55/45	70/30
5	50/50	45/55	44/56	44/56	41/59	52/48
6	30/70	27/73	26/74	28/72	38/62	29/71
Average % deviation:		±3	±4	±2	±10	±2

^a Ratio calculated from the recipe.

^b From Shield et al.¹⁸

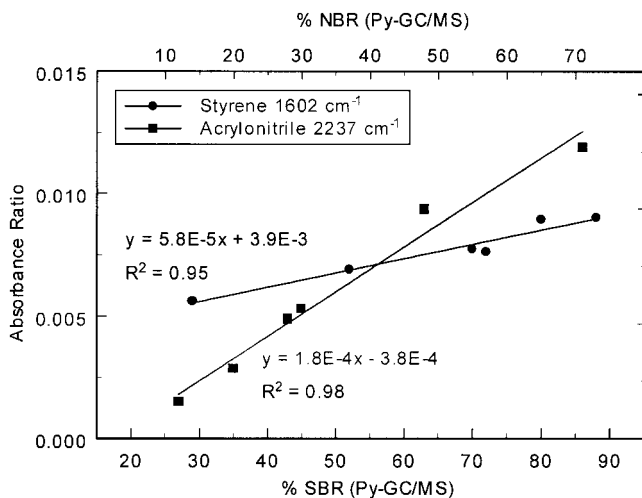


Figure 7 ATR-FTIR absorbance versus polymer content in SBR/NBR test samples as determined by pyrolysis-GC/MS. The absorbance at 1602 cm^{-1} is plotted versus % SBR on the lower x -axis and the absorbance at 2237 cm^{-1} is plotted versus % NBR on the upper x -axis.

spectroscopy, employing both the mid-IR and the near-IR regions.

Results of this study show that FTIR spectroscopy is an excellent tool for characterizing the elastomeric composition of elastoblends. An absorbance ratio for peaks characteristic of the polymers was used to determine the SBR and NBR content of the elastoblends. For applications where preparing a film is not practical, ATR-FTIR was used to eliminate the inaccuracies in measuring the pathlength. In this technique, the absorbance of the characteristic components was monitored as a function of concentration. The NIR method, using a PLS algorithm with appropriate standards, was used as a tool to accurately determine the polymer composition of the elastoblends. The average deviation of these techniques was found to be comparable to the results obtained from well-accepted TGA and pyrolysis-GC/MS techniques.¹⁸

Blends are widely used in the polymer industry, and there is a wide array of methods available for their characterization. One main concern when selecting an analytical test method for characterizing rubber is the potential interference from rubber additives such as oils, organic acids, antioxidants, crosslinking agents, resins, binders, accelerators, carbon black, and other fillers. Thermal analysis techniques such as TGA and pyrolysis-GC/MS are commonly used to characterize samples that contain these components. However, to obtain reproducible results using these thermal analysis techniques, the energy parameters, such as tem-

perature, heating rate, and heating time, must be accurately controlled. In addition, sample uniformity is always an issue because of the small sample size used in these techniques. Although infrared-based techniques are not typically capable of accurately and quantitatively characterizing filled rubber (unless the sample is dissolved and fillers are filtered out), these techniques offer a relatively faster analysis. Because the analysis time of the IR methods is relatively short, the error attributed to the nonuniformity of the sample matrix can be minimized by analyzing several sections of the sample. Results of this study show that FTIR and NIR are useful tools for studying blends of SBR and NBR. The FTIR techniques (MIR transmission, ATR-FTIR, and NIR) investigated in this study can be used in a variety of applications and provide a convenient means of accurately characterizing polymer blends.

The authors acknowledge the Ameripol Synpol Corp. for support of this work. This work was adapted from a paper presented at the 160th Rubber Division of the American Chemical Society Meeting in Cleveland, OH, October 16–19, 2001.

References

- Ghebremeskel, G. N.; Zhao, J.; Peasley, J. *Rubber World* 1998, 219, 37.
- Ghebremeskel, G. N.; Zhao, J.; Peasley, J. *Kautsch Gummi Kunstst* 2001, 3, 84.
- Zhao, J.; Ghebremeskel, G. N.; Peasley, J. *Kautsch Gummi Kunstst* 2001, 5, 223.
- Ghebremeskel, G. N.; Zhao, J.; Peasley, J. *Rubber Technol Int* 1999, 22.
- Coran, A. Y.; Patel, R. *Rubber Chem Technol* 1980, 53, 781.
- Coran, A. Y.; Patel, R. *Kautsch Gummi Kunstst* 1982, 35, 194.
- Coran, A. Y.; Patel, R. *Gummi Asbest Kunstst* 1984, 37, 378.
- Bhowmick, A. K.; De, S. K. *Rubber Chem Technol* 1980, 53, 960.
- Krause, S. J. *Macromol Sci Rev Macromol Chem* 1972, C7, 251.
- Heggs, R. P.; Marcaus, J. L.; Markham, R. L.; Managaraji, D. *Plast Eng* 1988, June, 29.
- Dunn, J. R.; Vara, R. G. In *Proceedings of the 128th Rubber Division Technical Meeting*, Cleveland, OH, October 1–4, 1985.
- Jofmann, W.; Verschut, C. *Kautsch Gummi Kunstst* 1982, 35, 95.
- Bertram, H. H. In *Developments in Rubber Technology*, 2nd ed.; Whelan, A.; Lee, K. S., Eds.; Elsevier Applied Science: Amsterdam/New York, 1981; p. 51.
- Stollfuss, B. Perbunan N., Technical Information Bulletin No. 2.7.1; Bayer A-G: Germany, September 1977.
- ASTM D3677. *Annu Book ASTM Stand* 1990, 09.01.
- Frisone, G. J.; Schwarz, D. L.; Ludwigsen, R. A. *Rubber Plast News* 1997, 21.
- Parker, J. R.; Waddell, W. H. *J Elastom Plast* 1996, 28, 140.
- S. R.; Shield, Ghebremeskel, G. N.; Hendrix, C. *Rubber Chem Technol*, to appear.