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Quantification of natural rubber blends by reflection/reflectance infrared and confocal Raman spectroscopy: a comparison of statistical methods

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Abstract: The blend of butadiene and acrylonitrile copolymer (NBR) with natural poly-cis-isoprene (NR) shows increased resistance to swelling in solvents in comparison to the individual components. In aerospace, NBR rubber is used as thermal protection for rockets and shall not contain other polymers, even in low contents, otherwise, it can affect the protection performance and rocket safety by causing detachment of the elastomer/propellant interface; therefore, this investigation presents methodologies to determine the NR/NBR contents. This study explores different analytical techniques, such as Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy, in the mid-infrared (MIR) by reflection and in the near-infrared by reflectance (NIRA) modes, Furthermore, quantification strategies by univariate, bivariate and multivariate (chemometric) models are evaluated and compared. A proposed methodology, based on multivariate Raman microscopy with partial least squares regression (PLS), showed high linearity (R^2 > 0.99) and low error (< 0.82 %). The validation of FT-MIR data for the CH_3, which presented lower error (1.3%) than vinylidene band (6%), showed that both methodologies (reflection and NIRA reflectance) can be used for the quantification of NR in NR/NBR. These results constitute a contribution to the state of the art in researching industrial and aerospace elastomeric applications.

Key words: NBR, NIRA, NR, quantitication, spectroscopy, UATR.

INTRODUCTION

Elastomers are materials of great interest to the industry, as they enable new solutions such as the development of blends. Rubber blends bring gains in system properties, thus achieving better cost-effective (Novaes 2010). Natural poly-cis-isoprene (NR) and styrene-butadiene copolymer (SBR) rubbers are examples of elastomers that benefit from the formation of blends, as their flaws are compensated by the added polymer. NR rubber is a naturally biosynthetic polymer, and shows an attractive range of properties, such as excellent physical properties and good processing characteristics. However, NR has low heat resistance and resistance to ultraviolet (UV) rays. SBR-based elastomers provide good mechanical properties, good resistance to abrasion, ozone and weathering, but has low resistance to oils (Novaes 2010).

NR is applied in the aerospace sector as flexible joint, which generally consist of elastomeric material layers alternated with reinforcing rings of metallic material (Mohan et al. 2011). SBR rubber is commonly used in the automotive industry (Rocha et al. 2007) and is sometimes added to the formulation of other rubbers to reduce costs. The use of SBR or any elastomer other than that specified for the aerospace applications is undesirable in aerospace applications because certain properties may be impaired, even with the addition of low contents. This mixture is especially deleterious to properties in high performance applications, as in the case of thermal protections for rocket engines. In this context, the development of methodologies that allow establishing the limit of quantification of elastomers in binary rubber blend and that ensure the quality control of materials is widely desired (Azevedo et al. 2018).

The butadiene and acrylonitrile copolymer (NBR) is also an important material in the industrial scenario and is used in thermal protections for rocket engines (Palmério et al. 2017, Pedreira et al. 2016). The preparation of the NBR/NR blend results in well-balanced properties (mechanical and chemical resistance), also useful for other applications. NR is a non-polar rubber with good mechanical properties; however, it presents relatively poor swelling resistance in hydrocarbon oil. In contrast, NBR is polar and its unfilled vulcanizate shows low mechanical properties; nevertheless, shows good swelling resistance in hydrocarbon oil (Salih et al. 2018).

Improperly adding of unsuitable elastomers for the proper application to lower the cost of rubber formulations is a risk, including in aerospace applications. In this case, the quality of the product delivered by the supplier will possibly not meet the specification necessary for aerospace use. Non-conforming materials might compromise the integrity of the rubber/propellant interface and lead to debonding. Therefore, the proper quantification of components is extremely necessary to investigate the presence of the suitable content of elastomers in the blends. This is also valid in the automotive industry, for example in SBR or NR rubber blends (Azevedo et al. 2018).

Instrumental techniques have been used for the characterization and quantification of different polymeric blends (Barros et al. 2022, Saboor & Safajou-Jahankhanemlou 2022, Zhao et al. 2022, Abd El-Kader et al. 2021, Paduvilan et al. 2021, Rigoli et al. 2021, 2019, Riba et al. 2019, Hariwongsanupab 2017, Dutra et al. 2004). Several techniques are used, such as: scanning electron microscopy (SEM) and transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR).

FT-IR spectroscopy is used in a recent qualitative investigation (Zhao et al. 2022) of vulcanized thermoplastic silicone rubber (TPSiV®), with different contents of methyl vinyl silicone rubber (MVSR), styrene copolymer ethylene butene styrene (SEBS) and styrene butadiene styrene copolymer (SBS). Compatibility and distribution of the MVSR phase and the SEBS/SBS phase were qualitatively characterized by attenuated total reflection (ATR)/FT-IR spectroscopy. Basically, results show wavenumber shifts, and that decreasing the relative silicone rubber content led to more pronounced shifts. However, according to the authors, the results of the FT-IR analysis only indicate that the MVSR and SEBS/SBS blend systems have some compatibility, and that quantitative conclusions cannot be drawn about the compatibility of MVSR and SEBS/SBS in relation to the different blend contents.

In an investigation by Saboor & Safajou-Jahankhanemlou (2022), a ternary rubber containing natural poly-cis-isoprene or natural rubber, copolymer of butadiene and styrene and polybutadiene (NR/SBR/BR) is prepared with the respective contents 25/25/50 (phr).

The effect of adding carbon black, nanoclay and nanosilica is evaluated by its mechanical and morphological properties. Results reveal that nanosilica provides greater elongation at break. TEM analysis is performed on crosslinked samples to ensure exfoliation of nano additives in the matrix. Results confirm the proper distribution and dispersion of nanoparticles in the composite samples.

As FT-IR spectroscopy, associated with other techniques (Rigoli et al. 2019) or not (Rigoli et al. 2021, Riba et al. 2019, Azevedo et al. 2018), was suitable for the determination of elastomer content in rubber blends, this instrumental technique was employed in this study in association with Raman spectroscopy, for the characterization of chemical structures and quantification of binary rubbers based on NBR and NR.

The previously cited articles employed mostly mid-infrared (MIR) and conventional modes of obtaining spectra: transmission and ATR. Even though a few of these studies used less conventional reflection techniques, such as universal attenuated total reflection (UATR), there are gaps to be explored in the characterization and quantification of blends, such as reflectance analysis in the near infrared region (NIRA) for NR/NBR.

Some studies discuss error or address strategies for optimizing quantification limits of spectroscopic methods for the quantification of elastomeric systems. Linear models based on the Lambert-Beer law have been used for quantitative determinations in elastomers, exploring the direct relationship between the intensity/height of the component band as a function of its concentration. In this case, the error is determined as a function of median intensities in replicate sample preparations. These methods, in general, present equipment precision (error) around 2% (Hórak & Vítek 1978) and are indicated for quantitative determinations in components with contents higher than 10% by mass (Barros et al. 2022, Rigoli et al. 2019, Azevedo et al. 2018, Ferreira et al. 2018).

The application of Lambert-Beer law for quantifications by using non-linear calibration models has also been reported. FT-IR quantification of SBR/NBR system showed a non-linear relationship between the characteristic band ratios, however a better calibration was achieved by polynomial regression (Fernández-Berridi et al. 2006). Multivariate models based on partial least squares regression (PLS) have been reported with success in the quantification of elastomeric systems. In multivariate analyses, errors are determined by cross-validation, followed by error calculation by the root mean square error (RMSE) method. These methodologies have been used for the determination of base polymer, additives and impurities (Weigel et al. 2021, Riba et al. 2019, Wang et al. 2019).

Considering that different industrial sectors, including aerospace, benefit from elastomeric blends, the development of new qualitative and quantitative methodologies applied to these materials, with the use of spectroscopic techniques such as FT-IR/Raman, and applying non-conventional methods of obtaining spectra and chemometric methods, is important for predicting the properties of these materials. In addition, robust, fast and accurate methods meet the pursuit of companies for characterization (structure/property relationship) and quality control.

MATERIALS AND METHODS

The aim of this study is to compare the validation results of different methodological proposals where the experimental error (accuracy), reproducibility (precision) and quantitative response linearity were compared. Nine (9) vulcanized sheets of elastomeric blends, with different NR and NBR contents, respectively, 10:90; 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20 and 90:10, were prepared. Five (5) replicates (N=5) of each sample were analyzed. Elastomers were kindly provided by Tenneco.

The complete formulations of the elastomeric blends, with additives, were not reported because the object of this study is the quantitative analysis of only the elastomers. The nominal contents of the elastomers in the blends are sufficient, considering that the necessary care was taken in the preparation of the samples for the analysis in the infrared (treatment with suitable solvent) so that the additives did not influence the determination.

A PerkinElmer Frontier Model spectrometer was used for the quantitative study by FT-IR, equipped with the UATR accessory with zinc selenide/diamond crystal, in the MIR spectral range, from 4000 to 550 cm^{-1}, resolution 4 cm^{-1} and 20 scans. The NR/NBR samples were pyrolyzed in a Bunsen burner, and the pyrolyzate was transferred directly to the UATR crystal using a stainless-steel spatula.

The quantitative Raman study was carried out using a Raman Horiba microscope, model LabRAM HR Evolution, in the spectral range of 50 to 3200 Raman shift cm^{-1}, resolution 1 cm^{-1}, acquisition time of 20 seconds and 3 scans. Measurements were performed directly on the surface of the samples, without any previous treatments.

Nine (9) different methodologies were used for the comparison study, based on FT-MIR/UATR spectroscopy techniques and dispersive Raman Microscopy. Table I presents the differences of each proposed methodology.

The analytical band, which is associated with the functional group to be determined, was chosen according to the characteristic bands of each elastomer described in the literature (Wake 1983). The concept of relative band is associated with the Lambert-Beer law that governs quantitative analysis by infrared spectroscopy (Smith 1979). From the

Table I. **Methodologies evaluated for the quantification of the NR/NBR system.**

Methodology	Technique	Processing	Model	Regression	Analytical or relative band/rubber
A	FT-MIR/UATR	Median of spectra	Univariate	Linear	A_{2237} (*) (NBR)
B	FT-MIR/UATR	Median of spectra	Univariate	Linear	A_{1376} (*) (NR)
C	FT-MIR/UATR	Median of spectra	Univariate	Linear	A_{887} (*) (NR)
D	FT-MIR/UATR	Median of spectra	Bivariate	Linear	Relative band: A887/A2237
E	FT-MIR/UATR	Median of spectra	Bivariate	Linear	Relative band: A1376/A2237
F	FT-MIR/UATR	Median of spectra	Bivariate	Polynomial	Relative band: A887/A2237
G	FT-MIR/UATR	Median of spectra	Bivariate	Polynomial	Relative band: A1376/A2237
H	FT-MIR/UATR	SNV Normalization	Multivariate	PLS	Multiples
I	Raman (514nm)	Derivative 1st Order	Multivariate	PLS	Multiples

(*) baselines: band 2237 cm^{-1} – 2300-2126 cm^{-1}; band 887 cm^{-1} – 920-860 cm^{-1}; band 1376 cm^{-1} - 1394 to 1354 cm^{-1}.

absorbance and concentration relationship, it is possible to eliminate the interference of the sample thickness variation. This variation must be avoided because it can cause errors in measuring the intensity/height of the analytical bands. The solution involves the use of a relative band, which can be composed by an analytical band and a reference band (which does not change the intensity with the variation of the content of a certain component), or even by two analytical bands, as was done in this study. The use of relative band also helps in the most adequate measurement of height/intensity in reflection spectra, such as those obtained in this investigation. In this case, the optical path is variable, influencing the band intensity (Barros et al. 2022, Ferrão 2001).

The 9 (nine) methodologies (Table I) were compared in terms of accuracy (difference from the nominal value), precision (methodological error related to reproducibility) and coefficient of determination (related to the ability of spectral variations to estimate NR and NBR contents).

This study evaluated the performance of PLS regression with band selection using full spectra of the FT-MIR and Raman spectroscopy, the optimization and variable selection were determined by cross-validation using the Sartorius multivariate analysis software SIMCA version 15, and the statistical treatments were performed using the statistical analysis software JMP Statistical Discovery, version 16, from SAS Institute Inc.

For the validation of the FT-IR/UATR results (univariate model) in relation to the MIR band of methyl at 1376 cm^{-1} (assigned to the NR), which presented the best error, the nine samples were tested using reflectance analysis in the near infrared region (NIRA), employing the same PerkinElmer Frontier Model spectrometer, in the NIR spectral range, from 6500 to 4000 cm^{-1}, 4 cm^{-1} resolution and 20 scans. The samples were previously extracted in methanol, which is the suitable solvent for rubbers containing NBR, and then pyrolysed (Wake 1983). The chosen analytical band is the one found at 4063 cm^{-1}, which can be probably related to the NR CH and methyl group combination band (Workman & Weyer 2008, Goddu 1960).

The variabilities, accuracy and precision of the developed methodologies were calculated according to Chai & Roland (2014) and Hórak & Vítek (1978), respectively. The Hórak & Vítek methodology considers the median for spectroscopic error calculations and the calculation of the error based on the median of errors or relative deviations and has been widely adopted in previous works (Barros et al. 2022, Rigoli et al. 2021, Dutra & Soares 1998).

RESULTS AND DISCUSSION

FT-IR/UATR analysis of the NR/NBR blend

Figure 1 presents the FT-MIR/UATR spectra of the NR/NBR samples with different contents. The individual spectra of NR and NBR elastomers were also added, to visualize their analytical bands. The band intensity around 2237 cm^{-1} (marked*), from the stretching ν C≡N group, declines with the decreasing of the NBR content in the blend. The opposite happens with the band intensity around 887 cm^{-1} (marked 0), from the wagging (ω) of the NR vinylidene group. The intensity of the band around 1380 cm^{-1} (marked #), from the symmetrical bending (δ_s) of the CH_3 group, also increased and was evaluated for the NR content as well. These data are in accordance with the Lambert-Beer law (Smith 1979), which indicates that the quantitative determination of this system is possible.

The weak NBR bands are consistent with its molar absorptivity characteristics (Smith 1979). Obtaining spectra in reflection mode, by UATR, also contributes to results with weak intensity

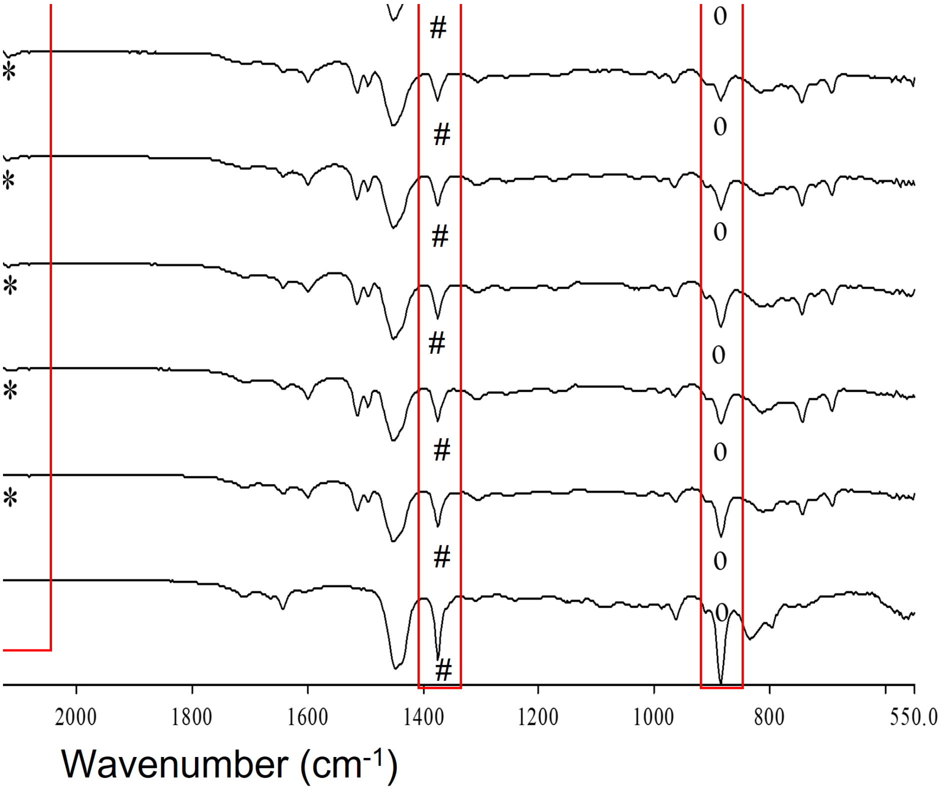

Figure 1. Comparison of FT-MIR/UATR/Bunsen burner pyrolysis spectra of NR/NBR.

when bands with higher wavenumber are analysed, due to the low penetration of the IR beam (Ferrão 2001). Nevertheless, this band was chosen because it is easier to measure as it is located outside of the fingerprint region (1500 – 400 cm^{-1}), which has several adjacent bands.

Raman analysis of the NR/NBR blend

Figure 2 shows the Raman spectra obtained with a 514 nm laser of the NR/NBR binary samples, in different contents, to assess the analytical regions for quantification of each elastomer. Results show that samples with higher NR levels present better responses regarding analytical bands. However, it was not possible to assign the functional groups related to the Raman Shifts because there is no information in the consulted literature about it. Also, no direct association between the intensity of the bands and the elastomer contents is observed, only a baseline variation. Thus, two regions were chosen, A and B, respectively, between 100-1600 cm^{-1} and 2800-3200 cm^{-1} (Raman shift), which were used to build the quantitative chemometric model.

Comparison of FT-IR/UATR and Raman results

Table II presents the consolidated accuracy results for each methodology. An adaptation of the method proposed by Horak & Vitek in 1978, which considers the median of intensity between replicas, was employed in the PLS regression methods. Since chemometric models consider multiple intensities, accuracy was determined based on prediction results so that all quantitative methodologies (univariate, bivariate or multivariate) were compared to the same precision assessment method. This adaptation does not affect the interpretation of the results or even the foundation proposed by Hórak & Vitek, in 1978, since the precision is related to the variation of the repeated measures. Hence, for the univariate or bivariate

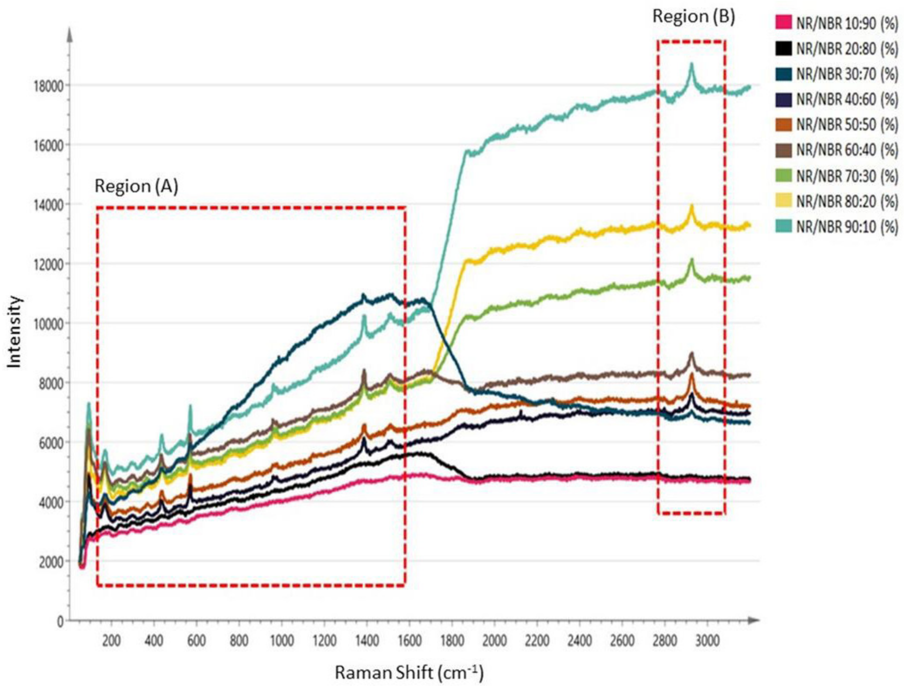

Figure 2. Comparison of NR/NBR Raman spectra.

models, precision means repeatability among signal intensity obtained for a same sample as well as for the multivariate models means repeatability among prediction responses for a same sample.

As the comparison between the proposed methodologies depends on accuracy, linearity and accuracy, no inference on methodological superiority is approached individually for these parameters.

Regarding the linearity of the developed methodologies, the selection of the analytical band and the type of processing of the spectra influences directly the quantitative relationship between the absorptions and the elastomer content (NR/NBR). Figure 3 demonstrates in a consolidated form the different regressions obtained by each proposed methodology.

A comparison between the nominal values and the results of each regression was performed for all obtained spectra and treatment models to determine the accuracy of each model. Table III presents the results of the accuracy of each model, expressed in percentage error.

In order to evaluate the analytical validation parameters described by accuracy, precision and linearity, the following scale, based on “Evaluating the Measurement Process” proposed by Wheeler (2004) was adopted: method considered EXCELLENT (Error % Precision/Accuracy < 2%; R^2 > 0.95); ADEQUATE methods, with restrictions (Error % Precision/Accuracy < 10%; R^2 > 0.90); INADEQUATE methods (Error % Precision/Accuracy > 10%; R^2 < 0.90). Table IV shows the comparison between the methodologies.

FT-NIR/NIRA and FT-MIR/UATR validation of the NR/NBR system

Initially, Figure 4 of the NR/NBR system was created containing some FT-IR spectra by NIRA reflectance (univariate), compared to NR and NBR spectra, to choose the best analytical bands to be used in the determination of the elastomers content. Not all sample spectra were used, to avoid flattening the bands in the figure, which would make it difficult to visualize the individual bands.

Table II. Consolidation of error (%) in terms of precision, calculated by the median method of errors (Hórak & Vítek 1978).

Methodology	Technique	Model	Regression	Band used	Error (%) in terms of precision
A	FT-MIR/UATR	Univariate	Linear	A_{2237}	6.1
B	FT-MIR/UATR	Univariate	Linear	A_{1376}	1.3
C	FT-MIR/UATR	Univariate	Linear	A_{887}	6.0
D	FT-MIR/UATR	Bivariate	Linear	A_{887}/A_{2237}	7.8
E	FT-MIR/UATR	Bivariate	Linear	A_{1376}/A_{2237}	6.6
F	FT-MIR/UATR	Bivariate	Polynomial	A_{887}/A_{2237}	7.8
G	FT-MIR/UATR	Bivariate	Polynomial	$A_{1376/}A_{2237}$	6.6
H	FT-MIR/UATR	Multivariate	PLS	Multiples	1.4
I	Raman 514nm	Multivariate	PLS	Multiples	0.8

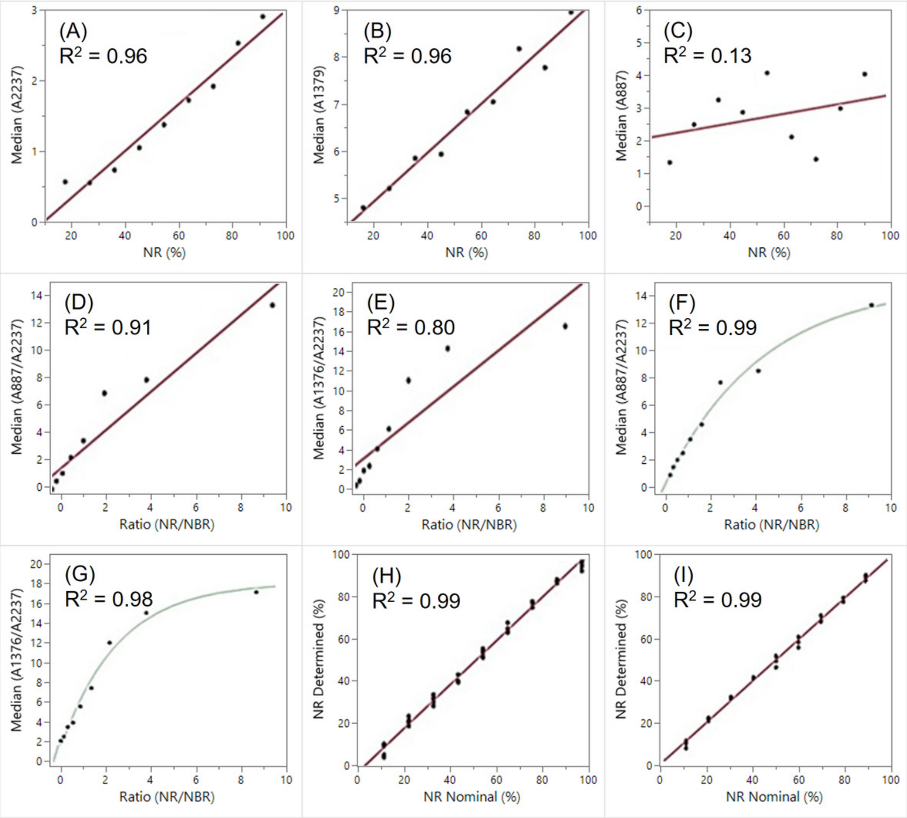

Figure 3. Linearity for the different methodologies.

NIRA results were used to validate the FT-IR/MIR-UATR study (univariate) of the NR/NBR blend in the NIR region, in relation to the 1376 cm^{-1} band of the methyl group, which presented the lower error for the NR rubber (1,3% in relation to 6% of vinilydene group in the 887 cm^{-1}- Table II). The corresponding analytical band in the NIR region is the one found at 4063 cm^{-1}, probably assigned to the combination band of CH group and NR methyl group (Workman & Weyer 2008, Goddu 1960) and whose intensity increases with the increase of NR content, obeying the law of Lambert-Beer (Smith 1979). A band around 4480 cm^{-1} was also observed, which apparently

Table III. Error (%) in terms of accuracy calculated by the RMSE method.

Methodology	Technique	Model	Regression	Band used	Error (%) in terms of accuracy
A	FT-MIR/UATR	Univariate	Linear	A_{2237}	8,5
B	FT-MIR/UATR	Univariate	Linear	A_{1376}	8.2
C	FT-MIR/UATR	Univariate	Linear	A_{887}	15.7
D	FT-MIR/UATR	Bivariate	Linear	A_{887}/A_{2237}	4.7
E	FT-MIR/UATR	Bivariate	Linear	A_{1376}/A_{2237}	9.6
F	FT-MIR/UATR	Bivariate	Polynomial	A_{887}/A_{2237}	5.3
G	FT-MIR/UATR	Bivariate	Polynomial	$A_{1376/}A_{2237}$	5.7
H	FT-MIR/UATR	Multivariate	PLS	Multiples	1.9
I	Raman 514nm	Multivariate	PLS	Multiples	1.6

Table IV. Consolidated results of methodologies used to quantify the NR/NBR system.

Met.	Technique	Model	Regression	Band used	Precision error (%)	Accuracy error (%)	Linearity (R^2)	General Evaluation
A	FT-MIR	Univariate	Linear	A_{2237}	6.1 (A)	8.5 (A)	0.95 (A)	Adequate, with restrictions
B	FT-MIR	Univariate	Linear	A_{1376}	1.3 (E)	8.2 (A)	0.96 (E)	Adequate, with restrictions
C	FT-MIR	Univariate	Linear	A_{887}	6.0 (A)	15.7 (I)	0.13 (I)	Inadequate
D	FT-MIR	Bivariate	Linear	A_{887}/A_{2237}	7.8 (A)	4.7 (A)	0.91 (A)	Adequate, with restrictions
E	FT-MIR	Bivariate	Linear	A_{1376}/A_{2237}	6.6 (A)	9.6 (I)	0.80 (I)	Inadequate
F	FT-MIR	Bivariate	Polynomial	A_{887}/A_{2237}	7.8 (A)	5.3 (A)	0.99 (E)	Adequate, with restrictions
G	FT-MIR	Bivariate	Polynomial	$A_{1376/}A_{2237}$	6.6 (A)	5.7 (A)	0.98 (E)	Adequate, with restrictions
H	FT-MIR	Multivariate	PLS	Multiples	1.4 (E)	1.9 (E)	0.99 (E)	Excellent
I	Raman (514nm)	Multivariate	PLS	Multiples	0.8 (E)	1.6 (E)	0.99 (E)	Excellent

Note: the abbreviations (E), (A) and (I) were used to briefly demonstrate the parameters classified as "EXCELLENT", "ADEQUATE" and "INADEQUATE", respectively.

decreases in intensity as the NBR content decreases, and is probably assigned to the first overtone of the nitrile group (Workman & Weyer 2008, Goddu 1960). However, this absorption was not evaluated due to its low intensity, which may result in greater errors for measuring the height of the analytical band for lower rubber contents.

Table V presents the median values of the absorbances of the analytical band A_{4063} of the NR rubber for the reflectance methodology (NIRA), as well as the calculations of deviations and error of the methodology, according to Hórak & Vítek (1978). The same methodology was adopted for the values obtained by UATR for the same binary system, whose results have already been shown in Table II.

Figure 5 shows the NIRA calibration/Bunsen burner pyrolysis curve, with the median values of the analytical band A_{4063} versus the NR content (%) in NR/NBR. Equation 1 is proposed from the calibration curve:

$$y = 0.0013x + 0.0446 \tag{1}$$

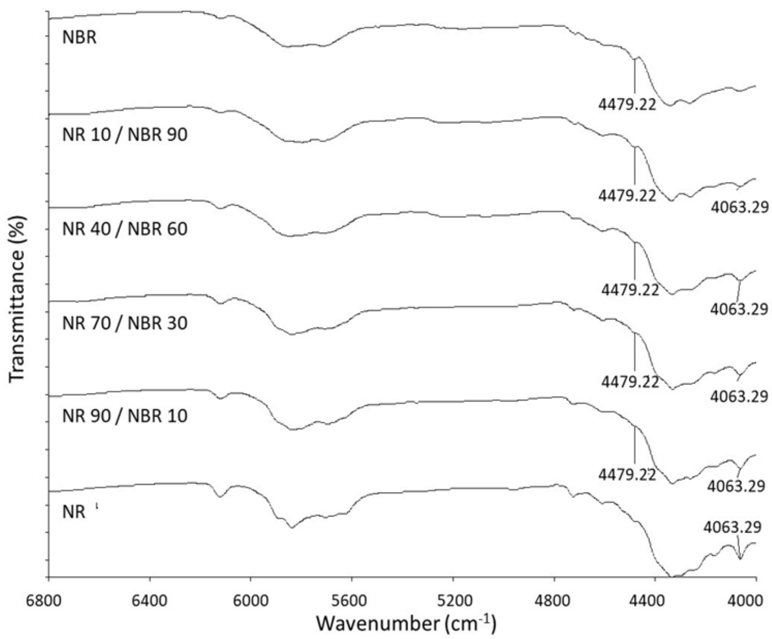

Figure 4. FT-IR/NIRA-reflectance of neat NR and NBR and selected binary blends -spectral range (6500-4000 cm^{-1}).

where y = median value of the band A_{4063} *versus* the content of NR (%)

Good data correlation is observed (R= 0.996), and about 99% (R^2) of the data obtained are explained by this methodology, which indicates that the NIRA analysis is effective for the proposed type of determination.

To validate the absorbance data in a wide FT-IR spectral range and considering that the band of the methyl group (A_{1376}) in the NR/NBR blend had already been investigated in the MIR region by reflection (UATR), the data found by this methodology was compared to that obtained by NIR/NIRA transflectance with a band also assigned to the methyl group (A_{4063}) (Table VI and Figure 6).

Although the absorbance values of the A_{1376} band are relatively high compared to the NIRA analysis (Table VI), Figure 6 shows that the NIRA data validate those obtained in the MIR region, suggesting that these data can be related to the NR content. The parameters of the calibration curve (R = 0.978 and R^2 = 0.956, that is, approximately 96% of the data are explained by the methodologies) indicate that NIRA (A_{4063}) and MIR/UATR (A_{1376}) data are validated, and endorse both FT-IR methodologies developed for the FT-IR determination of NR in NR/NBR, in a wide spectral range. The errors of the MIR/UATR (1.3% - Table II) and NIRA (1.95% - Table V) methodologies are within the accuracy limits of the FT-IR equipment (≤ 2%, according to Hórak & Vítek 1978).

As the modes of obtaining spectra have similar characteristics (reflection and reflectance) and the sample preparation technique is the same (Bunsen burner pyrolysis) used in the MIR analysis of NR/NBR, the differences are attributed only to the region spectral. This type of data comparison is considered valid, because the quantitative analysis conditions must be as similar as possible (such as using the same equipment, same operator, as well as similar way of obtaining and sample preparation technique) (Smith 1979). Therefore, this validation of IR data in different spectral regions for the analysis of the same system is a good practice, and has already been adopted in other studies (Barros et al. 2022, Carvalho et al. 2021, Janzen et al. 2021), for the validation of the FT-IR spectral data.

Table V. FT-IR/NIRA/Bunsen Burner Pyrolysis (A_{4063}) Results and Related Errors.

Sample NR/NBR (NR %)	ANALYTICAL BAND A_{4063} (NR)	MEDIAN A_{4063}	STANDARD DEVIATION	AVERAGE STANDARD DEVIATION	RELATIVE DEVIATION (RD) (%)	METHODOLOGY ERROR (%)
10	0.060	0.060	0.006	0.003	5.00	1.95
	0.054					
	0.057					
	0.069					
	0.067					
20	0.067	0.067	0.002	0.001	1.49	
	0.067					
	0.073					
	0.072					
	0.067					
30	0.075	0.079	0.003	0.001	1.26	
	0.079					
	0.082					
	0.081					
	0.076					
40	0.096	0.096	0.006	0.003	3.12	
	0.101					
	0.088					
	0.088					
	0.103					
50	0.104	0.107	0.004	0.002	1.87	
	0.109					
	0.099					
	0.109					
	0.107					
60	0.123	0.121	0.008	0.004	3.30	
	0.134					
	0.121					
	0.116					
	0.120					
70	0.143	0,138	0,004	0,002	1,45	
	0.135					
	0.138					
	0.138					
	0.134					

Table V. Continuation.

80	0.133	0.146	0.007	0.003	2.05	
	0.150					
	0.146					
	0.143					
	0.150					
90	0.155	0.154	0.006	0.003	1.95	
	0.154					
	0.162					
	0.153					
	0.149					

Note: baseline for the band A_{4063} - 4110 to 4000 cm_{-1}. Standard deviation - Where, R = highest value - lowest absorbance value. KR = 0,430 for 5 measurements (Hórak & Vítek 1978). Where, n= number of measurements
Relative deviation (RD) - Where, µ is the median absorbance value.

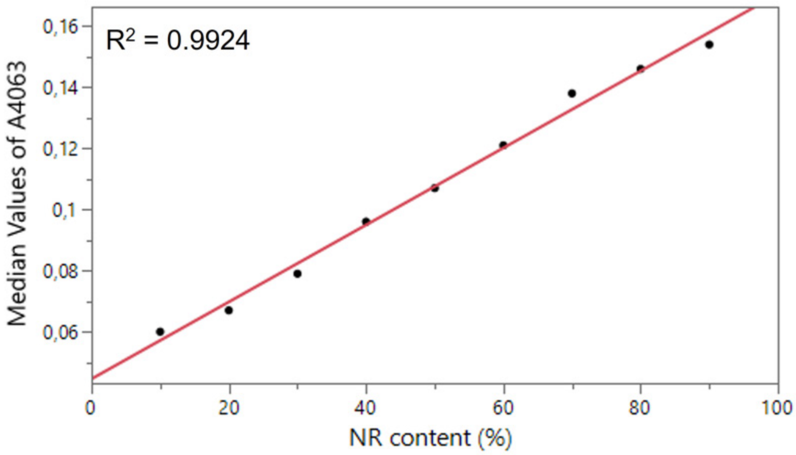

Figure 5. NIRA calibration/Bunsen burner pyrolysis curve, with median values of analytical band A_{4063} *versus* NR content (%) in NR/NBR.

Table VI. MIR/UATR data (A_{1376}) compared to NIRA (A_{4063}) for the determination of NR in the NR/NBR blend.

Sample NR/NBR (% NR)	A_{1376} (median values) Analytical Band MIR/UATR	A_{4063} (median values) Analytical Band NIR/NIRA
90	8.890	0.154
80	7.800	0.146
70	8.170	0.138
60	7.130	0.121
50	6.930	0.107
40	6.100	0.096
30	6.020	0.079
20	5.430	0.067
10	5.050	0.060

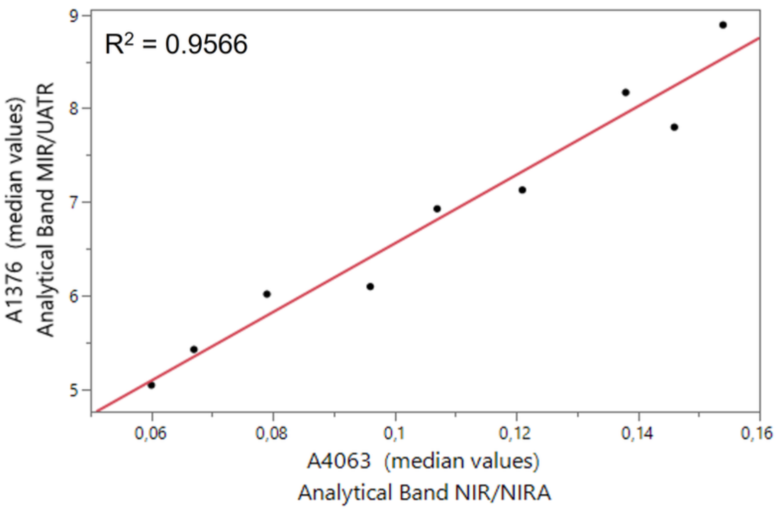

Figure 6. MIR/UATR absorbance data (A_{1376}) compared to FT-NIRA (A_{4063}) for the determination of NR in the NR/NBR blend.

CONCLUSIONS

The focus of this study was the comparison of different data processing models and spectroscopy methods. Then, we decided to approach with equal relevance those models that worked and those that did not show good results. The relevance of this publication is to demonstrate how different data processing strategies can better maximize the accuracy and precision of analytical methods.

By comparing the different proposed methodologies, it is possible to reach some conclusions:

1) The analytical techniques FT-MIR/UATR and Raman Microscopy (514nm) provide excellent quantitative results with the use of calibration by chemometric models.
2) The results of chemometric models are superior to calibrations by models with a direct relationship between the intensities of the analytical or relative bands. However, even with the use of traditional univariate and bivariate models, it was possible to obtain adequate quantitative models with errors smaller than 10% that could be adequate for process control of elastomeric blends.
3) Regarding the choice of NR analytical bands, which are in all cases in the fingerprint region of the FT-MIR spectrum, the band at 1376 cm^{-1} ($-CH_3$) proved to be superior to the at 887 cm^{-1} band (vinylidene), in terms of precision, accuracy and linearity. This probably happens because the methyl group has a relatively stronger intensity, less interference from neighboring bands, and a more suitable baseline for measuring even the lower NR contents, which may result in weaker bands (see Figure 1).
4) Regarding the choice of calibration models, the models that consider relative bands (ratios between bands) show a tendency towards polynomial behavior. The use of polynomial regressions, instead of linear ones, shows a slight superiority in terms of the studied quantification parameters.
5) Regarding the limits of quantification, the RMSE method provides information about the minimum limits for a methodology to be considered accurate. Thus, the method I (Raman Microscopy (514 nm) with chemometric modeling) reached the lowest limit of quantification, 1.6% of content of the NR/NBR system.

6) It was not possible to determine the minimum limit of quantification, but all methods were able to identify both elastomers present in the blend (NR and NBR).
7) The FT-NIRA validation of the data obtained in the MIR region by UATR, for bands of the methyl group (A_{1376} and A_{4063}), which presented the best results in terms of error.
8) (univariate model), accredits the two methodologies developed for the determination of NR content in NR/NBR blends.

The results demonstrate that the developed methodologies contribute to the state of the art of research on the characterization and quantification of elastomeric blend systems, which are materials that provide new and different technological solutions, whether in the automotive or in the aerospace sector.

The use of spectroscopic techniques such as FT-IR/Raman associated with modes of obtaining reflection spectra, non-conventional, chemometric methods or not, constitutes important resource for predicting the properties of the mentioned materials. It is also believed that data of this nature contribute to the development of robust and faster methodologies, which shows potential with a multiplying effect for the analysis of similar materials, aiming to gain in their subsequent quality control, to reach new levels of excellence.

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