

Quantification by FT-IR (UATR/NIRA) of NBR/SBR blends

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Abstract

Rubber blends are important materials in automotive industry, as well as in other sectors. However, there are implications when suitable use of a polymer in an artifact is not made. In the automotive area, for example, the use of an elastomer without the fuel resistance requirement would result in component degradation, potential fuel leakage, and danger of fire. The use of polymer blends may be the solution to this problem. Fourier transform infrared spectroscopy (FT-IR) can be used for the knowledge of the polymer content of these blends. Then, FT-IR quantitative methodologies for determining acrylonitrile-butadiene copolymer (NBR) copolymer and butadiene-styrene copolymer (SBR) contents were developed by the transmittance accessory, NIRA, and the transmission mode, being the sample analyzed by transmission and universal attenuated total reflection (UATR) in the medium infrared (MIR). UATR and NIRA methodologies showed better accuracy. However, the MIR analysis showed a detection limit between 10-20% of NBR.

Keywords: *content, NBR, NIRA, SBR, UATR.*

1. Introduction

In contrast to the deceleration in the new polymers production, there is a growing interest in the processes research and development for the modification of existing polymers^[1]. In this context, polymer blends are available for specific applications. According to the literature, the necessary condition is that the lower content of one of components must exceed at least 5%^[2,3].

Blends are often used to improve properties of each polymer involved in the product, process and/or reduce cost. There are many applications in several industries, such as aeronautics, naval, automotive, graphics, real estate, among others. Therefore, studies involving polymers and their blends are attractive, since the methodologies developed can be used in different sectors^[1,4].

Butadiene-based copolymers are widely used in automotive industry. Among these, the SBR and NBR copolymers are outstanding. SBR plays a major role in the market due to its application in tires production. When SBR is used in conjunction with the BR-high cis butadiene homopolymer, excellent properties are obtained for application to tire tread. Since year 2000, automobile and tire manufacturers have been concerned about the environment and which led them to invest in new cleaner synthetic processes for production of these elastomers. Butadiene is a monomer used in the manufacture of elastomers of great economic interest worldwide. According to their properties, the polymers are assigned to a specific type of use^[5].

There are several blends available in the world market, but for the purpose of this paper, the blend composed of NBR and SBR copolymers was selected based on its properties which are suitable on lowering costs by improving certain properties of NBR rubber, which has good chemical and oil resistance. However, these properties vary according to a considerable number of rubber products. Higher the acrylonitrile (AN) content, greater the oil resistance, however lower the flexibility. It is possible to use a NBR blend of high content AN with SBR rubber to obtain an oil resistance degree as such a NBR with low content of AN, with an overall economy in cost. NBR products with high AN content tends to shrink in contact with lubricating oils, in high temperature. The manufacture of NBR/SBR blends constitutes a solution for the final artifact achieve desired properties. SBR can also improve NBR processing^[6].

In the automotive industry, NBR is usually applied in hoses that have direct contact with fuels or gases^[5]. NBR is also used in the aerospace industry, as rocket motor thermal insulation^[7]. It comes to our attention that the quality of the product delivered by the supplier might not meet the specification needed, consisting only by NBR. This may lead to detachments compromising the integrity of the rubber / propellant interface.

NBR rubber also benefits aeronautics industry on appliances as such hoses, seals, and self-sealing fuel and oil tanks. It is applied in the nuclear industry to make protective gloves. NBR property of withstanding a temperature range

of -40 to 108°C makes it the ideal material for aeronautical applications. Still, NBR can be applied to create molded products, adhesives, sealants, sponges, expanded foams and carpets^[8].

A variation in polymerization, AN ratio to butadiene, processing properties and vulcanization are characteristics added in NBR / SBR blend by NBR rubber worth to mention. The AN content is one of the main criteria to define the basic properties of an elastomer. Nitrile group polarity grants to elastomers resistance to oils and hydrocarbon-based solvents, flexibility and abrasion resistance^[5]. In this paper, a NBR rubber with AN content of 37-41% was used according to NBR supplier. Additionally, a FT-IR methodology developed by the group^[9] was applied to precisely acquire the AN value.

The AN content determination in NBR have been performed by FT-IR transmission with values reference obtained by Kjeldhal method^[10], measuring contents up to around 40%. FT-IR transmission and reflection (UATR) techniques^[9] were used for determining contents up to around 50%, with good results, indicating that UATR methodology presents better linear correlation and less analysis time.

One of the most common blend elastomer is the SBR responsible for nearly 40% of all synthetic rubber used in the world. According to data from 2007, approximately 2.4 million tons of SBR per year were already produced in the world^[5]. SBR rubber characteristics depend on styrene content, which can vary between 10 and 85%. Formulations with low styrene content exhibit an elastomeric behavior, whereas those with high styrene content have a thermoplastic

nature^[11]. SBR-1502 was object of this study, with 23.5% styrene, obtained by cold polymerization (10°C maximum) in emulsion of fatty and resinous soaps, coagulated in a salt / acid or acid system and stabilized with a non-smelly antioxidant.

SBR rubber has good mechanical properties, high resistance. Likewise, it has good resistance to abrasion, ozone and weathering, but regarding to oil resistance it presents a gap, making this mixture with NBR beneficial for both copolymers, dependent on the suitable application of the final artifact^[12].

The property variations are dependent on the functional groups content of the polymers and also compounds present in the product composition. Therefore, the possibility of using blends to reach a specific application indicates the need for suitable characterization and/or quantification of these materials. Instrumental techniques, mainly Fourier transform infrared spectroscopy (FT-IR), associated or not with other techniques, is mentioned in the literature for this goal, including also studies of polymers used in the automotive and aerospace industry, such as NBR, SBR and their polymer blends^[13-18].

Table 1 shows some studies. Although good results were achieved in these studies, some observations were made in this study, which served as a basis for the elaboration of the methodology currently developed.

It is observed that the MIR region is the most used, just as the technique obtaining FT-IR spectra is the conventional one, which means transmission and the use of other instrumental

Table 1. Main aspects cited by studies on polymers and their blends characterization.

Author	Year	Main conclusion	Comments
Shield et al. ^[19]	2003	FT-MIR Analysis (medium infrared) and FT-NIR (near infrared) were used to NBR/SBR determination. Obtaining modes: MIR - transmission and ATR/ NIR - optical fiber - NBR band - 2240 cm ⁻¹ and SBR - 1600 cm ⁻¹ . NIR range - 5443 - 6103 cm ⁻¹ . Methodology errors MIR - 4% and NIR - 2%.	Although the relative error of methodology was compared with methods as TGA (10%), a medium intensity band (1600 cm ⁻¹) was used for SBR, which may probably cause a greater error than if it were used at 700 cm ⁻¹ , for lower contents of this polymer.
Dutra et al. ^[17]	2004	NR/SBR blends were analyzed by FT-IR transmission/ controlled pyrolysis and TGA/DTG, with linear correlation 0.998 and methodology error 1.73%, within the accuracy limits of the equipment.	Controlled pyrolysis technique, while accurate, involves elaborate sample preparation and requires reasonable analysis time. Using thermal analysis technique to validate data, although more accurate, is more complex, depending on the rubbers degradation temperatures being adequate, that is the degradation of one rubber finish before the other begins.
Berridi et al. ^[20]	2006	NR/SBR blends were analyzed by FT-IR transmission / pyrolysis in Bunsen burner and TGA/DTG. FT-IR was more effective in the determination.	Pyrolysis technique in Bunsen burner is less precise than the controlled one, however, relative bands were used. There was no comment on methodology errors.
Chakraborty et al. ^[11]	2007	Determination of acrylonitrile (AN) content in NBR gum (without additives) by FT-IR transmission/cast film, with reference values obtained by the Kjeldhal method, measuring contents up to around 40%.	Cast film technique involves solvent use, elaborated sample preparation, and there may be interference associated with the solvent/polymer interaction, and requires reasonable analysis time. Validation by Kjeldhal or any other instrumental method, although more precise, implies knowledge of both techniques for elaboration of the calibration curve.
Lee et al. ^[21]	2007	NR, SBR and BR content determination in a ternary mixture of these elastomers by transmission/pyrolysis FT-IR in Bunsen burner, TGA, DSC and by gas chromatography and mass spectrometry coupling by pyrolysis (Py-GC/MS). This last method was more precise, there was interference of one elastomer in the other, with the other techniques.	There was considerable variation in contents determination, especially by TGA and FT-IR, but it should also be considered that the use of coupling techniques requires specialists in both areas, in this case, chromatography and mass, for better results interpretation.

Table 1. Continued...

Author	Year	Main conclusion	Comments
Sanches et al. ^[9]	2008	Determination of acrylonitrile (AN) content in NBR non-vulcanized/vulcanized by FT-IR transmission / pyrolysis in Bunsen burner and controlled, with solvent extraction and by UATR, as received, measuring contents up to around 50%. Techniques presented similar precision, but UATR was more adequate to the determination, due to the shorter analysis time and the smaller amount of sample used.	UATR method was used to determine the AN content in the rubber used in this study.
Harada ^[22]	2016	It focuses on rubber analysis techniques, such as infrared, TGA, Py-GC/MS, but in the FT-IR analysis the focus is on qualitative reflection analysis for component verification.	The quantitative part is also centered on the Py-GC/MS analysis. FT-IR is cited qualitatively.
Ujianto et al. ^[23]	2017	It focuses on FT-IR of NR	Qualitative analysis, aiming at the evaluation of spectrometric changes, resulting from devulcanization.
Datta et al. ^[24]	2017	Determination of NR, SBR and BR contents in ternary mixture by FT-IR and TGA. Bands 1375 (NR), 699 (SBR) and 738 (BR) cm^{-1} and relative bands were used in the FT-IR methodology.	The vinylidene band at 885 cm^{-1} , which would be more characteristic of NR, could have been tested.

techniques. However, it validates the FT-IR data and makes the methodology more complex and time-consuming. Methodological errors are not generally compared. In this paper, it was proposed a FT-IR methodology in the MIR region, with data validation in the NIR region, by means of less conventional spectral modes, such as UATR and NIRA, compared to data obtained by transmission. The samples were prepared by pyrolysis in a Bunsen burner, with evaluation of FT-IR methodology error.

2. Materials and Methods

2.1 Samples

Nine samples of NBR/SBR blends were prepared at Tenneco Automotive Brazil, with materials kindly provided by the company, in the proportions 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10, according to the formulation found in Table 2.

2.1.1 Preparation of rubber samples

The raw material was weighed on a precision scale and all components, except sulfur and accelerators, tetramethylthiuram disulfide (TMTD), (1,3-Dimethylbutyl)-N'-phenyl-phenylenediamine (6PPD), N-(cyclohexylthio) phthalimide (PVI) and 4,4 Dithiomorpholine (DTDM), which were mixed in banbury of 2 liters per 240 seconds, with a pound pressure of 4 kgf/cm^2 , rotation of 70 rpm and initial temperature of 40°C, for production of master batch. It was processed into a roller form six times in a lab open mill with a rotation of 40 rpm. Later, the master batch was accelerated at banbury, with the rest of the weighted components (TMTD, 6PPD, PVI, DTDM and sulfur) for 120 seconds, with 4 kgf/cm^2 pound pressure, 70 rpm rotation and initial temperature of 40°C. Then the rubber was homogenized in roller form six times in an open mill lab with a rotation of 40 rpm and withdrawn into blanked. For the preparation of vulcanized rubber sheet, a hydraulic press with vulcanization time of 6 min, plateau temperature of 160°C and 150 kgf/cm^2 of closing pressure was used.

2.2 Equipment of characterization/conditions

2.2.1 FT-IR analysis

The samples were analyzed in Spectrum One PERKINELMER FT-IR spectrometer (MIR regions of 4000 to 400 cm^{-1} and NIR of 12000 to 4000 cm^{-1} , 4 cm^{-1} resolutions, gain 1, 20 scans), being spectra obtained by transmission techniques (MIR and NIR) and reflection (MIR), using the UATR accessory, and in NIR region, also using the Frontier PERKINELMER FT-IR spectrometer, NIRA accessory, being all samples of different methodologies, prepared by pyrolysis in Bunsen burner.

In Bunsen's pyrolysis, samples of each rubber blend were cut, extracted for 8 hours in a Soxhlet extractor, using methanol as solvent^[25]. After solvent evaporation in the oven, it was put a quantity of about 0.5 g of sample in each pyrolysis tube. The tubes were flamed in Bunsen burner, at the same flame height (marked with the aid of an universal device and a claw to determine the same pyrolysis position). For the transmission analysis, by pyrolysis, was used the 0.025mm spacer.

By reflection, using the UATR accessory, in the same way that was done in a recent study by Rigoli et al.^[26], the pyrolysis samples were analyzed by placing them in contact with the diamond-coated zinc selenide crystal surface with 120N (Newton) torque application.

For MIR analysis, the nine NBR/SBR samples (composition already shown in Table 2), prepared by pyrolysis in Bunsen burner and analyzed by transmission and reflection (UATR), were used to prepare $A_{\text{NBR}}/A_{\text{SBR}} \times [\text{NBR}]/[\text{SBR}]$ analytical curve, aiming the NBR and SBR contents determination, through the relative band A_{2237}/A_{700} . This band is composed by analytical absorptions of stretching (ν) C \equiv N of NBR (2237 cm^{-1}) and bending (δ) C-H of SBR (700 cm^{-1}). The baselines used were: 2275-2150 cm^{-1} (band 2237 cm^{-1}) and 2150-590 cm^{-1} (band 700 cm^{-1}), for transmission / pyrolysis methodology, and 2275-2180 cm^{-1} (band 2237 cm^{-1}), 858-642 cm^{-1} (band 700 cm^{-1}) for UATR methodology.

Table 2. NBR/SBR Blend Formulation System.

Components	Functional group	Phr								
		900	800	700	600	500	400	300	200	100
NBR										
SBR		100	200	300	400	500	600	700	800	900
Naphthenic Oil							45			
Zinc Oxide	ZnO						37			
Stearic Acid							10			
Carbon Black N550	C						680			
Sulfur	S						8			
TMTD							8			
6PPD							18			
PVI							5.5			
DTDM							10			
Paraffin wax	$C_n H_{2n+2}$, n = around 50 – 75						20			

For the NIR methodology, the same number of reference NBR / SBR samples, prepared by pyrolysis in Bunsen burner and analyzed by transmission, were used to prepare the analytical curve $A_{4336}/A_{4060} \times [NBR]/[SBR]$. The bands chosen are in the region of combination or overtones of fundamental bands. In the case of NBR/SBR blend, the band A_{4336} is probably attributed to the first overtone of stretching (ν) of $C\equiv N$ group of NBR or of combination bands, and the A_{4060} to the second overtone of bending (δ) of SBR aromatic CH groups^[19,27]. The baseline used was 4540-4000 cm^{-1} (bands 4336 and 4060 cm^{-1}). For NIRA methodology, the same number of samples and the same analytical bands were used. The samples were also prepared by pyrolysis in Bunsen burner, and were analyzed by transmittance because they were in the liquid state^[28]. The baseline used was 4780 to 4000 cm^{-1} .

The data of all FT-IR/MIR and NIR methodologies, for each sample, represent the median of 5 values of analytical bands intensity chosen, being that the mean standard deviations (Equations 1 and 2) and the relative error (RD)

(Equation 3) were calculated by non-parametric treatment in agreement with Hórák^[29] and with the methodology adopted successfully in group quantitative studies for rubber and other materials^[17,28,30].

$$\hat{\sigma}_{\mu} = \frac{\hat{\sigma}}{\sqrt{n}} \quad (1)$$

$$\hat{\sigma} = K_R \times R \quad (2)$$

Where, $\hat{\sigma}$ is the mean standard deviation, n , the measurements number, R is the difference between the highest and the lowest values of absorbance. K_R is the coefficient to calculate the standard deviation ($\hat{\sigma}$) of a range of values, with $K_R = 0.430$ for 5 experiments^[29]. The RD of the measurements for each analyzed sample, given in %, was determined by Equation 3, where μ is the median value of A. The median of the relative errors represents the error of the methodology^[17,28,30].

$$RD(\%) = \frac{\hat{\sigma}_{\mu}}{\mu} \times 100 \quad (3)$$

3. Results and Discussion

3.1 FT-IR analysis

In this topic the following were addressed: a) the determination by UATR of AN content of NBR used in the blends, according to methodology previously developed by the group^[9], since only one range was furnished by the supplier. For SBR rubber, the determined value as reported by the supplier was used. These values were not used in the blends contents calculation, only used for the proper characterization of the raw materials used for the prediction of properties of blends, for future and specific applications. b) the determination of the NBR/SBR blends in two spectral regions, by different ways of obtaining spectra, aiming to evaluate the most suitable conditions for this type of analysis.

3.2 Determination by UATR of AN content of NBR used in the blend

In Table 3, the data for AN content in NBR calculation are inserted.

3.3 MIR/transmission analysis of NBR/SBR

In Figure 1, are the MIR/transmission spectra of some NBR/SBR blends studied. It can be observed that the bands intensities A_{2237} and A_{700} increase and decrease according to the content of NBR and SBR, respectively, as expected by Lambert-Beer Law, for quantitative analyzes^[32]. The data for elaboration of calibration curve are shown in Table 4 and Figure 2. To overcome liquid film thickness issues and to improve the data accuracy^[32], mean values of relative band A_{2237}/A_{700} were considered as a function of the relative NBR/SBR concentration.

From the calibration curve (Table 4), the following correlation (Equation 4 - $R = 0.98$, with 96% of the values explained by the methodology, $R^2 = 0.96$) is proposed:

$$A_{2237} / A_{700} = 0.17 [NBR] / [SBR] + 0.14 \quad (4)$$

To find the two elastomers contents of the unknown mixture, Equation 5 should also be used. This is valid for all the methodologies developed in this study.

Table 3. UATR data for determination of AN in NBR.

Sample	A_{2237}	A_{2237} (MEDIAN)	Mean standard deviation	RD(%)	Calculated acrylonitrile content ^[9] (%)(*)	Acrylonitrile content (%) range, reported by NBR gum supplier (**)
NBR	0.040 0.039 0.040 0.040 0.040	0.040	0.001	2.5	30 ± 1	37-41

(*) $y = 0.0014x - 0.002$ – calibration curve, where y = median value of A_{2237} ^[9];

(**) Only the range of AN content was reported by NBR (gum) supplier, without the determined value, nor what method was used. Therefore, the value considered for the material characterization was obtained, that is, $30 \pm 1\%$, of medium AN content^[31] by the FT-IR methodology, previously developed^[9], which is accurate, that is, with the relative error around 2%, under the conditions used (UATR, sample analyzed as received). It is interesting to note that the content found is also used for applications aerospace^[9], around 33%.

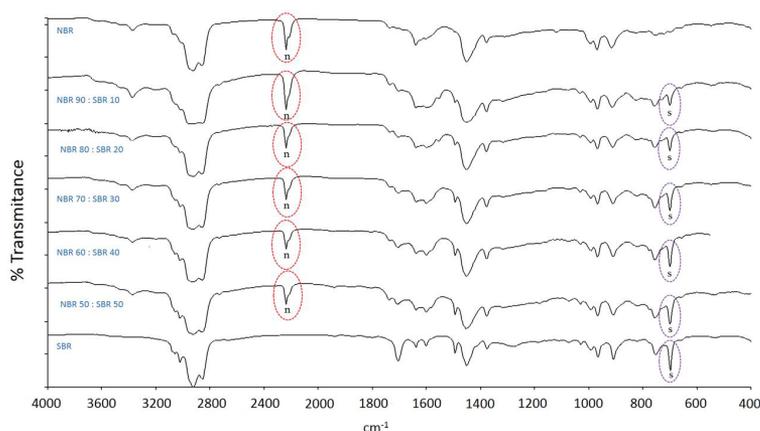
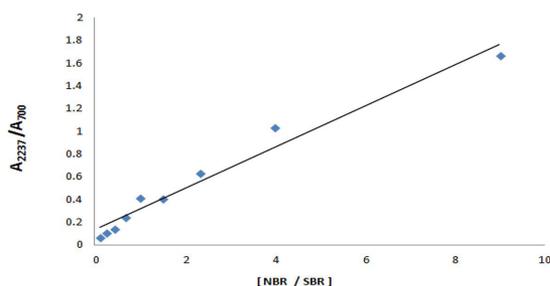


Figure 1. MIR/transmission spectra (Bunsen burner pyrolysis) of NBR/SBR blends, with AN and styrene bands, marked with n and s, respectively.

Table 4. MIR/transmission data (Bunsen burner pyrolysis) for calibration curve elaboration and associated methodology errors.

NBR/SBR (Relative Concentration)	A_{2237}/A_{700} Median	Mean standard deviation	RD %
90 / 10 (9.0)	1.563	0.013	0.83
80 / 20 (4.0)	0.984	0.007	0.71
70 / 30 (2.3)	0.608	0.004	0.66
60 / 40 (1.5)	0.394	0.011	2.79
50 / 50 (1.0)	0.401	0.024	5.99
40 / 60 (0.67)	0.239	0.010	4.18
30 / 70 (0.43)	0.142	0.007	4.93
20 / 80 (0.25)	0.108	0.007	6.48
10 / 90 (0.11)	0.067	0.010	14.93

**Figure 2.** MIR/transmission calibration curve A_{2237}/A_{700} versus relative concentration [NBR/SBR].

$$[NBR] + [SBR] = 100\% \quad (5)$$

The methodology error, which is relative errors median^[28] calculated in Table 4, already mentioned, 4.18%, can be considered good, compared to the reference value^[29], $\leq 2\%$, which is usually only found under fixed conditions, ideal for sample preparation, that is, in solution form and analyzed in closed cell, with thickness control. The error falls to 2.79%, closer to the accuracy limit of the equipment, $\leq 2\%$, for optimal condition, if the contents of 10-20% of NBR are not considered, may suggest a limit of detection in this range, by this methodology, probably due to the low intensity of the AN band, for these levels.

3.4 MIR/UATR analysis of NBR/SBR

In Figure 3, the MIR/UATR spectra of some studied NBR/SBR polymer blends are included. As for transmission MIR spectra, it can be observed that the intensities of

bands A_{2237} and A_{700} increase and decrease according to the NBR and SBR content, respectively, as expected by the Lambert-Beer Law. The data for calibration curve elaboration are shown in Table 5 and Figure 4. In this methodology, A_{2237}/A_{700} relative band was also used to improve the accuracy of the data.

From the calibration curve (Table 5), the following correlation (Equation 6 - $R = 0.98$, with 96% of the values explained by the methodology, $R^2 = 0.96$) is proposed:

$$A_{2237} / A_{700} = 0.05 [NBR] / [SBR] + 0.03 \quad (6)$$

The methodology error, which is the median of the relative errors (Table 5), 3.41%, can be considered good compared to the reference value, $\leq 2\%$. The error falls to 2.09%, closer to the accuracy limit of the equipment, $\leq 2\%$, for optimal condition, if the contents of 10-20% of NBR are not considered, and may also suggest a limit of detection in this band, by this methodology, probably due to the low intensity of the AN band, for these levels.

3.5 NIR/transmission analysis of NBR/SBR

In Figure 5, the NIR/transmission (pyrolysis in Bunsen burner) spectra of some NBR / SBR polymer blends studied are shown. As for MIR and UATR spectra, it can be observed that the intensities of the bands A_{4336} and A_{4060} increase and decrease according to the NBR and SBR content, respectively, as expected by the Lambert-Beer Law.

In this methodology, the relative band A_{4336}/A_{4060} was chosen to overcome liquid film thickness issues and to improve the data accuracy. Table 6 shows the values used, as well as their mean and relative deviations.

Table 5. MIR/UATR data (Bunsen burner pyrolysis) for calibration curve elaboration and associated methodology errors.

NBR/SBR - (Relative Concentration)	A_{2237}/A_{700} (Median)	Mean standard deviation	RD (%)
90/10 (9.0)	0.431	0.009	2.09
80/20 (4.0)	0.263	0.005	1.90
70/30 (2.3)	0.187	0.003	1.60
60/40 (1.5)	0.111	0.002	1.80
50/50 (1.0)	0.088	0.003	3.41
40/60 (0.67)	0.047	0.003	6.38
30/70 (0.43)	0.030	0.002	6.67
20/80 (0.25)	0.014	0.001	7.14
10/90 (0.11)	0.010	0.003	30.00

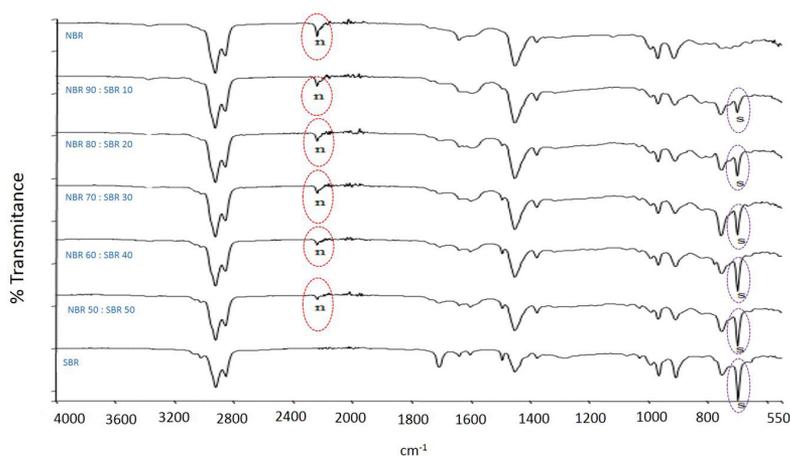


Figure 3. MIR/UATR spectra of NBR/SBR blends, with the AN and styrene bands, labeled with n and s, respectively.

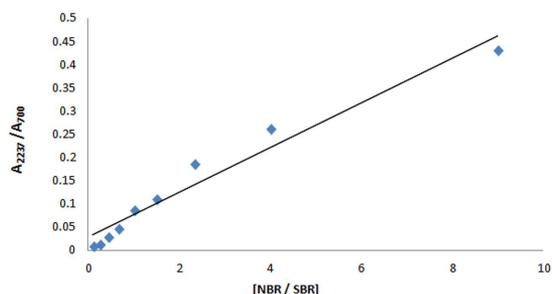


Figure 4. MIR/UATR calibration curve A_{2237}/A_{700} versus relative concentration [NBR/SBR].

Figure 6 shows the calibration curve of NIR / transmission (Bunsen burner pyrolysis) A_{4336}/A_{4060} versus [NBR]/[SBR] (% w/w). From the calibration curve (Table 6), the following correlation (Equation 7 - $R = 0.92$, with 85% of the values found, being explained by the developed methodology) is proposed:

$$A_{4336} / A_{4060} = 0.26 [NBR] / [SBR] + 2.58 \quad (7)$$

The methodology error was 1.33% (Table 6). Although the error is within the limits of the equipment accuracy, $\leq 2\%$, there being no evidence of NBR low levels detection

limit, the linearity is not as good as that found for the MIR, transmission and UATR methodologies.

3.6 NIRA analysis of NBR/SBR

To improve the results of NIR methodology, using the reflection method, the samples were analyzed by transmittance in this region (NIRA). The analytical bands chosen were the same. Figures 7-8, Table 7 and Equation 8 shows the results obtained. The methodology error was 0.74% (Table 7), with good linearity $R = 0.96$, and 92% of the data found were explained by this methodology. The error is within the limits of equipment accuracy, $\leq 2\%$, and there is no evidence of limit of detection of low levels of NBR.

$$A_{4336} / A_{4060} = 0.30 [NBR] / [SBR] + 2.46 \quad (8)$$

To know the contents of unknown samples it is enough to analyze 5 aliquots of the rubber and to use the suitable calibration curves established in the developed methodologies, depending on the region of the infrared available in the laboratory. For example, Table 8 shows the evaluation of the MIR methodologies developed by means of analysis of unknown concentration NBR / SBR sample.

Although the test sample has been analyzed by the analyst, without the knowledge of its concentration, the

Table 6. NIR transmission data (Bunsen burner pyrolysis) for calibration curve elaboration and associated methodology errors.

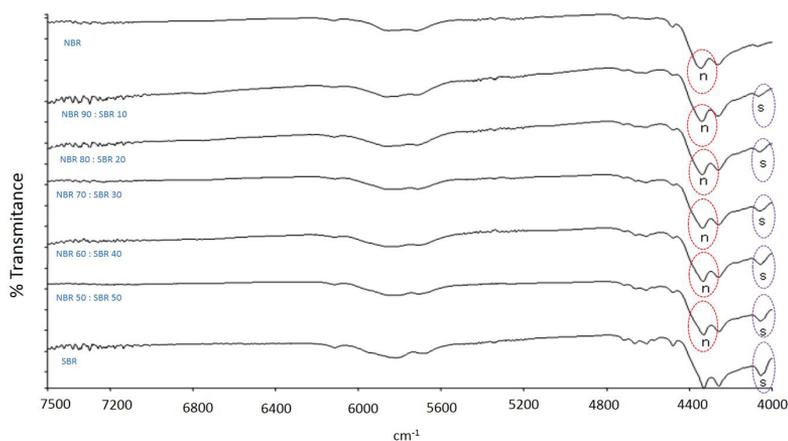
NBR/SBR (Relative Concentration)	A_{4336}/A_{4060} (Median)	Mean standard deviation	RD (%)
90/10 (9.0)	4.625	0.058	1.25
80/20 (4.0)	4.000	0.160	4.00
70/30 (2.3)	3.733	0.043	1,15
60/40 (1.5)	3.231	0.045	1.39
50/50 (1.0)	2.893	0.025	0.86
40/60 (0.67)	2.714	0.036	1.33
30/70 (0.43)	2.484	0.059	2.38
20/80 (0.25)	2.400	0.025	1.04
10/90 (0.11)	2.200	0.030	1.36

Table 7. NIRA data (pyrolysis in Bunsen burner) for calibration curve elaboration and associated methodology errors.

NBR/SBR (Relative Concentration)	A_{4336}/A_{4060} (Median)	Mean standard deviation	RD (%)
90/10 (9.0)	4.865	0.067	1.38
80/20 (4.0)	3.973	0.039	0.98
70/30 (2.3)	3.42	0.126	3.68
60/40 (1.5)	3.171	0.127	4.01
50/50 (1.0)	2.877	0.021	0.73
40/60 (0.67)	2.632	0.007	0.27
30/70 (0.43)	2.459	0.016	0.65
20/80 (0.25)	2.305	0.012	0.52
10/90 (0.11)	2.161	0.016	0.74

Table 8. Data of unknown NBR/SBR sample (X/Y) for validation of MIR methodologies developed.

NBR/SBR(nominal relative concentration)/ methodology	A_{2237}/A_{700}	A_{2237}/A_{700} (median)	Calculated concentration	RD (%)
Unknown sample (X/Y)/MIR/transmission	0.569	0.632	NBR = 74.29 SBR = 25.71	2.53
	0.592			
	0.632			
	0.644			
Unknown sample (X/Y)/MIR/UATR	0.155	0.155	NBR = 71.43 SBR = 28.57	5.81
	0.155			
	0.146			
	0.192			
	0.165			

**Figure 5.** NIR transmission spectra (Bunsen burner pyrolysis) of NBR/SBR blends, with AN and styrene bands, labeled with n and s, respectively.

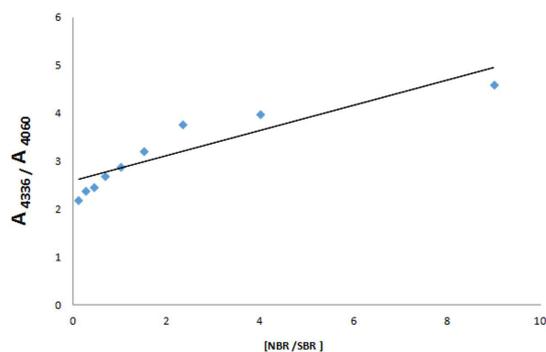


Figure 6. NIR calibration curve A_{4336}/A_{4060} versus relative concentration [NBR/SBR].

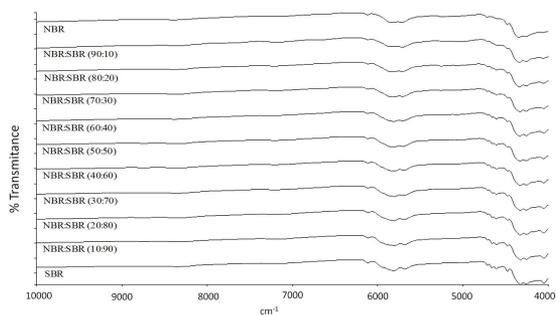


Figure 7. NIRA Spectra (pyrolysis in Bunsen burner) of NBR/SBR blends.

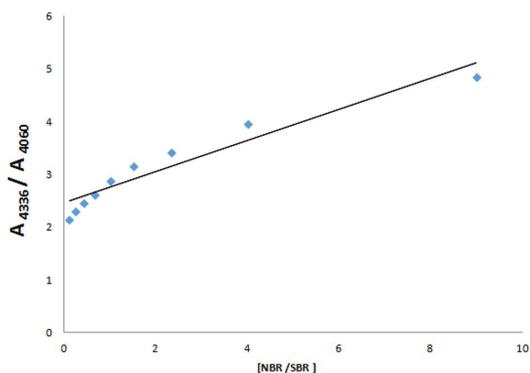


Figure 8. NIRA calibration curve A_{4336}/A_{4060} versus relative concentration [NBR/SBR].

nominal value that should have been found would be around NBR70 / SBR30. Thus, both methodologies presented satisfactory values, with the best result for which UATR was used.

4. Conclusion

Summarily, all MIR and NIR methodologies were useful for NBR and SBR contents determination in the analyzed blends. The best correlation in the MIR region was found for the UATR methodology (pyrolysis in Bunsen burner), although there may be a detection limit between 10-20% NBR and an error around 3%. In the NIR region, the NIRA

methodology showed better correlation, with no limit of detection and with error around 1%, within the limits of the FT-IR spectrometer. Both methodologies MIR/NIR are fast, therefore useful as quality control in different industrial and research scenarios.

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