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Infrared quantification of binary rubber blends with overlapping bands

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Abstract: Quantification of elastomer content for the ethylene-propylene diene monomer/polybutadiene blend are seldom subjects in the literature, mainly due to rubber compatibility problems. However, suitable blend contents can lead to desirable properties. Infrared spectroscopy can quantify this type of blend even if some bands overlap, which can be resolved with the proper choice of spectrum obtaining mode and non-overlapping analytical bands. This study evaluates the ethylene-propylene diene monomer/polybutadiene blend quantification by transmission, reflection and transflectance infrared. Even though all of the methodologies showed satisfactory results, transmission mode provided better accuracy. The methodology is simple and suited for the rubber industry. The sample with the higher BR content provided the best result. The band at 743 cm^{-1} is weak and results in even weaker absorptions when measuring samples with low BR content. On the other hand, the developed methodologies provided an accurate determination of low EPDM contents. For infrared spectroscopy researchers, these results not only encourage using different spectra obtaining modes application, including less conventional ones such as transflectance in the near infrared region for quantitative determination, it also contributes to a wide discussion of errors in the developed methodologies, which are also seldom discussed in publications.

Key words: determination, EPDM/BR, FT-IR, reflection, transflectance, transmission.

INTRODUCTION

Rubbers offer an extensive industrial application range, including aerospace, as thermal protections (George et al. 2020), automotive, as tires components (Globe Newswire 2020, Murakami et al. 2019, Watanabe & Nakano 2018). In rocket motors, for example, ethylene-propylene-diene monomer (EPDM) rubber is extensively used as thermal protections.

Concerning the synthetic rubber production capacities worldwide, according to Watanabe & Nakano (2018), the production capacity of EPDM rubber is similar to that of styrene butadiene rubber (SBR) and butadiene rubber (BR). Recent data predict that the global EPDM market will increase at a considerable rate between 2021 and 2025 (Freeman 2021). Therefore, due to the production and application opportunities in different industrial sectors, studies involving EPDM and BR-based rubbers are interesting.

The EPDM advantages in structure and properties propel its use in blends and elastomers mixtures, in order to achieve success in different industrial sectors (Mayasari et al. 2020, Ajitha & Thomas 2019, Azevedo et al. 2018). However, mixture heterogeneity prevents its application to a higher extent. The difficulties intensify even more when there are differences in polarity level and unsaturation between

the elastomers. As a result, some mixtures combination can be impaired (Ghosh & Basu 2003).

The elastomers in the EPDM/BR blend, for instance, are incompatible. There are few studies published on this blend (Roland 2013), especially about determination of elastomer content by instrumental techniques. Infrared spectroscopy, when applied, is usually on qualitative analysis. Due to the incompatibility and immiscibility of EPDM/BR blend, there are also few studies published on its use. However, some studies address the use of coupling agents to solve this problem. According to Go & Ha (1996), the EPDM/BR blend was studied to develop suitable materials for engine mount. The objective was to obtain materials with balanced properties of low oxidation degradation and high resilience; however, compatibility problems caused processing difficulties. Go & Ha (1996) evaluated the addition of a mixture of aromatic and aliphatic hydrocarbon resin, which was very effective for the EPDM/BR mixture plasticization and in improving compatibility between components.

El-Nemr et al. (2018) designed a study considering EPDM and BR advantages (EPDM - resistance to thermal aging, chemical resistance, impact resistance, mechanical properties, and dielectric property; BR - excellent elasticity, good flexibility, and abrasion resistance) and disadvantages (EPDM - slow curing speed; BR- low stress and tear resistance, and difficult processing). They evaluated the effect of ionizing radiation to induce cross-linking on mixtures of EPDM/BR (100/0, 70/30, 50/50, 30/70, 0/100) and their mechanical and physico-chemical properties.

In the same study, El-Nemr et al. (2018) also applied Fourier Transform Infrared Spectroscopy (FT-IR) to evaluate the characteristic bands of the EPDM/BR blends and the functional groups introduced by the radiation treatment. Results showed that mechanical properties such as tensile strength (TS), elongation at break (EB) and tensile modulus (M) increased with EPDM addition in the mixture. On the other hand, TS and M increased with radiation, while EB decreased. Physico-chemical properties, such as gel fraction and volume fraction of rubber in swollen gel (Vr) increased with EPDM addition, while swelling and soluble fraction decreased when increasing EPDM content. Oppositely, Vr increased with the radiation dose. The mechanical results showed that the EPDM/BR (50/50) blend provided moderate properties among those of the mixture primitive components. Thermogravimetric Analysis (TGA) indicated that the EPDM/BR (70/30) blend has greater thermal stability than BR or EPDM, separately.

The development of a methodology that provides individually rubber content in a blend would be an important step to better evaluate these types of mixtures. In addition, for the aerospace industry, it could guarantee the absence of undesired elastomers in the mixture introduced by the supplier to lower costs. These unsolicited mixtures can be very harmful to the properties required for specific aerospace projects. Since EPDM based systems continue to be studied as rocket engines thermal protection, the development of a methodology that identifies and quantifies the presence of another elastomer will be an original contribution to the state of art in research.

Studies on the determination of BR rubber in ternary elastomeric blends have been cited in the literature (Datta et al. 2017, 2019, Lee et al. 2007). For example, the determination of the NR, SBR and BR contents in a ternary blend has been cited. However, differently than this research, those studies were carried out by coupling different instrumental techniques (Datta et al.

2017, Lee et al. 2007), employing the attenuated total reflection mode (ATR), and pyrolysis as the sample preparation technique.

In the study by Lee et al. (2007), the determination of NR, SBR and BR contents in a ternary mixture of these elastomers was performed by several instrumental techniques, such as FT-IR, DSC, TGA and chromatography/mass by pyrolysis (Py-GC/MS). Results showed that the Py-GC/MS methodology was the most accurate. Datta et al. (2017) used derived thermogravimetry (DTG) and ATR reflection FT-IR, with samples analyzed as received. Also, an algorithm-based infrared band height/intensity correction was used.

Datta et al. (2019) used an infrared parameter for rubber $P_{H(IR)}$, which is a characteristic of each elastomer. It has been proven to be a constant for a given rubber and is independent of the number and amount of compounding ingredients in the blend. This parameter can be used to predict the percentage by weight of this rubber in a blend vulcanized with one or more rubbers. It only requires a unique baseline subtracted from the characteristic height of the IR band of the rubber in question. Results were achieved using an algorithm for baseline subtraction. The only limitation of this work, cited by the authors, resides in the overlapping of bands from two rubbers, that is, one can have a characteristic IR band that is also produced by the other elastomer, for example, SBR and BR. Thus, this method can only work properly for materials that present distinct bands in the same mixture.

Transmission FT-IR analysis, particularly in the middle infrared region (MIR), provides good results for the determination of elastomers content by the identification of the functional groups (Rigoli et al. 2017, Damazio et al. 2015, Sanches et al. 2008). This technique also is useful for the evaluation of elastomers in binary mixtures, without overlapping of the analytical bands (Rigoli et al. 2021, Riba et al. 2019, Azevedo et al. 2018). However, there is a researching gap regarding the MIR region for analysis of elastomers blends with overlapping bands, such as EPDM/BR. This blend presents C=C vinyl and trans groups in both elastomers.

FT-IR analysis in the near infrared region (NIR) also presents studying gaps. NIR analysis provide good results for polymer analysis (Workman 2006), including EPDM, however it requires the application of algorithms (Tang et al. 2018, Miller 1989). This fact endorses further studies in the NIR region for evaluation of binary rubber blends, especially in transflectance mode. Near-infrared reflectance analysis (NIRA) is less explored than conventional NIR transmission mode.

Furthermore, there are only a few studies using reflection techniques by Universal Attenuated Total Reflectance Accessory (UATR), in the MIR region, and transflectance in NIR region (NIRA) for the quantification of elastomer, which creates additional researching opportunities. NIRA has already shown good results for the analysis of different polymeric systems with two or three components (Carvalho et al. 2021, Mello et al. 2018, Azevedo et al. 2018), which encourages this type of analysis in studies of elastomers in binary blends with EPDM, with and without overlapping of IR bands.

In a recent study, Rigoli et al. (2021) evaluated an EPDM blended with polychloroprene (CR), which has applications in the aeronautical industry and with great potential in the defense sector. The few prior studies relating to EPDM and CR used complex instrumental methods for the quantification analysis. FT-IR analysis was able to evaluate the elastomeric contents of the EPDM/CR blend in a faster and more accurate process. Rigoli et al. (2021) cite in the paper that transmission mode is the most widely used

spectra obtaining technique; however, studies usually fail to inform the methodology error.

Therefore, Rigoli et al. (2021) proposed the quantification of EPDM/CR blends by using infrared analysis with the reflection UATR technique, combined with sample pre-treatment (pyrolysis). Results showed that the UATR/pyrolysates methodology provides accurate results, which was confirmed by a test sample analysis. Other elastomeric systems can benefit from the developed FT-IR methodology, which could be valued for reverse engineering of thermal protections. As a future trend, It was highlighted that polymers recent studies by NIRA analysis, without chemometrics application, have been successfully carried out in cases where there are no overlapping bands (Magalhães et al. 2020, Mello et al. 2018). Therefore, it can be used in other polymers analysis, such as rubber blends.

Other studies relating to the characterization of binary rubber blends have been carried out by FT-IR, some of which integrated with thermal analysis techniques (Ferreira et al. 2018, Dutra et al. 2004, Shield & Ghebremeskel 2003); however, these FT-IR studies were performed exclusively in the MIR region.

The FT-IR characterization of more than one elastomer becomes more complex when occur overlapping of the MIR bands, as in the EPDM/BR blend, with respect to the vinyl and trans C=C bands, between 1000 and 900 cm^{-1}, common to both elastomers. Deconvolution processes constitute a possible attempt to solve analysis conditions for overlapping bands (Canevarolo 2017). This process consists in increasing the spectral resolution, in a narrow spectral range while maintaining bands position, but changing their respective areas. Therefore, the deconvolution process should not be applied to quantitative analysis (Canevarolo 2017).

The problem with the overlapping bands in quantitative IR analysis can be overcome with the appropriate choice of spectra obtaining mode and analytical bands in the MIR region of interest, with validation of results in the NIR region. Other solution would be associating FT-IR with another instrumental technique, although it would result in higher costs of analysis and demand different specialists' knowledge.

FT-IR methodologies development was studied for EPDM binary blends (EPDM/BR) characterization and quantification, with overlapping analytical bands. Different industry sectors applying reflection (UATR) and transflectance (NIRA) non-conventional techniques in comparison with conventional transmission techniques might benefit from this research. It evaluates the intensity/bands height calculation, detection limits and precision without manipulating overlapping absorptions deconvolution (qualitative process), which reduce examination steps and, therefore, analysis time.

MATERIALS AND METHODS

Materials

Five (5) EPDM/BR samples with different contents (EPDM 10/BR 90, EPDM 30/BR 70, EPDM 50/BR 50, EPDM 70/BR 30, EPDM 90/BR 10), in phr (parts per 100 rubber parts, in mass), were analyzed according to the methodologies described below. The EPDM Keltan 6950 (ethylene (ET): 48% and 5-ethylidene-2-norbornene (ENB):9,0%) and BR Buna CB 45B (C=C cis 38%, C=C vinyl 11% and C=C trans 53%) were supplied by LanXess (Table I).

The first phase of mixing was carried out on a tangential banbury (LUXOR 40L). The elastomers were added with naphthenic oil and zinc oxide in the banbury, with a piston pressure of 6 kgf/cm^2, rotation of 45 rpm, and mixed for 200 seconds. Afterward, the carbon black and

Table I. EPDM/BR formulation (90/10; 70/30; 50/50; 30/70 and 10/90).

Components	Content (mass %)
EPDM Keltan 6950 (ET: 48% e ENB: 7.5%)	5.1 ; 15.4 ; 25.7 ; 36.0 ; 46.3
Polybutadiene (Buna CB 45B)	46.3 ; 36.0 ; 25.7 ; 15.4 ; 5.1
Naphthenic Oil NH-140 (plasticizer)	10.3
Carbon black N550 (charge)	30.8
Zinc oxide (activator)	3.1
Stearic Acid	1.0
Dispersion additive	1.0
Sulfur (vulcanizing agent)	1.5
TMTD (accelerator)	0.8

antioxidant were added, at the same rotation, and mixed for more 100 seconds. After the first phase of homogenization, the mixture was unloaded on an open-mill, and with the aid of a stock blender, it was cooled to add the rest of additives and cut the compound.

The vulcanization process was set in a sheet device according to ASTM D 3182 (150 mm x 150 mm x 2 mm), with 4.5 minutes at 180° C and closing pressure of 100 kgf/cm^2. The vulcanization time was defined by the rheometer curve.

FT-IR methodologies (transmission, reflection, transflectance)

The analysis conditions were as follows: Spectrum One spectrometer (PerkinElmer), in MIR region (4000-400 cm^{-1}) and partial NIR region (7800-4000 cm^{-1}), 4 cm^{-1} resolution and 20 scans. Transmission, UATR (80N) (reflection), and NIRA (transflectance) were the spectra obtaining modes. EPDM/BR samples were pyrolyzed in a Bunsen burner after pretreatment with acetone and, then, analyzed as liquid films.

Pyrolysis (thermal degradation) is highly suitable for IR analysis of rubbers, and was employed as a sample preparation technique. Its process consists of separating the polymer from most of the formulation additives, isolating the base polymer (elastomer) structural unit to obtain adequate intensity IR bands for spectrum interpretation (Smith 1979, Rigoli et al. 2021). The extraction is performed by an adequate solvent, which remove the soluble rubber additives.

The pyrolysis conditions can be well controlled in relation to time and temperature; however, at higher costs; or without control of time and temperature directly in a Bunsen burner. This study employed the latter method associated with use of band intensity ratio to minimize errors in the methodology, a feature explained posteriorly.

The pyrolysis on a Bunsen burner basically consists of heating approximately 0.5 g of rubber sample chopped into small pieces, previously extracted with a suitable solvent (in the case of EPDM/BR, the best solvent is acetone) in a pyrolysis tube. The thermal degradation that occurs produce a viscous liquid (pyrolysate) that contains the elastomer. This liquid is transferred to an infrared cell (KBr), without spacer, for analysis. The band intensity ratio was used to control the effect of the bands thickness variation or height measurements.

In the case of the elastomer sample being unknown, pyrolysis must be carried out without previous extraction to identify the elastomer characteristic bands and choose the appropriate solvent. The solvent correctly chosen is important to only remove the additives and not attack the

rubber. After the extraction, the rubber sample is pyrolyzed again. In this study, the composition was previously known and acetone was the proper solvent.

For the development of the quantitative methodology, analytical bands were chosen according to the Lambert-Beer law. The analytical bands are associated with the absorptions from each elastomer functional groups. The Lambert-Beer law establishes a linear relationship between compound absorbance (A) and its concentration (Smith 1979, Custódio et al. 2018). For the determination of A, as done in previous studies, the height of the analytical band (intensity) from each elastomer was measured (Rigoli et al. 2019, 2021, Carvalho et al. 2021).

The control of thickness is important for measuring properly the band intensity (height). This control can be performed by inserting a spacer or by using the band intensity ratio. This ratio (A_1/A_2) is composed of an analytical band (A_1) and a reference band (A_2), and the latter stays unchanged. Two analytical bands, as observed in other studies, can also constitute a band intensity ratio, to eliminate the interference of sample thickness variation, which can instigate errors in measuring the intensity of the band (Rigoli et al. 2019, 2021, Carvalho et al. 2021, Ferreira et al. 2020).

Different MIR analytical bands were evaluated for EPDM (1376 and 887 cm^{-1}, respectively assigned to CH_3 bending and vinylidene groups wagging) (Smith 1979), and BR (~1000, 970, 900, relative to C=C vinyl wagging and 743 cm^{-1}, C=C cis group wagging) (Takahashi & Polito 1997, Smith 1979). As stated previously, the analytical bands refer to the groups that characterize the rubbers. Band intensity ratio ($A_{887}/A_{743;}$ A_{887}/A_{909}; A_{887}/A_{966}; A_{887}/A_{990}, and A_{1376}/A_{743}) formed by two analytical bands, one from each elastomer, were established for thickness control and better accuracy of the results (Smith 1979). The selected MIR baselines to measure bands intensity/height were: 930–860 cm^{-1}, for the bands at 887 and 909 cm^{-1}; 775-732 cm^{-1}, for the band at 743 cm^{-1}; 1048-931 cm^{-1}, for the bands at 966 and 990 $cm^{-1}$and 1380-1331 cm^{-1}, for the absorption at 1376 cm^{-1}.

For NIRA analysis, it was considered the band intensity ratio A_{5690}/A_{4600}. The selected baselines were: 6065 to 4790 cm^{-1} for the band at 5690 cm^{-1} and 4695 to 4560 cm^{-1} for the band at 4600 cm^{-1}. The probable assignment of NIR bands is in results and discussion, to a better understanding of the results.

The criteria that guided the choice of the best band intensity ratio were the calibration curve best linearity (R), data percentage explained by the methodology (R^2) and the methodology error, as exemplified in previous papers (Rigoli et al. 2021, Carvalho et al. 2021). For the EPDM/BR blend, it is non-overlapping bands.

Initially, regarding the EPDM/BR analysis, a MIR investigation was carried out by transmission to choose the best band intensity ratio. Secondly, the study proceeded with UATR and NIRA analysis of each sample for the elastomers quantification, including methodology errors. Calculations were carried out in accordance with the non-parametric statistical method (Eq.1-3) (deviations related to the median) (Horák & Vítek 1978), which are applied in different FT-IR spectroscopic data investigation (Rigoli et al. 2019, 2021, Carvalho et al. 2021, Ferreira et al. 2018, 2020, Azevedo et al. 2018).

$$\hat{\sigma} = K_R \ .R \tag{1}$$

where $\hat{\sigma}$ is the standard deviation, R is the difference between the absorbance highest value and the absorbance lowest value and K_R equals 0,430 for 5 data points (Horák & Vítek 1978).

$$\hat{\sigma}_{\hat{\mu}} = \frac{\hat{\sigma}}{\sqrt{n}} \tag{2}$$

where $\hat{\sigma}_{\hat{\mu}}$ is the mean standard deviation, *n* is the number of observations, that is, number of data points.

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

where *RSD* is the relative standard deviation given in percentage, μ is the median of absorbance values.

The calculation of the methodology error considered the median of relative errors, according to previous researches (Rigoli et al. 2021, Carvalho et al. 2021, Azevedo et al. 2018, Damazio et al. 2015, Dutra & Soares 1998).

Test samples were also analyzed to verify the effectiveness of the developed MIR methodologies. The samples were coded and sent to an analytical research laboratory for IR analysis under the same conditions as the prepared calibration curves samples. It was considered the most suitable analytical bands of the developed methodologies, as well as their corresponding calibration curves. Five aliquots of each test sample were analyzed, and the median value was applied in each calibration curve. Measurement errors were also calculated, according to the methodology employed to prepare each curve.

RESULTS AND DISCUSSION

EPDM/BR - FT-IR analysis/transmission/ Bunsen burner pyrolysis

Table II shows the assignment of the typical absorption bands of each elastomer that constitute the EPDM/BR blend (Takahashi & Polito 1997, Smith 1979). The region around 900-1000 cm^{-1} exhibited overlapping bands. Theoretically, absorptions bands at 887 and 1376 cm^{-1} (EPDM) and 743 cm^{-1} (BR) would be the most appropriate analytical band for quantitative determination of each elastomer in the blend (Figure 1). The band intensity increases as the elastomer content increases, especially for the band at 887 cm^{-1} of vinylidene (EPDM), indicating that the system can be analyzed quantitatively by IR, as it obeys the Lambert-Beer law (Smith 1979),

The band intensity ratio (A_{887}/A_{743}) does not present overlapping bands, so it was analyzed first. Table III indicates FT-IR results (A_{887}/A_{743}) for the calibration curve and the assessment of this methodology. It displays EPDM/BR content and calculated errors for the FT-IR/Transmission/ Bunsen burner pyrolysis methodology.

A methodology error of 9.04 % (Table III) is high in comparison to the equipment precision

Table II. EPDM and BR bands assigned to its functional groups and vibrational modes.

Rubber	Wavenumber (cm^{-1})	Functional group	Vibrational mode
EPDM	887	$RR'CCH_2$	Wagging
	910	C=C vinyl	
	966	C=C trans	
	993	C=C vinyl	
	1376	CH_3	Symmetric angular bending
BR	743	C=C cis	Wagging
	909	C=C vinyl	
	966	C=C trans	
	992	C=C vinyl	

limit ≤ 2 % (variation of the band intensity measure) (Horák & Vítek 1978). However, the equipment precision limit is obtained under conditions of ideal thickness control, such as transmission/solution/cell with spacer. This higher error value of approximately 9 % may be due to the 743 cm^{-1} band weak intensity, which makes measuring BR contents difficult, especially for lower contents of this elastomer. Nevertheless, this band was evaluated because it does not overlap with the EPDM bands.

Figure 2 shows the FT-MIR/transmission calibration curve (A_{887}/A_{743}) for EPDM and BR contents. From the calibration curve taken by FT-IR analysis, the following relationship is proposed (Eq. 4).

$$y = 7.4221x + 1.8796 \quad (4)$$

where *y* is the absorbance median value of the band intensity ratio A_{887}/A_{743}, and *x* is the relative content [EPDM]/[BR].

A good data correlation (R= 0.995) was observed, while about 98% (R^2) of the obtained data are explained by this methodology.

Using band intensity ratio *versus* relative content for calibration curves is good practice to improve precision and to avoid errors due to film thickness variation and to the optical path. It can benefit in transmission and reflection determinations (Ferreira et al. 2018, 2020, Mello et al. 2018, Gedeon & Ngyuen 1985).

The band intensity ratio A_{1376}/A_{743} is also a pair of bands that does not show overlapping, so it was analyzed in sequence. FT-IR results (A_{1376}/A_{743}) were used for the calibration curve for the EPDM/BR determination, as well as

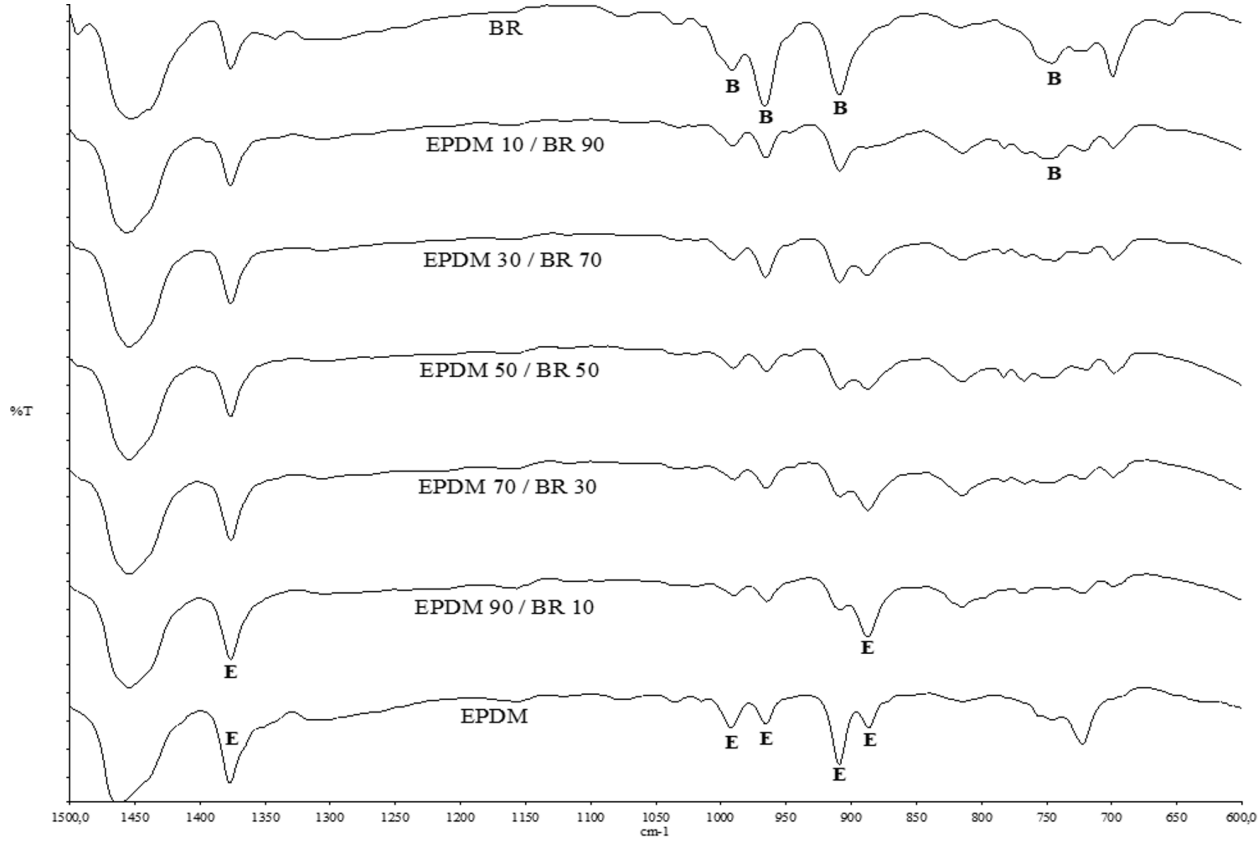

Figure 1. **FT-IR transmission spectra of pyrolyzed EPDM/BR sample overlayed with the EPDM and BR standard elastomers spectra, under the same conditions (EPDM-E; BR- B).**

the errors involved in the FT-IR/transmission/Bunsen burner pyrolysis methodology.

Calculations similar to those already shown in Table III were made and the methodology error of 8.06 % was observed using this band intensity ratio (A_{1376}/A_{743}). It can also be considered high if compared to the equipment precision limit (band intensity measure variation) ≤ 2% (Horák & Vítek 1978). It was employed as analogous to the band A_{887}/A_{743}, for the reasons already exposed.

Table III. FT-IR/transmission/Bunsen burner pyrolysis results (A_{887}/A_{743}) and errors related to the EPDM/BR blend quantification.

EPDM/BR (relative content)	A_{887}/A_{743}	Parameters
10/90 (0.11)	2.000	$\hat{\mu}$ = 1.833
	2.000	R = 0.565
	1.435	$\hat{\sigma}$ = 0.243
	1.500	$\hat{\sigma}_{\hat{\mu}}$ = 0.109
	1.833	RD = 5.95 %
30/70 (0.43)	3.600	$\hat{\mu}$ = 3.739
	3.143	R = 1.757
	4.214	$\hat{\sigma}$ = 0.755
	3.739	$\hat{\sigma}_{\hat{\mu}}$ = 0.338
	4.900	RD = 9.04 %
50/50 (1)	6.333	$\hat{\mu}$ = 7.571
	5.533	R = 3.550
	9.083	$\hat{\sigma}$ = 1.526
	7.571	$\hat{\sigma}_{\hat{\mu}}$ = 0.682
	8.923	RD = 9.00 %
70/30 (2.33)	24.111	$\hat{\mu}$ = 24.111
	35.500	R = 15.125
	22.375	$\hat{\sigma}$ = 6.504
	30.600	$\hat{\sigma}_{\hat{\mu}}$ = 2.909
	20.375	RD = 12.06 %
90/10 (9)	76.000	$\hat{\mu}$ = 67.667
	54.000	R = 45.333
	62.667	$\hat{\sigma}$ = 19.493
	67.667	$\hat{\sigma}_{\hat{\mu}}$ = 8.718
	99.333	RD = 12.88 %

Figure 3 illustrates FT-MIR/transmission calibration curve (A_{1376}/A_{743}) for EPDM and BR contents determination. From the calibration curve taken by FT-IR analysis, the following relationship is proposed (Eq. 5).

$$y = 9.2055x + 5.6622 \quad (5)$$

where *y* is the absorbance median value of the band intensity ratio A_{1376}/A_{743}, and *x* is the relative concentration [EPDM]/[BR].

It was detected a good data correlation (R=0.996), and about 99% (R^2) of the obtained data are explained by this methodology.

Band intensity ratios including BR with overlapping EPDM bands were also evaluated, using the same methodologies of error calculation and calibration curve employed for non-overlapping bands.

Table IV reunite all data for the best band intensity ratio evaluation, considering calibration curve linearity (R), data explained by the methodology (R^2), and methodology error (%). According to Table IV, in terms of linearity and results in percentage explained by the developed methodology, the band intensity ratios A_{1376}/A_{743} and A_{887}/A_{743} are the most suitable for determining EPDM/BR contents. Regarding the methodology error, the band at A_{887}/A_{909} is the most suitable. However, at 909 cm^{-1}, it can be observed an overlapping with the EPDM characteristic band.

Results show that intensity ratio A_{1376}/A_{743} and A_{887}/A_{743} are the most suitable for determination of EPDM/BR contents, considering the FT-IR transmission/pyrolysis data analysis, linearity, percentage of results explained by the methodology, and the circumstance of non-overlapping bands. The low intensity band at 743 cm^{-1} interfere with measuring BR content, especially low contents (10-20%), which may

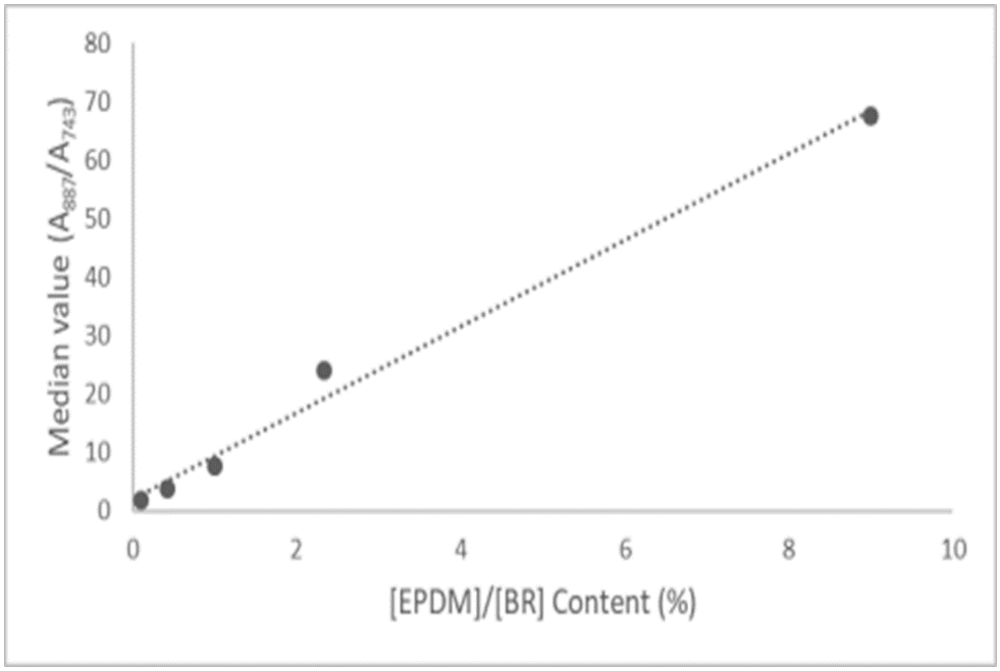

Figure 2. FT-MIR/ transmission calibration curve (A_{887}/A_{743}) *versus* [EPDM]/[BR].

indicate a limit of quantification. Although the methodological error is set between 8 to 9%, it is acceptable with the analysis conditions.

EPDM/BR - FT-IR/UATR/Bunsen burner pyrolysis analysis

Considering that this study investigates non-overlapping bands and that the band intensity ratio A_{887}/A_{743} shows good results for the pyrolysis/transmission mode, the UATR/ pyrolysis in a Bunsen burner methodology was tested. Figure 4 shows results plotted in a calibration curve. It was not possible to measure the band at 743 cm^{-1} of the sample with 10% BR, which indicates a limit of quantification for this BR content by this methodology. This may be due to differences in characteristics of reflection and transmission methodologies, because there is optical path variation in the first, and stronger bands in transmission spectra appear weaker in the reflection spectra (Magalhães et al. 2020, Ferrão 2001).

In order to determinate the EPDM and BR contents by FT-MIR/UATR/Bunsen burner pyrolysis, (Eq.6) is proposed based in the calibration curve plotted in Figure 4.

$$y = 23.024x + 1.9541 \quad (6)$$

where *y* is the absorbance median value of the band intensity ratio A_{887}/A_{743}, and *x* is the relative content [EPDM]/[BR].

Although UATR/Bunsen burner pyrolysis methodology responded for four samples, indicating a limit of quantification for BR contents lower that 30 phr, a good data correlation was observed (R = 0.995). Approximately 99% (R^2) of the data was explained by this methodology. Thus, there is a tendency to linearity and it meets the Lambert-Beer law in this detection limit. The methodology error was around 13% and this high value can be assigned to the difficulty of the UATR in measuring the band in 743 cm^{-1}. This band intensity is weaker than in the transmission/Bunsen burner pyrolysis methodology due to the technical characteristics (Magalhães et al. 2020, Ferrão 2001).

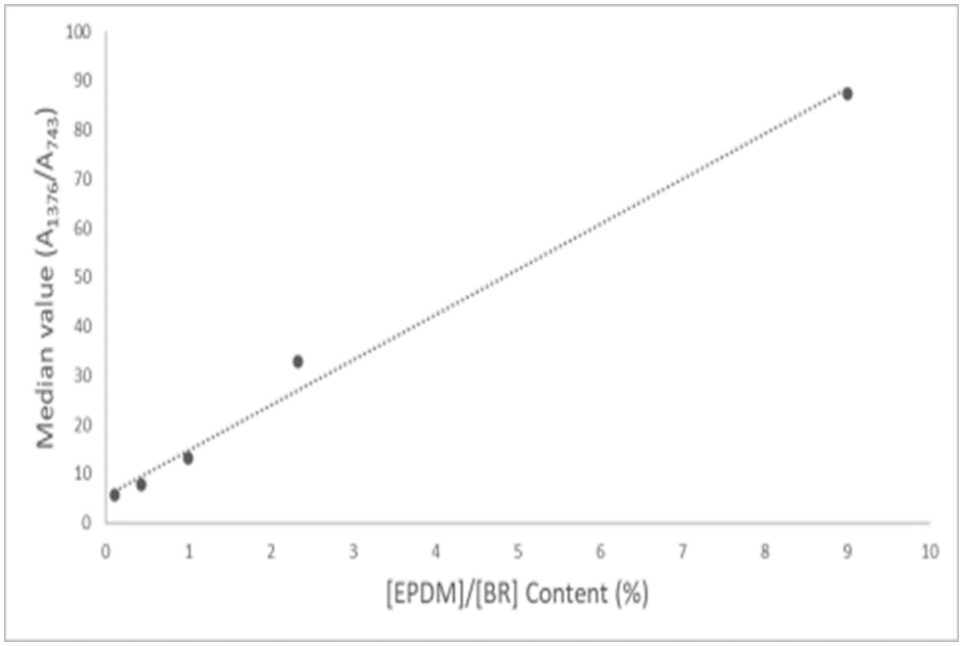

Figure 3. FT-MIR/Transmission calibration curve (A_{1376}/A_{743}) *versus* [EPDM/BR].

Table IV. FT-IR/transmission/Bunsen burner pyrolysis data assessment, using different bands intensity ratio for EPDM and BR contents determination.

Band intensity ratio	R (linearity)	R^2 (results percentage explained by the methodology)	Methodology error (%)	Methodology error comment
A_{887}/A_{743}	0.995	98	9.04	High error if compared to the equipment precision limit [39] (band intensity measure variation) ≤ 2%. which is mainly obtained under thickness control ideal conditions (transmission/solution/cell with spacer). This error of around 9% may be due to the weak intensity of the band at 743 cm^{-1}, which makes it difficult to properly measure BR contents. However, the band in 743 cm^{-1} was evaluated for having no overlapping with EPDM bands.
A_{1376}/A_{743}	0.996	99	8.06	This error of around 8% may also be due to the band intensity at 743 cm^{-1}, considered weak, which makes it difficult to measure BR contents. However, it was evaluated for having no overlapping with EPDM bands.
A_{887}/A_{909}	0.947	90	2.47	Error considered satisfactory if compared to equipment precision limit [39] (band intensity measure variation) ≤ 2%, but this band in 909 cm^{-1} overlaps with the EPDM characteristic band.
A_{887}/A_{966}	0.91	83	5.35	Since this band shows overlapping at 966 cm^{-1}, with EPDM characteristics, the error is considered satisfactory under the conditions of the conducted analysis.
A_{887}/A_{990}	0.900	81	3.67	Since this band shows overlapping at 990 cm^{-1}, with EPDM characteristics, the error is considered satisfactory under the conditions of the conducted analysis.

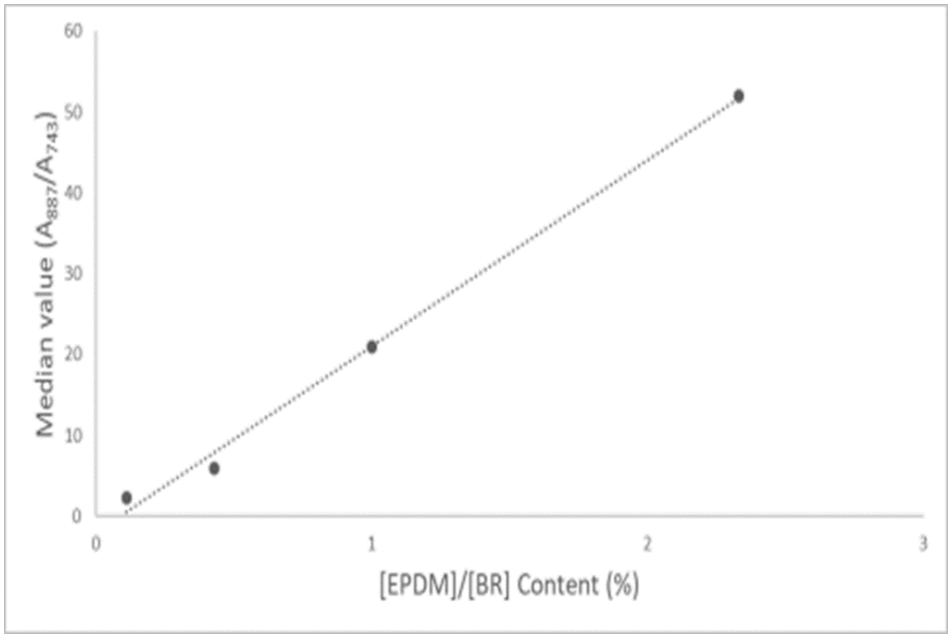

Figure 4. FT-MIR/UATR/ Bunsen burner pyrolysis calibration curve (A_{887}/A_{743}) *versus* [EPDM]/[BR].

EPDM/BR - FT-IR/NIRA/Bunsen burner pyrolysis analysis

Although the NIRA spectra of EPDM and BR are similar, probably due to the absorptions of the C=C groups present in BR and in the dienic part of EPDM, the analytical bands of each elastomer were chosen through the evaluation of their peak table, by comparing wavenumbers that are on one and not on the other spectrum, to avoid bands that overlap. The EDPM and BR spectra were evaluated, also, in relation to the blend spectra, and the variation in the intensity of the bands was observed as the variation in the content of the elastomers. Thus, the A_{5690}/A_{4600} band intensity ratio was chosen because the bands absorb at wavenumbers well apart, and because they have intensities that are possibly adequate for the blend elastomers determination.

The assignment of the characteristic NIRA absorptions of EPDM and BR in this study were: the band at 5690 cm^{-1} (EPDM) can be associated with the C=C bands second overtone, between 900 and 1000 cm^{-1}. The band at 4600 cm^{-1} (BR) is the combination of a region and can probably be assigned to the C=C and CH groups at 1000, 900 and 3100 cm^{-1} (Goddu 1960).

It was not possible to measure the band at 4600 cm^{-1}, characteristic of BR, in the EPDM90/BR10 sample due to its low intensity. Therefore, there must be a detection or quantification limit for the NIRA methodology in the analysis conditions, i.e, the analysis of the Bunsen burner pyrolysate and the use of the A_{5690}/A_{4600} band intensity ratio. Consequently, the maximum content that can be measured by NIRA analysis with these conditions is 30 phr of BR, caused by the low intensity of the BR characteristic band.

The error around 4% for the NIRA/Bunsen burner pyrolysis A_{5690}/A_{4600} methodology can be considered satisfactory based on the analysis conditions. The conditions are in the NIR region, with samples prepared by Bunsen burner pyrolysis without temperature control. If the sample were analyzed as received, it could provide bands with even lower intensity. However, the NIRA methodology transflectance mode, error (4%), is in accordance with what is mentioned in the literature for NIR analysis

by transmission (4%) (Carvalho et al. 2021, Vogelsanger et al. 2014).

This NIRA methodology error cannot be compared to the equipment accuracy limit (≤ 2%), because this value is only to be considered as a reference (Horák & Vítek 1978). The reference value can be easily reached by applying thickness control under ideal conditions. For example, investigating a liquid by transmission in the MIR region using a sealed cell with a spacer (Smith 1979).

Figure 5 displays the NIRA/Bunsen burner pyrolysis calibration curve, with the band intensity ratio A_{5690}/A_{4600} median values versus EPDM/BR relative content.

From the calibration curve shown in Figure 5, is proposed a linear equation (Eq. 7).

$$y = 2.1177x + 5.5931 \quad (7)$$

where y is the A_{5690}/A_{4600} median value, and x is the relative content [EPDM]/[BR].

Although the NIRA/Bunsen burner pyrolysis methodology only responded to four samples, a good data correlation was observed (R = 0.97), while about 94% (R^2) of the obtained data can be explained by this methodology. These values associated with the NIRA/pyrolysis/A_{5690}/A_{4600} developed methodology error, around 4%, and the limit of quantification demonstrate that it can be used for EPDM/BR contents determination, for values greater than 30 phr of BR.

FT-MIR/transmission and FT-MIR/UATR Bunsen burner pyrolysis methodology effectiveness

Since the band intensity ratio A_{1376}/A_{743} and A_{887}/A_{743} revealed similar results, the band intensity ratio A_{887}/A_{743} was chosen for the methodology effectiveness, as it involves the vinylidene group. This group is more characteristic of EPDM than that of 1376 cm^{-1}, which, despite being a band attributed to this structural unit of the elastomer, is associated with the methyl group (Rigoli et al. 2017) and can cause overlapping of bands.

Therefore, in order to verify the efficiency of the developed methodology using FT-IR/transmission/Bunsen burner pyrolysis, two EPDM/BR samples with nominal relative content (30/70) and (10/90), coded, respectively, as samples A and B, were analyzed under the

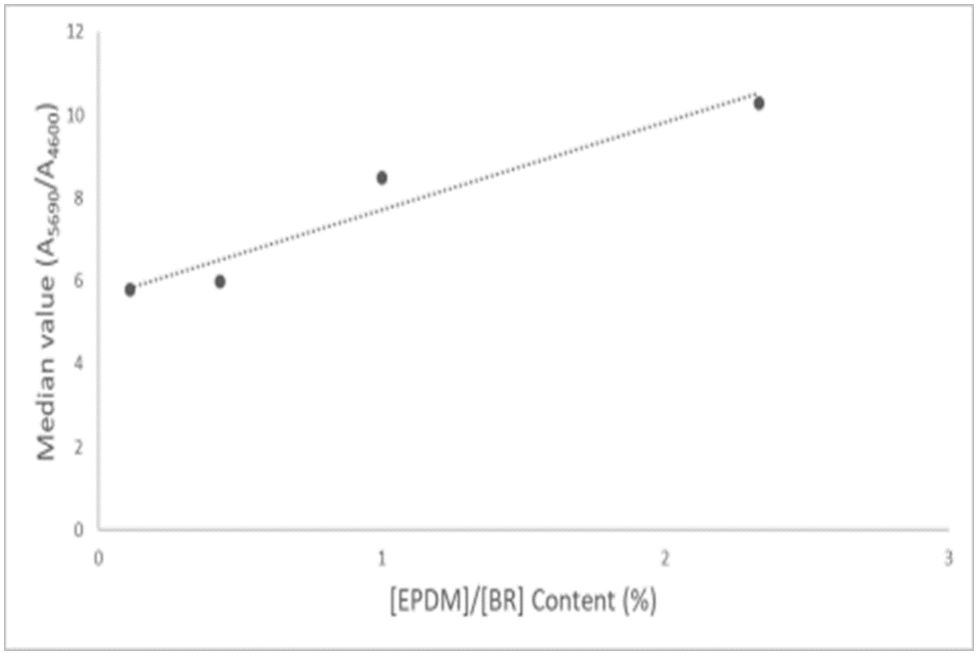

Figure 5. NIRA/Bunsen burner pyrolysis (A_{5690}/A_{4600}) calibration curve *versus* [EPDM]/[BR].

same conditions used to plot the A_{887}/A_{743} band calibration curve. In addition, to evaluate the efficiency of the methodology developed by FT-IR/UATR/Bunsen burner pyrolysis, the EPDM/BR sample with nominal relative content (10/90), coded as sample B, was also analyzed. The analysis followed the same conditions as those used to draw the calibration curve for the A_{887}/A_{743} band. Table V data assessment reflects that good results were achieved applying (Eq. 4, Eq 6 and Eq.8), since it was considered the relative content in the calibration curve.

$$[EPDM] + [BR] = 100 \quad (8)$$

Where [EPDM] is the EPDM content and [BR] is the BR content.

Table V shows that values are close to the nominal, especially for higher BR contents, with a relative error between 3-9%.

The sample with the higher BR content (Sample B) provided the best result, which is due probably to the methodology (transmission or UATR) being more suitable for measuring higher contents of this elastomer. The weak band at 743 cm^{-1} results in even lower absorptions when measuring samples with little rubber content, which could provide greater error. On the other hand, it can achieve an accurate determination of low EPDM contents. Therefore, this dataset can be useful for different applications.

The values obtained for the EPDM and BR contents, in sample A, are in the expected magnitude range, being considered acceptable at industries for the quality control of rubber blend. The methodology error, in the technological aspect, can be higher than the quantitative IR analysis reference (Horák & Vítek 1978), under ideal conditions (≤ 2%), because it is only restricted to one specification range for the material acceptance (Mello et al. 2018).

It can be concluded that the calibration curve that comprises the A_{887}/A_{743} band, without EPDM/BR band overlapping, shows the most suitable results for the determination of EPDM/BR content, even with the error between 3-9%

Table V. FT-IR/transmission and FT-IR/UATR Bunsen burner pyrolysis data assessment of EPDM/BR test samples using the A_{887}/A_{743} band intensity ratio curve.

SAMPLE EPDM/BR	A_{887} (EPDM)	A_{743} (BR)	A_{887}/A_{743}	A_{887}/A_{743} Median	Mean Standard Deviation	Relative Deviation (%)	EPDM Content (%)	BR Content (%)
SAMPLE A Nominal content: (30/70) - Transmission data	0.046	0.012	3.883	3.833	0.330	8.60	20.83	79.17
	0.037	0.008	4.625					
	0.032	0.011	2.909					
	0.047	0.016	2.937					
	0.071	0,016	4.437					
SAMPLE B Nominal content: (10/90) – Transmission data	0.042	0.013	3.230	2.737	0.162	5.92	10.40	89.60
	0.052	0.019	2.737					
	0.066	0.026	2.538					
	0.075	0.024	3.125					
	0.043	0.018	2.389					
SAMPLE B Nominal Content: (10/90) – UATR data	0.013	0.006	2.166	2.166	0.064	2.95	15	85
	0.013	0.006	2.166					
	0.013	0.006	2.166					
	0.012	0.006	2.000					
	0.011	0.006	1.833					

(due to BR band low intensity, making it difficult to measure with greater precision).

In an attempt to find greater precision in the EPDM and BR quantification, the NIRA analysis was evaluated. Samples were also pyrolysed in a Bunsen burner.

FT-MIR (transmission), reflection (UATR) and transflectance (NIRA) comparison data

Figure 6 shows the comparison of absorbance results for the different methodologies.

Figure 6a shows linearity (R = 0.99) and the explained data percentage (R^2 = 98%) demonstrate a good agreement between MIR (transmission) and MIR (reflection-UATR) absorbance values. This means that the methodologies with different characteristics (Ferrão 2001) provide similar EPDM and BR results. Consequently, the UATR methodology can be used to determine these elastomer's levels, respecting their detection limit, as mentioned previously. Figure 6b and Figure 6c results, respectively, (R = 0.93; R^2 = 86%) and (R = 0.97; R^2 = 94%), also showed good uniformity.

Therefore, the three methodologies (transmission, reflection, and transflectance) are able to evaluate the EPDM/BR content. By transmission, linearity values and explained data are more precise. It holds the advantage of not having a limit of quantification to determine low BR contents, which would be suitable for the aerospace industry, where a low content of another elastomer in EPDM could modify its thermal protection properties.

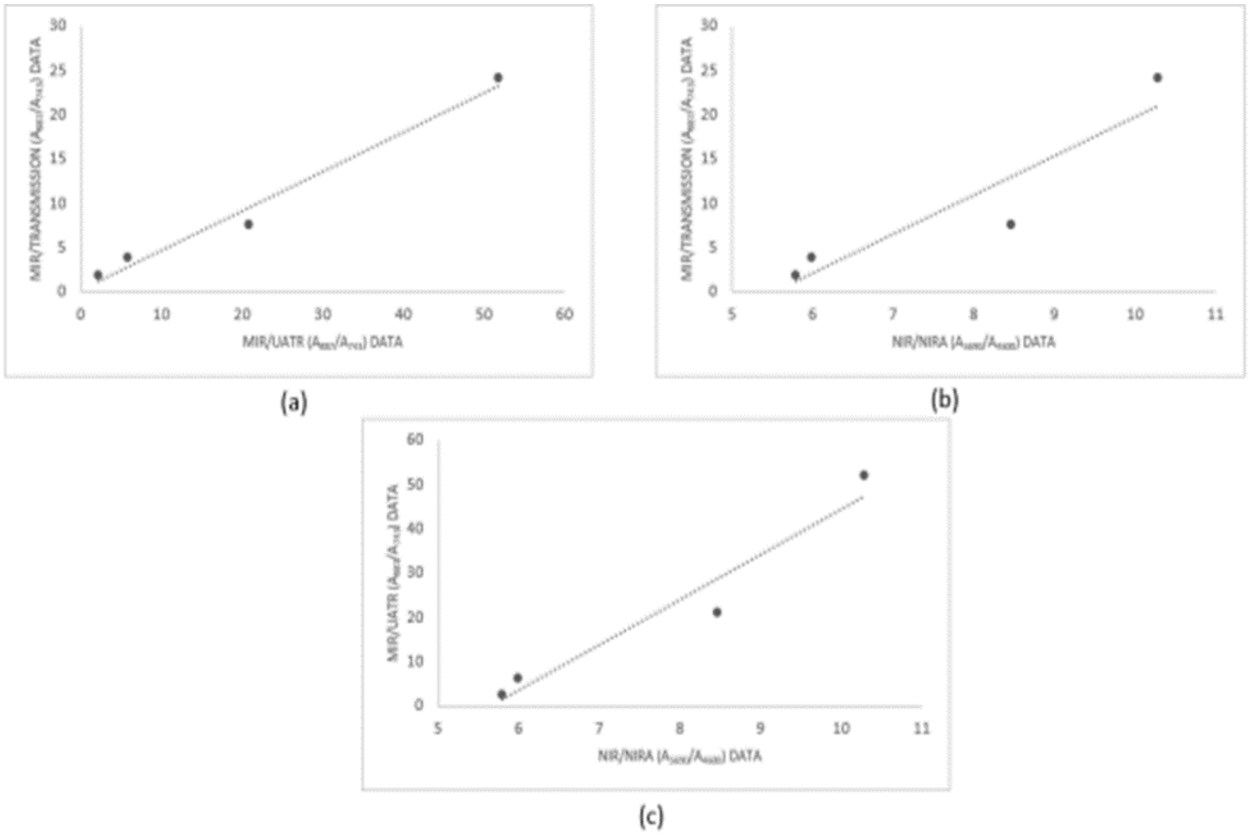

Figure 6. Comparison of methodologies: (a) A_{887}/A_{743} MIR transmission versus A_{887}/A_{743} MIR UATR. (b) A_{887}/A_{743} MIR transmission versus A_{5690}/A_{4600} NIRA. (c) A_{887}/A_{743} MIR UATR versus A_{5690}/A_{4600} NIRA.

CONCLUSIONS

For the determination of EPDM/BR contents using non-overlapping bands, by FT-IR transmission, reflection (UATR) and transflectance (NIRA), the criteria selected to choose the appropriate methodology included the calibration curve (R) linearity, the data percentage explained by the methodology (R^2), the methodology error (precision) and the detection limit.

In terms of R (linearity) and R^2 (the explained data percentage), transmission and reflection methodologies results showed good agreement. Regarding the methodology error, the one related to NIRA data shows the best value; however, reflection (UATR) and transflectance (NIRA) demonstrated a limit of quantification for values smaller than 30 phr of BR. Consequently, the most suitable methodology for the EPDM and BR determination, in a binary blend with no overlapping bands, is the transmission/pyrolysis (A_{887}/A_{743}).

Given that pyrolysis was applied as the sample preparation method for the three methodologies, the time of analysis did not influence in the choice of the most suitable methodology for the determination.

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