QUANTIFICATION OF AEROSPACE AND INDUSTRIAL EPDM/BR RUBBERS BY FT-IR: TRANSMISSION, REFLECTION AND TRANSFLECTANCE

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Abstract

The study focuses on quantifying mixtures of ethylene-propylene-diene monomer (EPDM) and polybutadiene (BR) using infrared (IR) spectroscopy, emphasizing the importance of selecting appropriate spectral acquisition methods and analytical bands to avoid overlapping and ensure accuracy. Three methodologies were tested: transmission, reflection, and transflectance, each using suitable analytical bands. The transmission method, with the relative band A_887/A_743, showed the highest precision, particularly in detecting BR content below 30 phr, which is crucial for aerospace applications where even minimal amounts of another rubber are undesirable. In addition to being a less complex technique, making it suitable for the rubber industry, the study also contributes to the scientific discussion on various IR spectroscopy methods, including less conventional ones like transflectance, and addresses the methodological errors associated with these techniques.

Keywords: content determination, EPDM/BR**,** FT-IR.

Area of Knowledge: Exact Earth Sciences - Chemistry

Introduction

The text discusses the wide industrial application of rubbers, such as ethylene-propylene-diene monomer (EPDM) and butadiene rubber (BR), which are used in sectors such as aerospace and automotive. (EPDM), for example, is used as thermal protection in rocket engines due to its thermal stability and balanced mechanical properties. However, due to the absence of polar groups in its structure, (EPDM) presents compatibility challenges when mixed with other rubbers.

(EPDM) production is comparable to that of other synthetic rubbers, such as styrene butadiene rubber (SBR) and butadiene rubber (BR) and the global (EPDM) market is expected to grow significantly. Blending (EPDM) with other rubbers, such as (NR), (SBR) and (NBR), can improve certain properties, such as ozone resistance, but compatibility between the components is still a challenge due to different polarity and unsaturation levels.

Recent research has focused on improving the compatibility of (EPDM) blends with other rubbers, such as (BR), using compatibilizing agents and surface modifications of (EPDM). Fourier transform infrared spectroscopy (FTIR) techniques are applied to characterize and quantify rubber blends, with promising results, especially when overlapping analytical bands are avoided.

This study aims to develop (FTIR) methodologies for the characterization and quantification of binary (EPDM) and (BR) blends, considering overlapping analytical bands. The objective is to use unconventional techniques, such as reflection (UATR) and transflectance (NIRA), to improve accuracy, reduce analysis time and eliminate errors resulting from band overlap. This seeks to contribute to the advancement of scientific research and industrial applications of (EPDM) based systems, optimizing the

characterization and quantification of binary rubber mixtures. Transflectance analysis (NIRA) is used to validate the methodology (FTIR) by transmission or reflection.

Methodology

FT-IR methodologies (transmission, reflection, transflectance)

Analysis was conducted under the following conditions: 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 applied. EPDM/BR samples were pyrolyzed in a Bunsen burner after acetone treatment and were analyzed as liquid films.

Pyrolysis (thermal degradation) was conducted as a sample preparation technique, as it is more suitable for rubbers IR analysis. Its process consists in separating the polymer from most formulation additives, regenerating the base polymer (elastomer) structural unit, resulting in adequate intensity IR bands for spectrum interpretation.

Analytical bands can be referred to those bands associated with the functional group or compound to be determined. Seeking the quantitative methodology development, analytical bands were chosen for each elastomer following Lambert-Beer law. Lambert-Beer law establishes a linear relationship between compound absorbance (A) and its concentration. For the calculation of A, not only in this paper but also in recent researches each elastomer analytical band height (intensity) was considered, which is suitable for the research.

Thickness control is important for the band intensity (height) proper measurement. This control can be accomplished by inserting a spacer or by relative band. A band intensity ratio (relative band) (A_1/A_2) is composed of an analytical band (A_1) and a reference band (A_2), and the last one does not change with the process. A relative band can also be formed by two analytical bands, as observed in other papers to eliminate the interference of sample thickness variation, which can instigate errors in the band measuring intensity.

Different analytical MIR bands were evaluated for EPDM (1376 and 887 cm^{-1}, respectively assigned to CH_3 bending and vinylidene groups wagging) and BR (~1000, 970, 900, relative to C=C vinyl wagging and 743 cm^{-1}, C=C cis group wagging). From the analytical bands, relative bands ($A_{887}/A_{743;}$ A_{887}/A_{909}; A_{887}/A_{966}; A_{887}/A_{990}, and A_{1376}/A_{743}) were established for thickness control and better accuracy of data obtained. 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 relative band 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, aiming at a better understanding of the data.

The criteria that guided the choice of the best relative band were the calibration curve best linearity (R), data percentage explained by the methodology (R^2) and the methodology error as exemplified in previous papers. In the case of EPDM/BR, it is associated with non-overlapping bands.

Initially, regarding EPDM/BR analysis, MIR research was carried out by transmission with the purpose to choose the best relative band. Secondly, it proceeded with UATR and NIRA analysis for the elastomers quantitative determination in each sample, including methodology errors. Calculations were carried out in accordance with the non-parametric statistical method (**Eq.1-3)** (deviations related to the median),which are applied in different FT-IR spectroscopic data investigation.

All samples were kindly manufactured and supplied by Tenneco Automotive Brazil. For quantitative analysis.

Five samples of different EPDM and BR contents were analyzed, **Table 2.**

$$\hat{\sigma} = K_R \,.\, R \qquad \textbf{(1)}$$

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.

$$\hat{\sigma}_{\hat{\mu}} = \frac{\hat{\sigma}}{\sqrt{n}} \quad \textbf{(2)}$$

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

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

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

The median of relative errors was used for the calculation of the methodology error, according to previous scientifical articles.

Test samples were also analyzed to verify the effectiveness of the developed MIR methodologies. Basically, 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 based to prepare each curve.

Results

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 relative band 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 although it is a band assigned to this elastomer structural unit, it is associated with the methyl group and can cause band overlap.

Therefore, in order to verify the efficiency of the developed methodology using FTIR/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 same conditions used to plot the A_{887}/A_{743} band calibration curve. On the other hand, 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 C, was also analyzed under the same conditions applied in calibration curve elaboration for the A_{887}/A_{743} band. **Table 1** data assessment reflects that good results were achieved applying (**Eq. 4, Eq. 5** and **Eq. 6**), since it was considered the relative content in the calibration curve.

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

$$y = 23.024x + 1.9541 \quad \textbf{(5)}$$

$$[EPDM] + [BR] = 100 \quad \textbf{(6)}$$

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

Table 1. FT-IR/transmission and FT-IR/UATR Bunsen burner pyrolysis data assessment of EPDM/BR test samples using the A_{887}/A_{743} relative band 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	0.046	0.012	3.883	3.833	0.330	8.60	20.83	79.17

Nominal content: (30/70) - Transmission data	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 C Nominal Content: (10/90) – UATR data	0.013	0.006	2.166	2.166	0.064	2.95	15.00	85.00
	0.013	0.006	2.166					
	0.013	0.006	2.166					
	0.012	0.006	2.000					
	0.011	0.006	1.833					

Source: prepared by the author (2024)

It can also be observed, **Table 1,** that values are close to the nominal, especially for higher BR contents, with a relative error between 3-9%.

The best result was found for the sample with a higher BR content (Sample B). This result is probably because the methodology (transmission or UATR) is more suitable for measuring higher contents of this elastomer, by the low intensity band at 743 cm^{-1}, when compared with low contents, which could provide greater error. On the other hand, it can reach an accurate determination of low EPDM contents. So, this dataset can be useful for different applications.

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

It can be concluded that the calibration curve which considers the A_{887}/A_{743} band, consisting of non-overlapping bands to the EPDM/BR relative content, shows the most suitable results for EPDM/BR contents determination, even with the error between 3-9% (due to BR band low intensity, making it difficult to measure with greater precision).

In an attempt to find greater precision in EPDM and BR quantification, NIRA analysis applicability was evaluated. Samples were also prepared by Bunsen burner pyrolysis.

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

Table 2. presents the FT-IR band intensity ratio absorbance data of following methodologies: MIR/transmission, MIR/reflection (UATR), and transflectance (NIRA) for EPDM/BR contents determination.

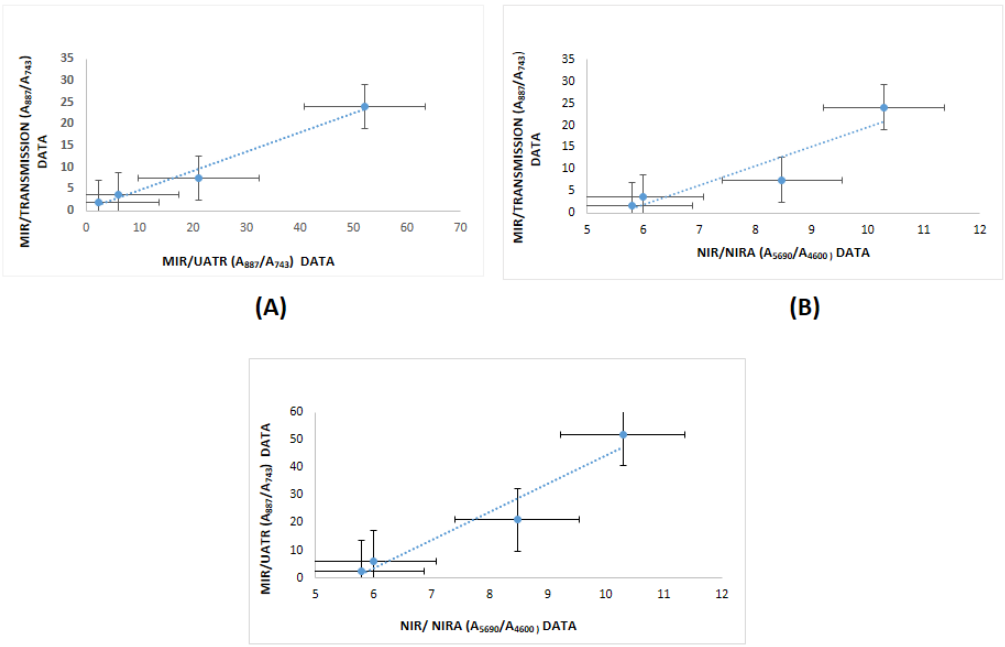
Table 2. MIR absorbance (transmission, reflection - UATR) and transflectance (NIRA) data for EPDM/BR contents determination.

EPDM/BR	MIR relative band (median)		NIR relative band (median)
	Transmission (A_{887}/A_{743})	UATR (A_{887}/A_{743})	NIRA (A_{5690}/A_{4600})
10/90	1.833	2.286	5.800
30/70	3.739	6.000	6.000
50/ 50	7.571	21.000	8.474
70/30	24.111	52.000	10.294

Source: prepared by the author (2024)

The methodologies absorbance data comparison is shown in **Fig. 1**

Figure 1. The methodologies absorbance data comparison for EPDM/BR system: (a) A_{887}/A_{743} relative band MIR absorbance (transmission) values versus A_{887}/A_{743} relative band MIR (UATR) absorbance values. (b) A_{887}/A_{743} relative band MIR (transmission) absorbance values versus A_{5690}/A_{4600} relative band NIRA absorbance values. (c) A_{887}/A_{743} relative band MIR (UATR) absorbance values versus A_{5690}/A_{4600} relative band NIRA absorbance values.



Source: prepared by the author (2024)

In **Fig. 1 (a)**, the 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 both methodologies, with different characteristics, estimate similar EPDM and BR levels. In addition, it states that the UATR methodology can be used to determine these elastomer's levels, respecting their detection limit, as mentioned before. Data from **Fig. 1 (b)** (R = 0.93; R^2 = 86%) and **Fig. 1(c)** (R = 0.97; R^2 = 94%) also showed good uniformity.

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

Discussion

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

The A_{5690}/A_{4600} relative band was chosen because they are at wavenumbers further apart, and because they have intensities that are probably adequate for the blend elastomers determination.

The probable assignment of the characteristic absorption bands of EPDM and BR considered in this study was: 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 bands region and can probably be assigned to C=C and CH groups combination band, at 1000, 900 and 3100 cm^{-1}.

It was not possible to measure the band at 4600 cm^{-1}, characteristic of BR, for the EPDM 90/BR 10 sample due to its low intensity. Therefore, it is possible to suggest that there must be a detection or quantification limit for the NIRA methodology in these methodology actual conditions, the analysis of Bunsen burner pyrolysate and the use of the A_{5690}/A_{4600} relative band. Consequently, the maximum content that can be measured by NIRA analysis under the mentioned 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 adopted conditions are NIR range, with samples prepared by Bunsen burner pyrolysis without temperature control. If the sample was analyzed as received, it could provide bands with even lower intensity. However, the NIRA methodology, by transflectance, error (4%) is in accordance with what is mentioned in the literature for NIR analysis by transmission (4%).

This NIRA methodology error cannot be compared to the equipment accuracy limit (≤ 2%), because this value is only to be considered as a reference. The reference value can be easily reached when applied thickness control under ideal conditions, for example, a liquid analysis by transmission, in the MIR region, using a sealed cell, that is, with a spacer.

Conclusion

For EPDM/BR contents determination 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 evaluation, the data percentage explained by the methodology (R^2), the methodology error (precision) and the detection limit.

In terms of R and R^2, transmission and reflection methodologies presented excellent results, similar and better than the NIRA data. Regarding the methodology error, the one related to NIRA data shows the best value (better precision). However, reflection (UATR) and transflectance (NIRA) methodologies demonstrate a detection limit for values smaller than 30 phr of BR. Thus, the most suitable methodology for 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 analysis time did not influence the choice of the most suitable methodology for the content determination.

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