INFRARED QUANTIFICATION OF EPDM/CR RUBBER BLEND: ADVANCES IN FT-IR SPECTROSCOPY TECHNIQUES

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Abstract

Ethylene-propylene-diene monomer (EPDM) and polychloroprene (CR) rubbers play a key role in the automotive and aerospace industries, where it is crucial to ensure the absence of undesirable components. Infrared (IR) spectroscopy, especially in the mid-infrared (MIR) region, has proven effective in quantifying binary mixtures, with the transmission technique being the most common. However, there are still gaps in the use of methodologies such as Universal Attenuated Total Reflection (UATR) and Near-Infrared Reflection Analysis (NIRA) to quantify these mixtures, opening up new research opportunities.The overlapping of bands in the (MIR) region makes it difficult to characterize different elastomers, such as (EPDM) and (CR), but this problem can be solved by appropriate selection of analytical bands and validation in the near-infrared (NIR) region. This study investigates (EPDM) and (CR) blends, highlighting that the (NIRA) transflectance technique offers greater precision for data validation, being particularly advantageous for aerospace applications that require greater accuracy in the detection of small component contents.

Keywords: Elastomers. Infrared spectroscopy. Quantitative analysis**.**

Area of Knowledge: Exact Earth Sciences - Chemistry

Introduction

EPDM/CR blends have great potential for application in several industries, such as the automotive industry. The combination of the properties of (CR) and (EPDM) elastomers offers significant advantages for different sectors, standing out for the strength, durability and versatility of the materials. These attributes make EPDM/CR blends attractive for industrial applications that require materials with high performance and longevity.

Quantitative analysis of these blends is essential, as the proportion of each elastomer directly influences the final properties of the material. Research suggests that the variation in the amounts of (CR) and (EPDM) significantly impacts the performance of the blend in several applications. Therefore, an accurate and detailed analysis is essential to understand how these proportions affect the behavior of the mixture and enable adjustments that maximize its performance under different conditions.

In the study by Rigoli et al. (2021), the quantitative determination of (CR) in EPDM/CR blends was investigated using Fourier transform infrared spectroscopy (FTIR). The analyses were conducted in the MIR region, using the UATR reflection mode and sample pyrolysis. The analytical band of 814 cm^{-1} of (CR) was used for quantification, and the study obtained a methodological error of approximately 2%, demonstrating the accuracy of the technique. The methodology, in addition to presenting advantages such as faster analysis, proved to be effective in the quantitative determination of these elastomers.

The accuracy of the methodology was validated with test samples, proving the effectiveness of the methodology developed as a future trend, the study by Rigoli et al. (2021) suggested exploring the (NIR) region, which is less studied compared to (MIR), especially using the (NIRA) transflectance technique. This type of approach is being explored in the present work for the EPDM/CR blend, complementing the information in the publication by Rigoli et al. (2021). The intention is to expand the knowledge of (IR) spectroscopy techniques and their applicability in the quantification of elastomer blends.

Methodology

The EPDM/CR samples were kindly prepared and provided by the company, Tenneco Automotive Brazil, for the previous study (RIGOLI. et al., 2021; RIGOLI. 2018) and used in this current work to complement the methodology, in the region (NIR), through analysis (NIRA). The nine (9) samples of the blends provided and analyzed contain the following nominal contents: EPDM/CR (10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10).

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. UATR (80N) (reflection), and NIRA (transflectance), were the spectra obtaining modes applied.

The EPDM/CR samples were prepared by pyrolysis in a Bunsen burner, after extraction in acetone, and analyzed by NIRA, completing the work, in partnership with RIGOLI et al. (2021). Pyrolysis (thermal degradation) was conducted as a sample preparation technique, as it is more suitable for IR analysis of rubbers, as already mentioned. Its process consists of separating the polymer from most of the formulation additives, regenerating the structural unit of the base polymer (elastomer), resulting in infrared bands of adequate intensity for spectrum interpretation and quantification of functional groups.

Analytical bands were chosen for each elastomer, for the development of the quantitative methodology, in accordance with the Lambert-Beer law, which, as mentioned, establishes a linear relationship between absorbance (A) and its concentration (c). To calculate A, in this study, as in other previous works, such as the study by Rigoli et al., 2021, the height (intensity) of the analytical band of each elastomer, appropriate for the study, was used.

For the EPDM/CR system, the NIRA qualitative analysis was performed using transflectance analysis (NIRA), with the characterization of bands, aiming at the appropriate choice of analytical bands suitable for the quantitative study, with the evaluation of absorptions for EPDM and CR. The probable assignment of all bands was included in the results and discussion item.

Analytical bands for EPDM (4330 cm^{-1}) and CR (4595 cm^{-1}) were quantitatively analyzed, depending on the band overlap. The baselines used for the EPDM bands were: 4464 to 4000 cm^{-1} for absorptions at 4330 cm^{-1} and 4766 to 4558 cm^{-1} for absorption at 4595 cm^{-1} of CR. The most accurate analytical bands of the developed methodologies were used, as well as their corresponding calibration curves.

Five aliquots of each test sample were analyzed and the median value was used in the application of each calibration curve. The errors involved in the measurement were also calculated for the transflectance methodology (NIRA) used to prepare each curve, in accordance with the specific statistical method for IR spectroscopic data (HÓRAK; VÍTEk, 1978), shown by Equations **(1-3).**

Formulas for nonparametric method, adapted from Hórak; Vítek (1978):

Standard deviation - $S = K_R \,.\, R$ **(1)**

where S 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.

Mean standard deviation - $S_X = \frac{S}{\sqrt{n}}$ **(2)**

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

Relative error or deviation (ER ou RD)

$$\mathrm{ER} = \left(\frac{S_x}{X}\right) . 100 \qquad \textbf{(3)}$$

Where X is the median absorbance value

The methodology, as mentioned, was considered as the median of relative errors (MAGALHÃES et al., 2020; RIGOLI et al., 2021; BARROS et al., 2023; DUTRA, SOARES, 1998).

Results

Table 1. shows the values of R, R2 and the errors of the methodologies for evaluating the bands, aiming at the best choice for determining the EPDM/CR contents.

Table 1, R, R2 values and methodological errors for evaluating the bands to determine EPDM/CR contentes

Parameter	EPDM A_{4330} (A)	CR A_{4595} (B)	EPDM/CR A_{4595}/A_{4330} (C)
	y = 0.0028x + 0.6698	y = 0.0003x - 0.0042	y = 0.0046x + 0.0067
R	0.980	0.977	0.945
R^2	~96 %	~96 %	~89 %
Methodology error (%)	2.31	9.09	7.14
Mean Standard Deviation	0.016	0.001	0.001

Source: prepared by the author (2024)

The median absorbance values of the EPDM analytical band A_{4330} of the transflectance (NIRA) methodology were inserted to determine the EPDM/CR contents. The data were adequate for the nine samples analyzed. Only for the sample with 80% EPDM content, there was a decrease in the median value. This may occur either because this sample does not really have this content, since it was not measured by another technique, its nominal value was used, or because of deviation from the Lambert-Beer law, showing evidence of a quantification limit for this content measured by the band at 4330 cm^{-1}-.The methodological error of 2.31% is close to the reference error, equipment precision limit, ≤ 2%, (HÓRAK; VÍTEK, 1978), for ideal thickness control conditions.

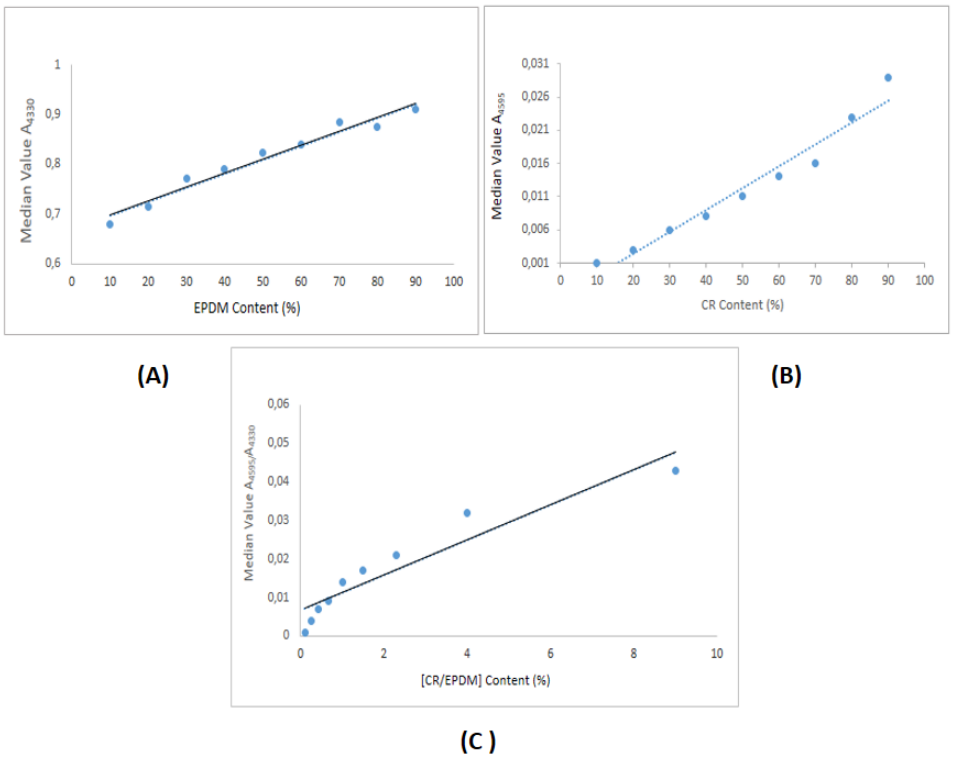
The median value of the absorbance of the analytical band A_{4595} versus the CR content (x) in [EPDM]/[CR]. An adequate correlation of data was observed (R = 0.977), and approximately 96% (R2)

of the data obtained were explained by this methodology. In an attempt to find an improvement in the precision of the methodology, the relative band resource was used, using the absorption at 4595 cm^{-1} for CR and applying the best band found for EPDM, at 4330 cm^{-1}. The name of the blend, due to the use of the relative band of CR and EPDM, A_{4595}/A_{4330}, was considered as CR/EPDM for both the title of Table 1 and for Figure 1, which takes into account the relative content of CR/EPDM.

The data related to the use of the relative band A_{4595}/A_{4330} were not entirely satisfactory regarding relative errors, however, it presented a smaller methodological error, around 7.0%, than that found using only the analytical band, A_{4595}, which generated around 9.0%. As already explained, this result may be due to factors related to the overlapping of EPDM and CR bands in the analyzed region, and to the weak intensity of the NIR band of CR combination. Thus, the errors increase significantly, progressively, suggesting a quantification limit for low CR contents, starting at 40%.

In **Figure 1,** the FT-IR calibration curves (A_{4595}/A_{4330}), (A_{4595}) and (A_{4330}) NIRA/Bunsen burner pyrolysis for the determination of CR and EPDM contents were shown.

Figure 1. Comparison of data from FT-IR/NIRA(A_{4595}/A_{4330}) calibration curves versus relative concentration CR/EPDM, EPDM (A_{4330}) and CR (A_{4595})



Source: prepared by the author (2024)

Discussion

Analyzing Table 1, it is possible to observe that the EPDM band can be considered as analytical, for the determination of its content in the EPDM/CR blend, the band at 4330 cm^{-1} is adequate, due to the error of the methodology (2.31%) being closer to the reference error, in the MIR region, ≤ 2%

(HÓRAK; VÍTEK, 1978). Therefore, it was considered in the evaluation of the relative band, for the determination of CR and EPDM. It should also be noted that the errors relative to the band for the determination of EPDM were smaller than the error found in the NIR region, for different systems, around 4% (CARVALHO et al., 2021) and closer to the reference value under ideal conditions, ≤ 2% (HÓRAK; VÍTEK, 1978). Regarding the determination of CR, by means of analytical or relative band, the first (A_{4595}) showed a more linear calibration curve (already presented in Figure 1), with more data explained by the developed methodology. The low intensity of the CR band may contribute to the inaccuracy of the measurements, especially for low CR contents, even suggesting a quantification limit of around 40% of this elastomer in the EPDM/CR blend, by the developed NIRA methodology.

Conclusion

The NIRA analytical band (4330 cm^{-1}) was analyzed to determine the EPDM content in EPDM/CR blends, which showed good results, with a methodology error of around 2%, lower than that found in NIR methodologies of different systems (4%). in terms of linearity of the curve R = (0.980) and data explained by this methodology 96% (R^2). in addition to the lowest methodology error, 2.31%, being considered the most suitable for this type of determination.

To determine the CR content, the analytical band A_{4595} was chosen. Although the methodological error was considered high, around 9%, probably due to the overlap of bands with the EPDM bands and/or the low intensity of the CR band, the calibration curve data presented good results in terms of linearity of the curve R= (0.977) and data explained by this methodology 96% (R^2). With the use of relative band, A_{4595}/A_{4330}, the methodological error dropped to 7%, but the relative errors remained high, suggesting a quantification limit for low CR contents, starting from 40%.

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