Determination of Polychloroprene Content in Rubber Blend Containing Ethylene Propylene Diene Monomer by Infrared Techniques

Paulo Santos Rigoli[1,2], Alexandra Helena de Barros[1], Rachel Farias Magalhães[1], Lidia Mattos Silva Murakami[3], Alexandre Estevão Carrara[1,*], Jorge Carlos Narciso Dutra[1], Elizabeth da Costa Mattos[1,4], Rita de Cássia Lazzarini Dutra[1]

1. Departamento de Ciência e Tecnologia Aeroespacial – Instituto Tecnológico de Aeronáutica – Divisão de Ciências Fundamentais – São José dos Campos/SP – Brazil. **2.** Departamento de Ciência e Tecnologia Aeroespacial – Instituto de Aeronáutica e Espaço – Divisão de Gerenciamento de Projetos – São José dos Campos/SP – Brazil. **3.** Tenneco Automotive Brasil – Setor de Engenharia de Desenvolvimento – Cotia/SP – Brazil. **4.** Departamento de Ciência e Tecnologia Aeroespacial – Instituto de Aeronáutica e Espaço – Divisão de Propulsão – São José dos Campos/SP – Brazil.

*Corresponding author: alexandre.ecarrara@gmail.com

ABSTRACT

Ethylene propylene diene monomer rubber is used as flexible thermal protection for rocket engines, as well as in blends with polychloroprene, which can be applied in the aeronautical sector, and with great potential in the defense sector. However, there is not a considerable number of studies considering both polymers as a blend. In general, elastomer content quantification in blends is done by more complex instrumental methods. When performed by Fourier transform-infrared spectroscopy, the conventional transmission mode is used, usually without including the developed methodology error. Therefore, the Fourier transform infrared spectroscopy (FT-IR) methodology is proposed using the universal attenuated total reflection mode, with sample treatment (pyrolysis) to determine polychloroprene content in the mixture with ethylene propylene diene monomer. In accordance with the infrared spectrometer precision limits and rubber blends studies data found in the literature, the methodology error analysis shows a value close to 2%. In addition, it has the advantage of being a less complex methodology. This actual study uses a simple FT-IR analytical tool, scarce, especially for the rubber research community, to determine the content of rubber minor phase within the major phase. It is valuable in weapons reverse engineering, aiming at the knowledge of new thermal protections.

Keywords: Blend; CR; EPDM; FT-IR; Transmission; UATR.

INTRODUCTION

In the aerospace sector, ethylene propylene diene monomer (EPDM) has been used in the search for a high-performance formulation. The use of EPDM in flexible thermal protection (TPS) for rocket engines has become an interesting alternative in relation to acrylonitrile-butadiene copolymer (NBR). Although NBR is more commonly used, the study of EPDM is aroused by some of its properties, such as low density, low processing cost and no release of toxic products during burning (Moraes *et al.* 2007).

It is known that structure and property relationship is crucial for different applications. Ethylene propylene diene monomer, for example, which has a saturated carbon-carbon "backbone", is nonpolar and has excellent resistance to oxygen, ozone, heat, as well as UV light. It also has excellent electrical resistivity and resistance to polar solvents. For this reason, it has wide application in electrical insulation, construction and automotive industry (Murakami *et al.* 2018).

Due to its importance, a significant number of papers on EPDM have been carried out in several fields (Miguel *et al.* 2020; George *et al.* 2020; Rigoli *et al.* 2019; Murakami *et al.* 2018; Choi and Kim 2011). Even though it shows adherence issues, plasma treatments, among others, can solve these difficulties, allowing EPDM applications, such as thermal protections, in the aerospace industry (Santos *et al.* 2014; Moraes *et al.* 2007).

It is also known that polymer blends are an alternative for obtaining materials with properties that, generally, are not found in a single material (Luna *et al.* 2015). The great advantage of mixing two elastomers is to try to minimize some negative characteristic or to optimize one of the qualities of the constituents.

Another reason for elastomer blends manufacture is the economic factor, since appreciable price difference exist between different rubbers (Ahmed *et al.* 2012). For example, the price of polychloroprene (CR) is high but its resistance to ozone is excellent. Therefore, blending CR with cheaper rubber is usually in practice for different applications.

Thus, elastomers mixtures are often used in the rubber industry, aiming to obtain well-balanced physical and mechanical properties, easy processability and relatively low production cost. It has been reported in the literature that rubber mixtures that have differences in polarity are very useful for obtaining a high compatibility degree, due to their well-defined interface (Rigoli *et al.* 2019; Chowdhury *et al.* 2016; Ding *et al.* 2015; Ahmed *et al.* 2012; Babbit 1978).

In this scenario, so that at least one of the characteristics is outlined or improved such as EPDM low adhesion, there is fundamental importance in studying and analyzing EPDM with CR (Fulin *et al.* 2007). With the inclusion of CR in the blend (from 15 to 20 phr) this problem tends to be overcome (Grison 2010).

On the other hand, CR with EPDM mixtures can improve the processability of CR and physicomechanical property of its vulcanizate (Fulin *et al.* 2007). Blend property depends on its ratio, among others. To improve CR processability, in the CR/EPDM blend, the usual ratio is from 90/10 to 70/30. Then, it is important to know the blend components content to predict its property.

These mixtures can be used, for example, in the automotive industry (Xu 2012). According to Ding *et al.* (2017), the combination of polychloroprene characteristics with those of ethylene-propylene-diene elastomer indicates a great potential for this blend application in various industrial and commercial areas.

As reported in these studies, the influence of both CR and EPDM elastomers content on the properties of their blends motivates quantitative study of these systems. However, there is not a satisfactory variety of published papers with qualitative analysis and even less with quantitative analysis on binary elastomer mixtures related to the EPDM/CR blend. Nevertheless, there are some studies on additives with the purpose to improve certain properties of this blend. Brotos and Moustafa (2002, 2003) characterized compatibilizers in order to improve the mixture properties, such as morphology and compatibility of the base elastomers.

Polychloroprene content effect in EPDM/CR blend was studied in a system containing cheaper additive in the formulation, such as Marble Sludge (MS) (Ahmed *et al.* 2012). It is exposed that MS powder can be used as a cheaper filler in EPDM/CR blends for the low cost of the final product. Marble Sludge filled EPDM/CR blends tend to reduce some properties, such as elongation at break, resilience, abrasion loss, among others. In contrast, it shows the opposite trend for scorch time, cure time, tensile strength, hardness values, for example, when increasing CR content in MS filled EPDM/CR blends.

Despite CR content determination was not the focus of the research, Ahmed *et al.* (2012) evaluated the influence of CR content in EPDM/CR blends. This fact imposes that the development of a faster and more accurate methodology continues to be necessary for the study of EPDM/CR-based polymers. Fourier transform infrared spectroscopy (FT-IR) analysis in different regions can support this type of research.

Although infrared spectroscopy (IR spectroscopy) was applied as an auxiliary method for EPDM/CR mixtures morphology, miscibility and physical properties analysis in Dubey *et al.* (2008) study, nondetailed IR method was used to evaluate the mixture composition characteristics. Using the absorption band related to the C-Cl bond at 650 cm^{-1} with the relative band concept, CR content was estimated with good approximation to the expected value. Fundamental information about the methodology error was not included in the discussion about calculations precision.

On the other hand, papers on rubbers characterization and quantification using instrumental methods and their couplings, such as thermal analysis, chromatography, mass spectrometry, generating a more robust methodology, but also more complex, can be found in the literature (Harada 2015). However, IR spectroscopy has shown satisfactory results in quantifying elastomer content in different elastomeric blends (Riba *et al.* 2019; Rigoli *et al.* 2019; Azevedo *et al.* 2018).

In general, it can also be noted that elastomers binary mixture quantitative FT-IR analysis uses spectra obtaining conventional mode, transmission, or even reflection by attenuated total reflection (ATR) (Riba *et al.* 2019). In spite of this, analysis condition details, such as sample preparation (treatment) or in ATR analysis case, the crystal type and analysis angle employed, number of analytical bands height or intensity measurements repetitions, as well as the developed methodology error, are usually not mentioned or are not properly explored.

In a recent research by Riba *et al.* (2019), a method using differential scanning calorimetry (DSC) was developed. It is based on a multivariate chemometric approach, compared to data obtained by FT-IR/ATR, by using algorithms to determine natural rubber (NR) and styrene butadiene rubber (SBR) blends content. However, in some cases where there are no bands overlapping and the absorption intensity increase is clearly related to concentration increase, chemometrics application is not needed (Mello *et al.* 2018).

The methodology error in Riba *et al.* (2019) was estimated in 2%. Although good results have been presented, a complex methodology was used to determine the rubber blend content and methodology error.

The last decades show a growing interest of the technological and scientific communities in polymer blend. This scenario is combined with the fact that sectors that are growing the most in this field are: automotive, electronics, packaging, construction, utensils, aeronautics and aerospace, encompassing very distinct characteristics. Therefore, this paper proposes a more modern quantitative FT-IR reflection methodology, universal attenuated total reflection (UATR), in comparison with transmission mode. While it discusses methodological errors, it purposes to minimize gaps observed in the existing methodologies developed for elastomeric systems quantification.

Good results were obtained by the simple proposed methodology in this actual paper, using UATR, showing good precision, confirmed by the analysis of test samples.

MATERIAL AND METHODS

Formulation preparation method

The EPDM/CR samples, formulation found in Table 1, were gently prepared and provided by Tenneco Automotive Brazil. Tenneco, an American company, is one of the largest manufacturers and suppliers of emission control systems, components for the suspension set, bushings, engine and transmission cushions, in addition to technical rubber metal parts for original equipment and aftermarket for the automotive industry.

Table 1. EPDM/CR formulation (90/10; 70/30; 50/50; 30/70 e 10/90).

Components	Content (mass %)
EPDM Keltan 6950 (ET: 48% e ENB: 7.5%)	56.3; 43.8; 31.3; 18.8 e 6.3
Polychloroprene (Neoprene W)	6.3; 18.8; 31.3; 43.8 e 56.3
Naphthenic Oil NH-140 (plasticizer)	14.1
Carbon black N550 (charge)	19.7
Stearic acid (activator)	0.6
Zinc oxide (activator)	1.1
6PPD (antioxidant)	0.4
Sulfur (vulcanizing agent)	0.5
TMTD (activator)	1.1

The processing took place with piston pressure of 4 kgf/cm², rotation of 70 rpm and initial temperature of 40 °C. Initially, all components were added in the mixer, except for sulfur and accelerators. After mixture homogenization, these additives were introduced. Four steps were taken: step 1 – mixture of elastomers – 35 s; step 2 – mixture of carbon black and additives – 70 s; step 3 – mixture of accelerators and sulfur – 30 s; step 4 – homogenization and cooling of compound in the cylinder – 120 s.

The vulcanization process of all EPDM/CR blends samples was set with a 7.5 kgf/cm² vulcanization press of steam for 6 minutes and closing pressure of 150 kgf/cm². Finally, samples were produced with the aid of roller cylinders in order to make samples approximately 10 cm long by 10 cm wide and 2 mm thick.

Fourier transform infrared spectroscopy methodology

In this topic, the methodologies developed for EPDM/CR blends characterization and quantification were described.

The following conditions were applied: FT-IR PerkinElmer spectrometer, Spectrum One model, spectral range from 4000 to 550 cm^{-1} [middle infrared region (MIR)], resolution of 4 cm^{-1}, 20 scans. The applied spectra obtaining modes were reflection, by UATR (80N), as well as transmission. The samples were prepared in the form of liquid pyrolysates, obtained by Bunsen burner, constituting liquid films.

Figure 1 shows a diagram that summarizes the FT-IR developed methodology, including the preparation technique and the ways of obtaining spectra that were employed.
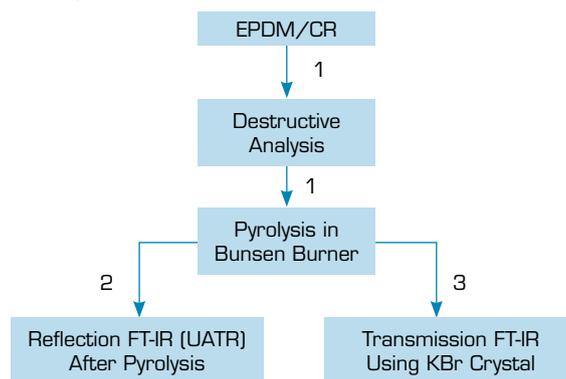

Figure 1. FT-IR qualitative analysis diagram of EPDM/CR samples, according to the developed methodology.

1. EPDM/CR blend was analyzed only using destructive technique to prepare samples, in this case, pyrolysis in Bunsen burner;
2. After treatment by pyrolysis, EPDM/CR samples were analyzed by UATR, a reflection technique; or
3. EPDM/CR samples were analyzed by transmission technique using potassium bromide (KBr) crystal or window.

Since pyrolysis is thermal degradation, the basic procedure consists of heating about 0.5 g of minced rubber sample. The sample is placed in a pyrolysis tube, similar to a thick-walled test tube. The rubber is heated in Bunsen burner to form a liquid product, the pyrolysate, which is collected in a KBr window. Another KBr window is placed on top in order to form a liquid capillary film, where the film thickness is defined. Then the film is analyzed by transmission (conventional way of obtaining IR spectra, where the IR ray passes through the sample, as a whole, revealing species in greater proportion; in the case of rubber, the base polymer, separated by pyrolysis). The liquid film pyrolysate was analyzed directly by reflection (UATR), also revealing the rubber base polymer.

Qualitatively, the materials were characterized by means of the characteristic bands of each elastomer. In other words, bands that define the characteristic functional groups were compared with the literature, according to Wake *et al.* (1983), and a reference spectra collection, so as to confirm what elastomer was involved.

As it is known, Lambert-Beer law (Smith 1979) governs the quantitative analysis in the infrared. It relates the height (intensity) of an analytical band, that is, to which one wants to determine the content of the corresponding functional group, to its content. The thickness control is important for the adequate measurement of the band intensity (height). In transmission experiments, this control can be done through the relative band.

A relative band is composed of an analytical band and a reference band to eliminate sample thickness variation interference, which can cause errors in the band intensity measurement.

Given that the CR pyrolysates spectra show bands of variable intensity (Wake *et al*. 1983), the challenge for quantifying this mixture was choosing the proper band for this elastomer. According to Smith (1979), C-Cl bond presents itself as a weak band in the region of 560 to 830 cm^{-1} (υ_{C-Cl}). Thus, the analytical band was found at 814 cm^{-1} (υ_{C-Cl}). Regarding EPDM, the analytical band around 885 cm^{-1} was used [vinylidene angular deformation (ω)] for the transmission analysis with the relative band concept.

For the calculations, an already developed IR methodology was applied. This approach was also manipulated in several previous publications of the group, since Dutra *et al*. 1996 until Rigoli *et al*. 2019, and also used in other recent research (Ferreira *et al*. 2020). The error data was calculated according to nonparametric statistical methodology for IR spectroscopy, as described in Horák and Vítek (1978), following a basic sequence of steps (Fig. 2).
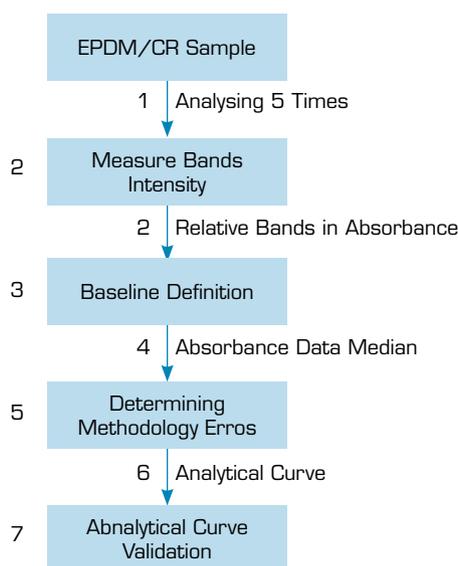

Figure 2. Fourier transform infrared spectroscopy quantitative analysis diagram of EPDM/CR samples, according to the developed methodology.

1. Analyze five times each sample which concentration is known;
2. Measure bands height or intensity (analytical and reference, which form relative bands) in absorbance;
3. Choose the best baseline;
4. Obtain the absorbance data median;
5. Calculate the errors involved in the methodology;
6. Elaborate calibration or analytical curve; and
7. Validate analytical curve when testing samples with unknown content, according to spectra obtaining mode and samples pretreating used, calculating the material content by means of the referred curve.

According to Horák and Vítek (1978), when there is a reduced number of experimental values, the median value ($\hat{\mu}$) should be used instead of the arithmetic mean. This way avoids the influence of values very different from others. Provided with such information, it is possible to calculate the methodology error or deviation with the following sequence: Eq. 1 (standard deviation), Eq. 2 (average standard deviation) and Eq. 3 (deviation or relative error).

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

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

$$RD = \left(\hat{\sigma}_{\hat{\mu}}/\hat{\mu}\right) \cdot 100 \tag{3}$$

where, R is the difference between the highest and the lowest absorbance values (x_n-x_1), K_R is the coefficient to calculate the standard deviation for 5 values ($K_R = 0.430$), $\hat{\sigma}$ is the standard deviation, n is the measurements number, $\hat{\sigma}_{\hat{\mu}}$ is the average standard deviation and RD is the relative error or deviation for each sample.

The methodology error is the median of the relative error (RD) calculated for each sample (Dutra *et al.* 1996; Ferreira *et al.* 2020). This variation is the limit allowed when measuring the analytical band intensity (height) of the same sample. It is associated to the spectrophotometer accuracy limit (Horák and Vítek 1978), under ideal conditions of thickness control ($\leq 2\%$).

RESULTS AND DISCUSSION

Characteristics of the two infrared techniques applied

In conventional transmission mode, infrared ray passes through the sample. As a result, it reveals species of both interior and surface, providing information especially of what is in higher content. In reflection mode, surface species are better detected. However, if they do not exist, the technique can also be used for the sample interior analysis (Azevedo *et al.* 2018; Smith 1979).

In the UATR technique, the IR beam passes through a reflection element. This element has a high refractive index, which consists of zinc selenide (ZnSe) covered with diamond, and reaches the sample surface (Magalhães *et al.* 2020).

There are differences regarding the optical path of the techniques. While in transmission, the optical path is constant for every wavenumber, in reflection the path can be variable. In spectrum regions where the sample weakly absorbs, the light penetrates deeper into the matrix, while the opposite happens where there is strong absorption (Ferrão 2001).

Therefore, in the comparison of spectra, obtained by transmission and reflection, it can be observed that the bands relative intensities are different. In other words, the weak bands in transmission spectrum appear stronger in the reflection mode (Ferrão 2001).

Universal attenuated total reflection technique allows an analysis of the sample as received, by means of a small quantity or with a minimum of sample preparation. However, one of the requirements of UATR reflection technique is the good contact between the crystal and the sample surface. Vulcanized rubbers are easily analyzed by UATR (Azevedo *et al.* 2018).

Because infrared ray does not penetrate deeply into the sample, UATR technique analyzes a very superficial layer of the sample, a few microns (Magalhães *et al.* 2020). Comparison of spectra and quantitative analyses need to be made under the same conditions, so becomes necessary to use the same torque to maintain pressure on the samples.

It is known that samples have to be prepared as thin films in order to measure their spectra in transmission (Magalhães *et al.* 2020; Smith 1979). There is no such limitation on measuring spectra by reflection.

Due to the differences presented between the two ways of obtaining spectra, it was decided to use these two techniques for EPDM/CR blend quantitative evaluation. In the transmission experiments, the relative band was used. Universal attenuated total reflection was performed without using relative band, most needed for thickness control in transmission analysis.

FT-IR/UATR analysis of EPDM/CR pyrolysates obtained in Bunsen burner

Figure 3 shows FT-IR (UATR) spectra obtained after EPDM/CR samples pyrolysis in Bunsen burner. From Fig. 3 analysis, it can be noted that C-Cl bands intensities around 814 cm^{-1} increased with the CR content in EPDM. In conformity with Lambert-Beer law, this behavior indicates that polychloroprene determination in the blend is possible by this band, even though according to Smith (1979), this band has weak intensity. In the UATR spectra, this band is better highlighted.

Thus, proceeding to the CR content determination in the blend (analytical band around 814 cm^{-1}), data for analytical curve elaboration, having A_{814} as a function of CR nominal content in the blend (Fig. 4), were calculated according to Eqs. 1-3 and displayed in Table 2.
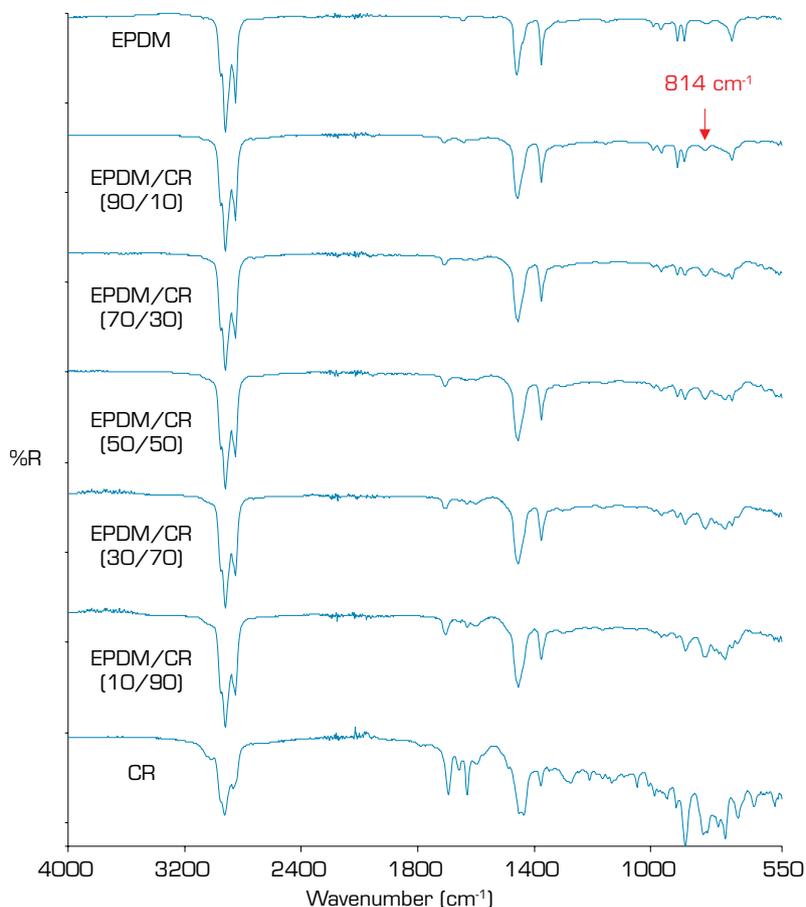

Figure 3. FT-IR/UATR spectra obtained after EPDM/CR blends pyrolysis in Bunsen burner with different contents, compared to EPDM and CR reference spectra.

The methodology error (relative errors median), 2.1%, indicated that the methodology is accurate, as it presented an error very close to the precision limit of the equipment, $\leq 2\%$ (Horák and Vítek 1978).

From Fig. 4 analysis, it can be noted that, on the analytical curve, the points satisfactorily approached the trend line ($R = 0.996$) with good linearity, $R^2 = 0.993$. In other words, about 99% of the obtained results were explained by this developed methodology. This confirmed the methodology accuracy for quantifying EPDM/CR mixtures, also noted by the methodology error mentioned previously. Thus, FT-IR (UATR) quantitative analysis after Bunsen burner pyrolysis for the EPDM/CR blend showed significantly accurate results.
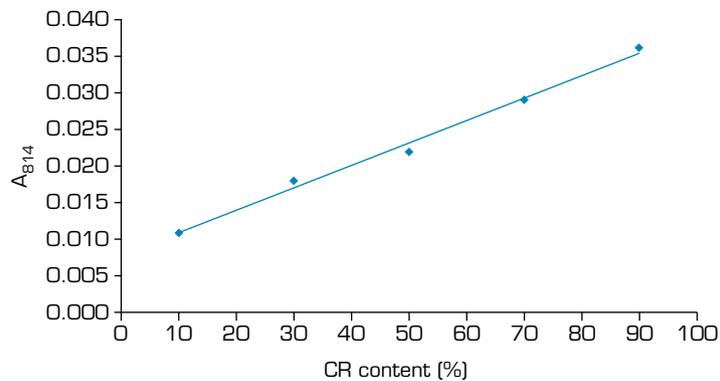
In sequence, in order to complete the quantitative process, analytical curve validation was performed by testing samples with unknown EPDM/CR proportions. This was justified, since UATR technique with sample treatment showed best results regarding methodology error, defining the best precision.

In this way, four samples were tested and identified as samples A, B, C and D (Tables 3-6). The samples were collected without the analyzer knowledge about each elastomer proportions in the samples.

Table 2. FT-IR (UATR) results after EPDM/CR samples pyrolysis in Bunsen burner.

EPDM/CR (%)	A_{814}	Parameters
90/10	0.010	$\hat{\mu} = 0.011$
	0.012	$R = 0.002$
	0.011	$\hat{\sigma} \approx 0.001$
	0.010	$\hat{\sigma}_{\hat{\mu}} \approx 0.0004$
	0.012	RD = 3.5%
70/30	0.018	$\hat{\mu} = 0.018$
	0.017	$R = 0.002$
	0.018	$\hat{\sigma} \approx 0.001$
	0.018	$\hat{\sigma}_{\hat{\mu}} \approx 0.0004$
	0.016	RD = 2.1%
50/50	0.024	$\hat{\mu} = 0.022$
	0.021	$R = 0.003$
	0.024	$\hat{\sigma} \approx 0.001$
	0.022	$\hat{\sigma}_{\hat{\mu}} \approx 0.001$
	0.022	RD = 2.6%
30/70	0.029	$\hat{\mu} = 0.029$
	0.029	$R = 0.002$
	0.029	$\hat{\sigma} \approx 0.001$
	0.029	$\hat{\sigma}_{\hat{\mu}} \approx 0.0004$
	0.027	RD = 1.3%
10/90	0.036	$\hat{\mu} = 0.036$
	0.036	$R = 0.004$
	0.033	$\hat{\sigma} \approx 0.002$
	0.037	$\hat{\sigma}_{\hat{\mu}} \approx 0.001$
	0.035	RD = 2.1%

Base line: 845 - 792 cm^{-1} - Analytical band: 814 cm^{-1}

Figure 4. FT-IR/UATR/pyrolysis in Bunsen burner analytical curve - band in function of CR content in EPDM/CR.

Each sample was analyzed five times (five aliquots) so that the median absorbance value (A), A_{814} (CR C-Cl band), of each sample could be inserted in the calibration curve equation (Eq. 4). These values were tested with the following equation:

$$y = 0.0003x + 0.0079 \tag{4}$$

where, y is the median absorbance, A_{814}, and x is the CR content in %.

Table 3. FT-IR/UATR/Bunsen burner pyrolysis analysis of EPDM/CR sample A.

A_{814} (5 measures)	Parameters	CR content – x (%)
0.014	$\hat{\mu}$ = 0.014	Applying Eq. 4:
0.014	R = 0.001	y = 0.014 → x = 20 %
0.015	$\hat{\sigma}$ ≈ 0.0004	
0.014	$\hat{\sigma}_{\hat{\mu}}$ ≈ 0.0002	Calculated CR content: 20%
0.014	RD = 1.3%	Calculated EPDM content: 80%

By applying Eq. 4 in sample A, it can be noted that the CR content value in the mixture was 20%. Consequently, the EPDM content was 80%, which indicates that this sample should have EPDM/CR in 80/20 ratio. This is the exact proportion informed by the sample supplier.

Table 4. FT-IR/UATR/Bunsen burner pyrolysis analysis of EPDM/CR sample B.

A_{814} (5 measures)	Parameters	CR content – x (%)
0.021	$\hat{\mu}$ = 0.020	Applying Equation 4:
0.020	R = 0.004	y = 0.020 → x ≈ 40 %
0.018	$\hat{\sigma}$ = 0.002	
0.020	$\hat{\sigma}_{\hat{\mu}}$ ≈ 0.001	Calculated CR content: 40%
0.022	RD = 38 %	Calculated EPDM content: 60%

In sample B, it can be noted that by applying Eq. 4, the value of "x" was very close to 40%, referring to the EPDM with CR mixture. This indicates that the sample should have EPDM/CR in the 60/40 ratio, which also represents the proportion reported by the sample supplier.

Table 5. FT-IR/UATR/Bunsen burner pyrolysis analysis of EPDM/CR sample C.

A_{814} (5 measures)	Parameters	CR content – x (%)
0.024	$\hat{\mu}$ = 0.024	Applying Eq. 4:
0.024	R = 0.001	y = 0.024 → x ≈ 54 %
0.024	$\hat{\sigma}$ ≈ 0.0004	
0.025	$\hat{\sigma}_{\hat{\mu}}$ ≈ 0.0002	Calculated CR content: 54%
0.024	RD = 0.8%	Calculated EPDM content: 46%

In sample C, 46/54 ratio was obtained by Eq. 4, approaching the sample supplier information, which is EPDM/CR in the 40/60 ratio.

Table 6. FT-IR/UATR/Bunsen burner pyrolysis analysis of EPDM/CR sample D.

A$_{814}$ (5 measures)	Parameters	CR content – x (%)
0.031	$\hat{\mu}$ = 0.032	Applying Equation 4:
0.032	R = 0.002	
0.033	$\hat{\sigma} \approx$ 0.001	y = 0.032 → x ≈ 80 %
0.033	$\hat{\sigma}_{\hat{\mu}} \approx$ 0.0004	Calculated CR content: 80 %
0.031	RD = 1.2%	Calculated EPDM content: 20 %

In this last unknown sample analysis, the given result by applying Eq. 4 indicated an EPDM/CR sample with 20/80 ratio. This result also matches the information reported by the supplier.

Fourier transform infrared spectroscopy transmission analysis of EPDM/CR pyrolysates obtained in Bunsen burner

Figure 5 shows FT-IR transmission spectra after pyrolysis of EPDM/CR samples in Bunsen burner.
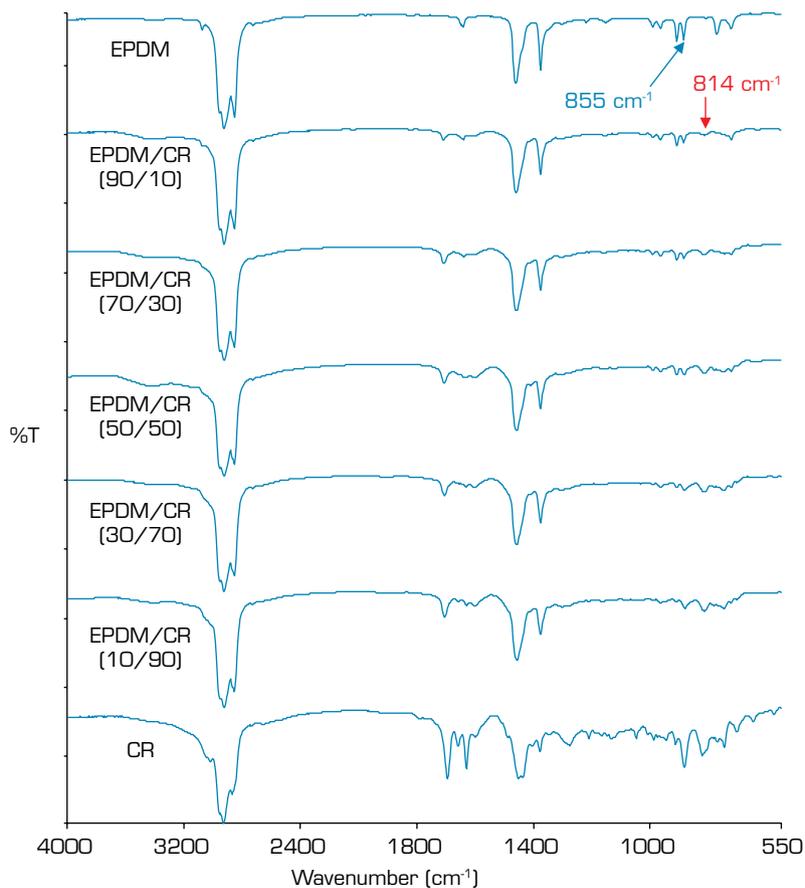

Figure 5. Fourier transform infrared spectroscopy transmission spectra obtained after EPDM/CR mixture pyrolysis in Bunsen burner with different contents, compared to both EPDM and CR reference spectra.

As in UATR methodology, although with less intensity, it can be seen in Fig. 5 that C-Cl bands intensities around 814 cm^{-1} increased with the CR content in the mixture. On the other hand, the 885 cm^{-1} intensity band, relative to the vinylidene group, decreases with the EPDM content.

For the CR content determination in the mixture, the bands around 814 and 885 cm^{-1} for the analysis and the relative band (A_{814}/A_{885}) were used in an attempt to avoid errors due to sample liquid film thickness variation. Data for elaboration of relative absorbance curve as a nominal CR content function in the blend were calculated and are presented in Table 7 (Fig. 6).

Table 7. Fourier transform infrared spectroscopy transmission results after EPDM/CR samples pyrolysis in Bunsen burner.

EPDM/CR (%)	A_{814}/A_{885}	Parameters
90/10	0.300	$\hat{\mu}$ = 0.450
	0.555	R = 0.255
	0.300	$\hat{\sigma}$ = 0.110
	0.473	$\hat{\sigma}_{\hat{\mu}}$ ≈ 0.049
	0.450	RD = 10.9%
70/30	0.720	$\hat{\mu}$ = 0.720
	0.739	R = 0.137
	0.613	$\hat{\sigma}$ = 0.059
	0.655	$\hat{\sigma}_{\hat{\mu}}$ = 0.026
	0.750	RD = 3.6%
50/50	0.893	$\hat{\mu}$ = 0.958
	0.958	R = 0.178
	0.950	$\hat{\sigma}$ = 0.076
	1.040	$\hat{\sigma}_{\hat{\mu}}$ = 0.034
	1.071	RD = 3.6%
30/70	1.167	$\hat{\mu}$ = 1.034
	1.034	R = 0.167
	1.062	$\hat{\sigma}$ = 0.072
	1.000	$\hat{\sigma}_{\hat{\mu}}$ = 0.032
	1.030	RD = 3.1%
10/90	1.172	$\hat{\mu}$ = 1.077
	1.077	R = 0.064
	1.114	$\hat{\sigma}$ = 0.027
	1.050	$\hat{\sigma}_{\hat{\mu}}$ = 0.012
	1.079	RD = 1.1 %

Base line: 845 - 792 cm^{-1} - Analytical band: 814 cm^{-1}; Base line: 898 - 845 cm^{-1} - Analytical band: 885 cm^{-1}

The methodology error calculation (relative errors median) resulted in 3.6%. This value indicates that the methodology was relatively accurate, as it presented an error just above the precision limit of the equipment, ≤ 2%. In this case, the errors presented higher values, as the absorbance values showed significant dispersion, probably due to the analytical band intensity not being as strong as in UATR analysis.

The error value (≤ 2%) is normally found in the literature for quantitative FT-IR studies, for liquids analysis, by transmission, in closed cell. In other conditions, in IR transmission analysis, with the samples prepared by pellet, for example, the error can reach up to 10% (Smith 1979), if there is no adequate thickness control. Transmission near infrared analysis (NIR) can show methodology errors up to around 4% (Vogelsanger *et al.* 2014).

As a consequence, the value (≤ 2%) should be used as a reference to find the best error in the developed methodology, according to the best analysis conditions available for the analyzed system. Comparatively, the methodology error obtained by UATR/pyrolysis (2.1%) was more adequate for the determination of CR in EPDM/CR.
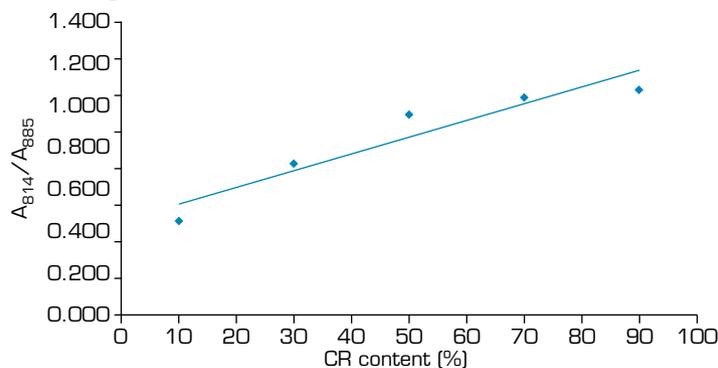

Figure 6. Fourier transform infrared spectroscopy/transmission/pyrolysis in Bunsen burner analytical curve – relative band (A_{814}/A_{885}) in function of CR content in EPDM/CR.

The calibration curve for transmission/pyrolysis in Bunsen burner methodology is described by Eq. 5.

$$y = 0.008x + 0.456 \tag{5}$$

where, y is the median absorbance A_{814}/A_{885} and x is the CR content in %.

From the analysis of Fig. 6, it can be noted that on the analytical curve the points were relatively close to the trend line (R = 0.947), with good linearity, $R^2 = 0.898$. This result means that about 89% of the obtained results were explained by the developed methodology. The results were satisfactory but not as the previous case, UATR analysis, which confirmed a lower transmission analysis precision of pyrolyzed samples, regarding EPDM/CR mixtures quantification.

Thus, FT-IR (UATR) quantitative analysis with treatment (pyrolysis) showed results significantly more accurate for EPDM/CR blend, even though relative band concept was applied in transmission methodology.

CONCLUSION

This study showed that FT-IR/UATR/Bunsen burner pyrolysis methodology reported the most accurate results (lowest relative error), confirmed by the test sample analysis. Conceptually, it is possible to state that this developed methodology, CR content in EPDM/CR blends, will contribute significantly with quantitative data obtained through IR spectrometry, so limited in the current scientific community.

Thus, it is highlighted that the methodology developed in this research will provide an important contribution to aerospace and defense material quality control. As the propellant in rocket engines is in contact with thermal protection, the methodology is interesting in the investigation of pieces of propellant adhered to the thermal protection. In parallel, it can also give evidence of proprietary formulations of protections using reverse engineering of unknown items.

TRENDS

Near infrared spectrum is composed with a lot of information, such as combination bands (sum or difference of MIR fundamental bands) and overtones (multiples of MIR fundamental bands). Both combination bands and overtones make it difficult to evaluate

the samples quality attributes through visual analysis. Therefore, statistical techniques, as well as spectrum processing, are applied in parallel to complement and enable a better spectrum analysis (Pissar *et al.* 2013). However, recent studies on polymers by near infrared reflectance analysis (NIRA) without chemometrics application have been successfully performed, because there was no band overlap (Mello *et al.* 2018; Azevedo *et al.* 2018; Magalhães *et al.* 2020). Therefore, it can be used for analysis of other polymers such as rubber blends and can be the subject of future papers.

AUTHOR'S CONTRIBUTION

Conceptualization: Rigoli PS; Dutra RCL and Mattos EC; **Methodology:** Rigoli PS;Dutra RCL and Mattos EC; **Investigation:** Rigoli PS; **Writing – Original Draft:** Rigoli PS; **Writing – Review & Editing:** Rigoli PS, Barros AH, Magalhães RF and Dutra RCL; **Funding Acquisition:** Dutra RCL; **Resources:** Murakami LMS; **Supervision:** Dutra RCL, Dutra JCN and Carrara AE.

DATA AVAILABILITY STATEMENT

All data sets were generated or analyzed in the current study.

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