Quantification of Aerospace Polymer Blends by Thermogravimetric Analysis and Infrared Spectrometry

Paulo Santos Rigoli[1]*, Lídia Mattos Silva Murakami[2], Milton Faria Diniz[3], Margarete Ferreira Prata Azevedo[3], Silvana Navarro Cassu[3], Elizabeth da Costa Mattos[3], Rita de Cássia Lazzarini Dutra[2]

Rigoli PS https://orcid.org/0000-0003-4291-2932

Murakami LMS https://orcid.org/0000-0003-2589-7769

Diniz MF https://orcid.org/0000-0003-0246-0660

Azevedo MFP https://orcid.org/0000-0003-1127-7032

Cassu SN https://orcid.org/0000-0002-6978-0266

Mattos EC https://orcid.org/0000-0002-9394-4910

Dutra RCL https://orcid.org/0000-0001-9958-1279

ABSTRACT: Ethylene-propylene-diene elastomer (EPDM) is employed as thermal insulation for rocket motors, as well as EPDM blends with ethylene vinyl acetate (EVA) have been used in the aerospace industry. The quantification of these blends is more common using Fourier Transform Infrared Spectrometry (FT-IR) by transmission mode, but without discussing sample preparation and methodology error. Considering this fact, a methodology was developed for determining EVA content in binary blend with EPDM samples, by Universal Attenuated Total Reflection (UATR) technique, associated to thermogravimetric analysis (TGA). This last one, it was applied to determine Vinyl Acetate (VA) content in EVA and to identify differences between EPDM/EVA blends. Samples of the analyzed blends showed two VA contents and five proportions of EPDM/EVA: 90/10, 70/30, 50/50, 30/70, and 10/90. The carbonyl stretching vibration band C=O at 1740 cm^{-1} was used as analytical band in FT-IR quantification. Finally, the results presented excellent accuracy with a good linear correlation coefficient (R > 0.940) and with relative error values lower than 2%, respecting the precision limits of the FT-IR spectrometer.

KEYWORDS: EPDM, EVA, FT-IR, Quantification, TGA.

INTRODUCTION

Several elastomers are common in industrial sectors such as aeronautics, space and defense. Seeking for high performance formulation, acrylonitrile-butadiene rubber (NBR), in addition to ethylene-propylene rubber (EPR) and ethylene-propylene-diene monomer (EPDM), are widely employed. It's known that the use of EPDM as thermal insulation in rocket motors has become a good alternative comparing to NBR, because of some properties such as low density, low processing cost, and no toxic products during burning (Dutra *et al.* 2006).

1.Departamento de Ciência e Tecnologia Aeroespacial – Instituto de Aeronáutica e Espaço – Divisão de Sistemas de Defesa – São José dos Campos/SP – Brazil.
2.Departamento de Ciência e Tecnologia Aeroespacial – Instituto Tecnológico de Aeronáutica – Divisão de Ciências Fundamentais – São José dos Campos/SP – Brazil.
3.Departamento de Ciência e Tecnologia Aeroespacial – Instituto de Aeronáutica e Espaço – Divisão de Propulsão – São José dos Campos/SP – Brazil.

*__Correspondence author:__ psrigoli@gmail.com

In addition, EPDM is also employed in other industrial sectors because it shows excellent properties like mechanical resistance, high temperature resistance, aging, and oxidation resistance, and allows incorporation of loads and plasticizers easily, showing a facilitated processing as well (Lanxess Rubber 2012).

The well-known relation structure-property is determinant to different applications. EPDM rubber has saturated structure of carbon-carbon and it's a non-polar polymer that has an excellent resistance against oxygen, ozone, heat and UV radiation, moreover, it has a good electrical resistivity and good resistance to polar solvents. Therefore, it has wide application in electrical insulation, construction and automotive industry. Due to its importance, a significant number of EPDM studies have been carried out in several areas (Choi and Kim 2011). On the other hand, it presents problem of adhesion, but treatment with plasma can overcome that difficulty, allowing applications of EPDM as thermal insulation in the aerospace industry (Dutra *et al.* 2006).

Elastomer blends are often used in the rubber industry to obtain balanced physical and mechanical properties, easy processability and relative low manufacturing cost. It has been reported in the literature that rubber blends with different polarities are very useful to achieve a high degree of conductivity, because of their well-defined interface (Ding *et al.* 2015).

There are many binary blends with EPDM. It's possible to cite as example, the binary blend of EPDM with chloroprene rubber (CR) or 2-chlorobuta-1,3-diene (Fulin *et al.* 2007), with NBR (Ding *et al.* 2015; Babbit 1978) and with ethylene vinyl acetate copolymer – EVA (Azevedo *et al.* 2009; Chowdhury *et al.* 2016; Babbit 1978).

EPDM/CR blends can improve the CR processability and vulcanizate physicochemical properties, generally from 10/90 to 30/70 ratio, moreover, the addition of CR tends to improve the adhesion to metal (Fulin *et al.* 2007).

As mentioned before, EPDM is a saturated non-polar rubber, but NBR contain polar groups $C \equiv N$ that improve the cohesive energy density among the chains. So, the selective distribution of conductive charges may also be a differential in EPDM/NBR blend to prepare a highly conductive rubber (Ding *et al.* 2015).

EPDM/EVA blends are considered interesting polymeric foams nowadays, because they have several applications, mainly due to their technical and commercial advantages. EPDM is a good alternative to be used with EVA for creating foams, since this last one provides low polarity, good compatibility with polyolefinic materials, and improve impact properties. Thus, foams are widely applied where lightness, softness, impact absorption properties and noise are required. According to these characteristics, foams are being extensively used in the aeronautics and automotive industry, sports equipment, footwear, toys, furniture, packaging and other applications (Azevedo *et al.* 2009).

The elastic feature from amorphous copolymers transferred to some compound or product can also be achieved with EVA containing higher vinyl acetate (VA) content. Obviously, EVA with higher VA content must be less crystalline (Azevedo *et al.* 2009).

However, Chowdhury *et al.* (2016) cite that in order to combine good properties, few EPDM/EVA blends have been prepared and studied, moreover, in a huge number of researches, these materials are made from just one type of EVA with only one specific VA content. Because of that, there is a lack related to distinguish blends by their contents, including measurement errors. Hence, determination of VA content in EVA and EVA content in EPDM represent important contributions to the scientific and technological communities, since those contents have different properties.

Considering only EVA copolymer, French *et al.* (1974) developed a methodology to determine VA content in EVA, comparing Attenuated Total Reflection (ATR) technique and transmission mode. They presented a method from baseline to calculate band intensity, but without details describing the method. In that paper, they commented about standard deviation in VA determination, but again, with no details.

Another quantitative methodology was developed by Higgins and Rein (2011). They used single reflection Diamond ATR (could be UATR) to measure styrene content in SBR and the ratio of ethylene to vinyl acetate in EVA copolymer. In that paper, they used a contemporary technique, but applied directly the software (MicroLab) from the equipment, with no details about how they calculated band intensity (median absorbance value or area method). In addition, they didn't comment about the methodology deviation. Regarding VA content determination in EVA, a methodology was developed in IAE (Instituto de Aeronáutica e Espaço) laboratory's, as well as vinyl mercaptoacetate (VMA) content determination in one of its derivatives, poly(ethylene-co-vinyl alcohol-co-vinyl mercaptoacetate) (EVALSH), by thermogravimetric analysis (TGA) and FT-IR-transmission technique. A calibration or analytical curve with the relative absorbance values (A_{1736}/A_{720}) versus esterification degree in EVALSH

samples determined by TGA showed a good linear relationship (Dutra *et al.* 1996). A similar methodology was employed to quantify EVA samples with different VA contents in EPDM blends, but by UATR technique, including analyzes about methodology errors.

There are some methodologies in the literature that use FT-IR when talking about quantitative analysis of binary elastomer blends. Usually, the transmission method is employed to obtain spectra. However, data such as sample treatment, number of repetitions, and methodology error are usually not cited.

D'Amelia *et al.* (2016) elaborated a quantitative experiment to determine the percent composition of VA in copolymers and blends with polyethylene (PE) and n-ninyl pyrrolidone (PVP). However, they used ATR and the data was analyzed using the Brucker OPUS® software. Their methodology considered area method to calculate band intensity, which can present some problems, such as influence of the neighbor bands. Unfortunately, as usual, they didn't give attention to the errors from their methodology.

There are a few papers describing methods to determine VA content in EVA, but this paper seeks to present a methodology to determine EVA content in EPDM/EVA blend, with two different VA contents.

Thus, considering a scenario that focus three points: a) the interest in polymer blends has been increasing during the last decades, especially in aeronautical, automotive, electronics, packaging, construction and household items (Luna *et al.* 2015), encompassing very distinct characteristics; b) there aren't many studies about VA content in EPDM/EVA blends, but functional groups determination has an extreme importance in polymers which belong to an elastomeric composition with specific properties; c) there are scientific lacks about contemporary FT-IR techniques. In this case, for blends quantification, as well as evaluation of methodology errors, this work proposes the characterization and quantification of EVA with two VA contents in EPDM blends, using non-conventional and more contemporary FT-IR reflection technique, such as UATR in association with TGA, besides evaluating the advantages of the new methodology, time analysis and its errors, establishing their accuracy at the end.

MATERIALS AND METHODS
MATERIALS

EPDM/EVA samples were kindly prepared and supplied by Tenneco. The components were weighed on an analytical scale and kept in closed containers. A roller mixer with 150 mm diameter and 350 mm length of Copé brand was used to prepare the blends. The temperature employed in the mixer was 90 °C, it was enough to plasticize EVA and to produce a steady blend with the other components. EPDM was added to the previous mixture after EVA plastification. In sequence, the inorganic additives were added until complete homogenization. After that, dicumyl peroxide and azodicarbonamide were added. At this stage, the mixing time did not exceed 5 min, avoiding the rubber crosslinking. After mixing, the materials were cut, cooled and separated until achieving room temperature.

The Copé hydraulic press was used for crosslinking at a temperature of 160 °C by electric heating and pressure of 60 kgf/cm². The pressing time determination was ensured using the rheometric curves from the Alpha Technologies rheometer, model MDR 2000. Determination tests were performed at the temperature of 160 °C for 10 min in EVA and EPDM.

Two types of EPDM/EVA blend were used, containing two different VA contents, but with the VA content undefined by the supplier. The blends samples contained five EPDM/EVA ratios (10/90, 30/70, 50/50, 70/30, and 90/10), according to supplier information. EVA samples with different VA contents were coded with the value in brackets, for example, EVA(x), where x represents the VA content in EVA.

METHODOLOGY

In Fig. 1 it's shown the TGA/FT-IR(UATR) off-line coupling methodology developed to quantify EVA in EPDM/EVA blends. The next items detail the conditions used and follow some steps as represented in Fig. 1.

1. Determine VA content in EVA samples by TGA;
2. Distinguish EPDM/EVA blends, comparing their mass losses (TGA);
3. Quantify EVA in EPDM/EVA blends by FT-IR(UATR) using C=O band:
   a. Calculate the methodology deviation (FT-IR);
   b. Elaborate analytical curves to obtain the equations and determine EVA content in EPDM/EVA blend (FT-IR);
   c. Verify analytical curves or calibration curves using the equations obtained for EPDM/EVA unknown samples (FT-IR). This last step confirms the precision of the methodology.
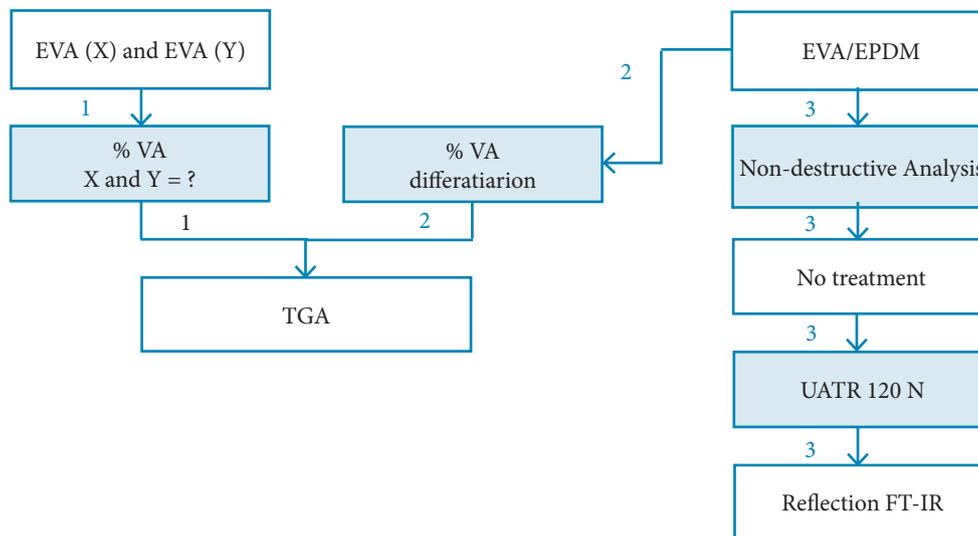

Figure 1. TGA/FT-IR(UATR) methodology analysis diagram.

TGA ANALYSIS

Thermogravimetry is a thermal analysis technique in which mass variation is determined as a function of temperature or time or both. In this technique, the material of interest is put into an oven with controlled atmosphere, with temperature variation or a selected temperature for a determined time. The entire process has mass variation monitored by the scale (Hale and Bair 1997).

The equipment used was the simultaneous thermal analyzer DSC/TGA, SDT Q600, TA Instruments. In this work, the samples had about 10 mg and they were analyzed two or three times, in nitrogen atmosphere, with a thermal range from 20 °C to 650 °C, and temperature-time rate of 10 °C/min.

FT-IR (UATR) ANALYSIS

FT-IR spectrometry measures the transmitted or incident energy at a defined number or wavelength (Smith 1979) by different ways of obtaining spectra, among them, the conventional one by transmission, where the radiation crosses the sample and provides the surface and inner species composition, emphasizing which is in greater proportion. More contemporary reflection techniques could be also employed. UATR technique shows good results for polymers quantitative analysis by absorption intensity measurements (Mello *et al.* 2017; Rodrigues *et al.* 2014).

Infrared spectrometry analyses were performed with a Spectrum One Perkin-Elmer spectrometer (spectral range from 4000 to 550 cm^{-1}, resolution 4 cm^{-1} and 20 scans), utilizing UATR accessory with 120 N force on the sample without treatment. The analytical band at 1740 cm^{-1} ($\upsilon_{C=O}$) was used to analyze a specific behavior in EVA copolymer. It was established the baseline with the wavenumber range from 1830 to 1620 cm^{-1}. In analytical curves, each median value of the analytical band (A_{1740}) represents a median of 5 repetitions in each sample, trying not to exceed the relative error of 2%, which represents the equipment accuracy limit (Hórak and Vítek 1978).

The errors calculations were carried out according to the specialized literature in infrared spectrometry by Hórak and Vítek (1978), as previously adopted in other researches of the same group with success, involving quantitative FT-IR analysis (Mello *et al.* 2017; Rodrigues *et al.* 2014; Siqueira *et al.* 2008; Dutra *et al.* 1996, Dutra and Soares 1998).

In the quantitative analysis, the median value (μ) was obtained from the five intensity values from the analytical band. The mean standard deviation ($\hat{\sigma}_\mu$) was calculated according to Eqs. 1 and 2. The relative error or deviation (RD) could be calculated using Eq. 3, in sequence. In order to calculate the methodology error, it was adopted the median value from the relative errors, according to previous studies (Mello *et al.* 2017; Rodrigues *et al.* 2014; Siqueira *et al.* 2008; Dutra *et al.* 1996; Dutra and Soares 1998). where the number of measurements is represented by *n* in Eq. 1 and standard deviation ($\hat{\sigma}$) came from Eq. 2.

$$\hat{\sigma}_\mu = \hat{\sigma} / \sqrt{n} \tag{1}$$

where R represents the difference between absorbance extremes values ($x_n - x_1$), and K_R represents the coefficient to calculate

$$\hat{\sigma} = K_R . R \tag{2}$$

the standard deviation in a range of values. In this case, for five points or values, $K_R = 0.430$ (Hórak and Vítek 1978). The relative deviation for each analyzed sample was calculated using Eq. 3.

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

where RD represents the relative error or deviation, in percentage.

RESULTS

TGA ANALYSIS

First of all, thermogravimetry was used to determine the VA contents in the EVA samples and to aid the FT-IR quantitative methodology to distinguish the VA content of EVA in the EPDM/EVA blends, comparing samples mass losses.

VA Content Determination in EVA Samples

Figure 2 presents the results from TGA analysis to compare the EPDM and EVA mass loss levels, moreover, to determine VA content in two distinct EVA samples. It's important to emphasize that EPDM and EVA are neat in this step.
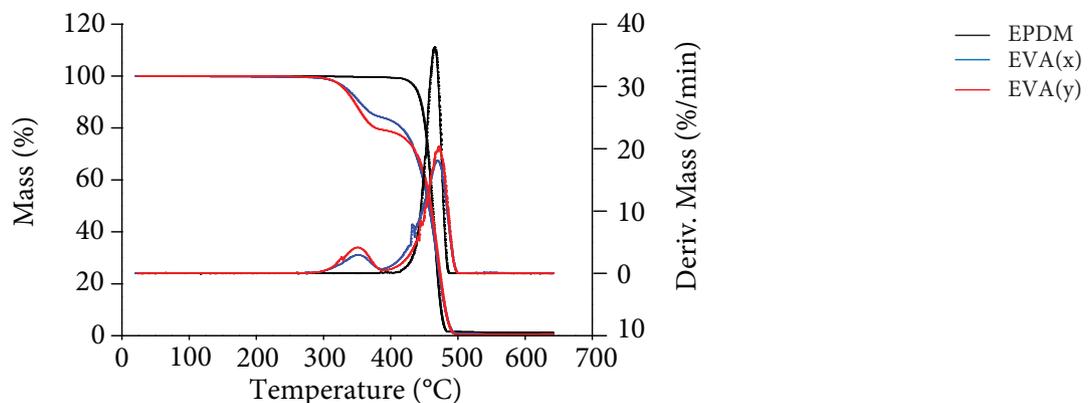

Figure 2. Thermal decomposition of EPDM, EVA(x) and EVA(y).

Figure 2 shows that neat EPDM presents thermal decomposition in only one stage, whereas neat EVA have two main stages, regardless of the VA content. This fact is confirmed with time derivative of mass curves.

It's known that the EPDM is an unsaturated hydrocarbon with non-polar character that has ethylene in its carbon chain. On the other hand, EVA has a polar character with ester function in its chain. During the EVA thermal decomposition in inert atmosphere, acetic acid was rapidly released at 350 °C, while the remainder was released at 430 °C (Hale and Bair 1997).

Therefore, VA content in EVA was determined by mass losses indicated in Fig. 2, resulting in x = 16% and y = 20%. So, there are two EVA samples (containing 16% VA and 20% VA), represented in this paper as EVA(16) and EVA(20).

Composition Analysis of EPDM/EVA blends by TGA

Table 1 shows the comparative results of EPDM/EVA blends thermal decomposition in five proportions (90/10, 70/30, 50/50, 30/70, 10/90), containing 16% and 20% of vinyl acetate. In Fig. 3 the blends thermal decomposition were compared containing EPDM/EVA(16) in 30/70 ratio and EPDM/EVA(20) in 30/70 ratio. It's noted that the blends thermal decomposition occurs in three stages. As mentioned before, this fact is also confirmed with time derivative of mass curves. The 3% mass loss obtained between 30 °C and 300 °C is related to the process additives employed in the rubber blends preparation, like azodicarbonamide, dicumyl peroxide, stearin, and calcium carbonate. The mass loss in temperature range from 300 °C to 380 °C is important, because it will be responsible for comparing blends.

Table 1. Thermal decomposition datasets from EPDM/EVA blends.

EPDM/EVA (%)	EVA (16)	EVA (20)
	Δm (%) (300 – 380 °C)	Δm (%) (30 – 380 °C)
90/10	1.5 ± 0.2	1.6 ± 0.1
70/30	3.2 ± 0.1	4.2 ± 0.1
50/50	5.3 ± 0.1	7.2 ± 0.1
30/70	7.7 ± 0.2	10.6 ± 0.1
10/90	9.4 ± 0.5	12.9 ± 0.2

Analyzing only the mass variation behavior from 300 °C to 380 °C relative to the release of acetic acid from EVA, observing the blends with 10% EVA (Table 1), it was noticed that there was almost no difference between the mass losses in blends containing EVA(16) and EVA(20), because EVA content was very low. For the other blends, the difference between the blends mass loss observed was higher, because those blends contained more than 10% EVA, allowing differentiating the EVA content present in the blends with EVA(16) and EVA(20). In Table 1, this tendency could be confirmed, because blends with EVA(20) presented higher mass losses compared to blends with EVA(16) with the same proportion, and it was expected due to higher VA content.
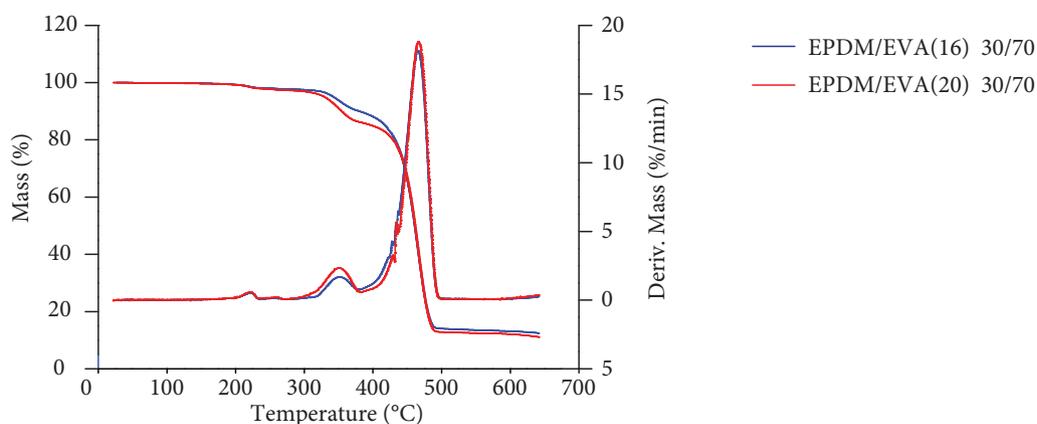

Figure 3. EPDM/EVA(16) mass loss: 7%; and EPDM/EVA(20) mass loss: 11%, on 30/70 proportion.

Moreover, for the same reason mentioned before, the higher EVA content in the blend, the greater mass loss. Therefore, it was possible to differentiate those blends using their VA contents.

FT-IR (UATR) ANALYSIS

EPDM/EVA Blends

Figures 4 and 5 show FT-IR(UATR) spectra of the EPDM/EVA(16) and EPDM/EVA(20) samples.
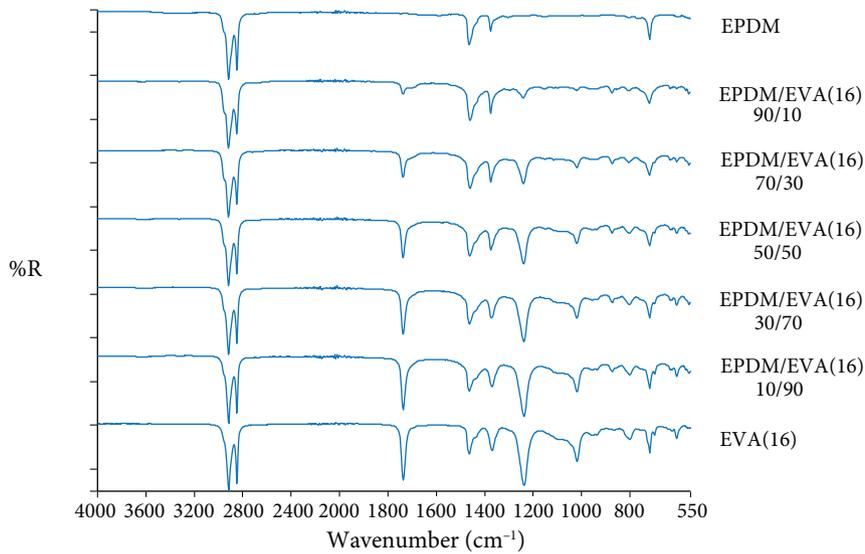

Figure 4. FT-IR (UATR 120N) spectra of EPDM/EVA(16) blend without treatment.
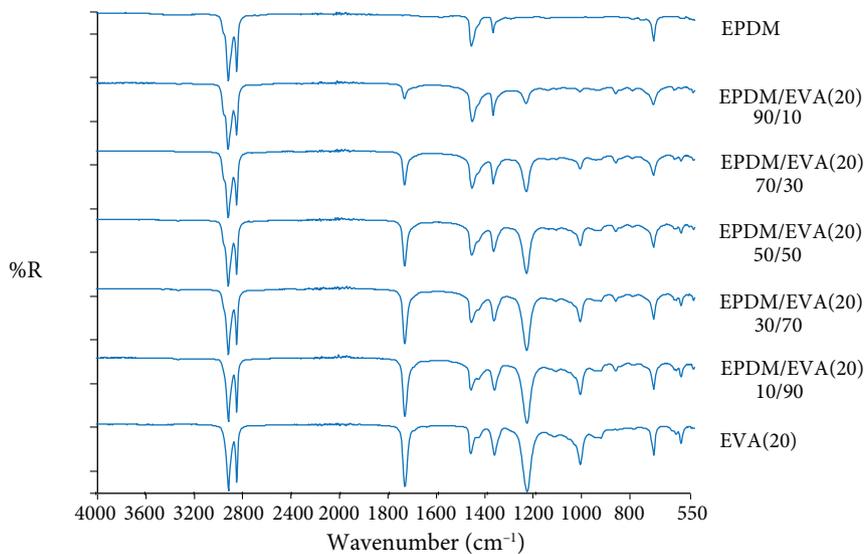

Figure 5. FT-IR (UATR 120N) spectra of EPDM/EVA(20) blend without treatment.

As shown in Figs. 4 and 5, the intensities of the C=O bands around 1740 cm^{-1} and C-O around 1240 cm^{-1} increase with EVA content in EPDM, obeying the Lambert-Beer law (Smith 1979). This indicates that it is possible to determine the polymer with carbonyl bond in the blend using those two bands. However, due to C-O band being in the fingerprint region (from 1500 to 550 cm^{-1}) with neighboring bands and damaging the best baseline, C=O band should present better results and therefore was chosen to the calculations.

Determination of EVA content in EPDM/EVA by A_{1740} Band

Table 2 shows the EPDM/EVA sample data for the analytical curve, A_{1740} versus nominal EVA content in EPDM (Fig. 6). A similar graph to the previous one is presented in Fig. 7, but with EVA content values measured by TGA. Because of that, it was possible to compare TGA and FT-IR (UATR) calculations accuracies.

Table 2. FT-IR (UATR) results of the EPDM/EVA samples with the band at 1740 cm^{-1}.

EPDM/EVA sample	A_{1740}/EVA(16)	A_{1740}/EVA(20)	EVA(16) parameters	EVA(20) parameters
90/10	0.054	0.079	$\mu = 0.054$	$\mu = 0.078$
	0.054	0.078	$R = 0.004$	$R = 0.002$
	0.055	0.078	$\sigma = 0.002$	$\sigma = 0.001$
	0.051	0.077	$\sigma_\mu = 0.001$	$\sigma_\mu \approx 0.001$
	0.053	0.079	$RD = 1.4\%$	$RD = 1.3\%$
70/30	0.135	0.186	$\mu = 0.132$	$\mu = 0.185$
	0.130	0.182	$R = 0.005$	$R = 0.006$
	0.133	0.185	$\sigma = 0.002$	$\sigma = 0.003$
	0.132	0.188	$\sigma_\mu = 0.001$	$\sigma_\mu = 0.001$
	0.132	0.185	$RD = 0.7\%$	$RD = 0.6\%$
50/50	0.208	0.275	$\mu = 0.208$	$\mu = 0.275$
	0.210	0.283	$R = 0.004$	$R = 0.01$
	0.209	0.273	$\sigma = 0.002$	$\sigma = 0.005$
	0.208	0.274	$\sigma_\mu = 0.001$	$\sigma_\mu = 0.002$
	0.206	0.275	$RD = 0.4\%$	$RD = 0.7\%$
30/70	0.270	0.374	$\mu = 0.268$	$\mu = 0.362$
	0.272	0.352	$R = 0.005$	$R = 0.022$
	0.268	0.362	$\sigma = 0.002$	$\sigma = 0.01$
	0.267	0.365	$\sigma_\mu = 0.001$	$\sigma_\mu = 0.004$
	0.268	0.354	$RD = 0.4\%$	$RD = 1.2\%$
10/90	0.317	0.414	$\mu = 0.315$	$\mu = 0.414$
	0.320	0.405	$R = 0.012$	$R = 0.036$
	0.315	0.397	$\sigma = 0.005$	$\sigma = 0.015$
	0.308	0.433	$\sigma_\mu = 0.002$	$\sigma_\mu = 0.007$
	0.309	0.427	$RD = 0.7\%$	$RD = 1.7\%$

The methodology error (median value from relative deviations in Table 2) was 0.7% to 16% VA and 1.2% to 20% VA, indicating that this methodology was accurate, because it presented an error no higher than the equipment limits of accuracy, $\leq 2\%$ (Hórak and Vítek 1978). The highest relative error with 20% VA is probably justified by the highest analytical band intensity.

From Figs. 6 and 7 it was observed that both methodologies presented precise results, because the points obtained were satisfactorily represented by trend lines (linear correlation coefficients very close to the unit). Thus, the quantitative analysis from FT-IR (UATR) methodology was successfully confirmed.
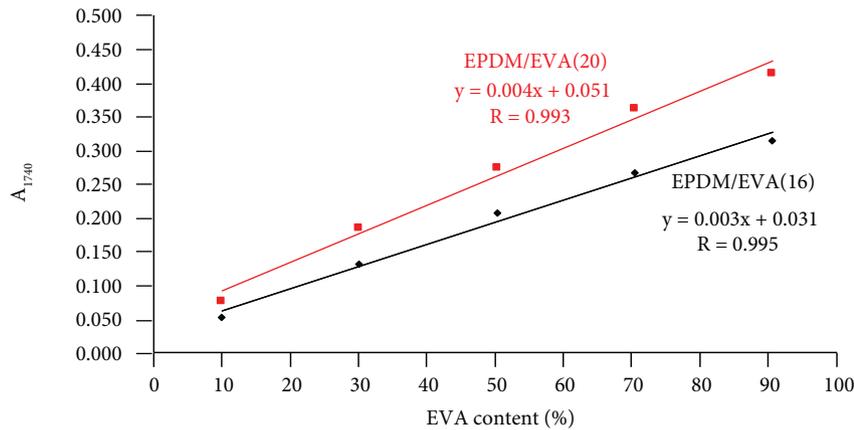
Figure 6. Absorbance A_{1740} versus EVA content in EPDM/EVA blend.
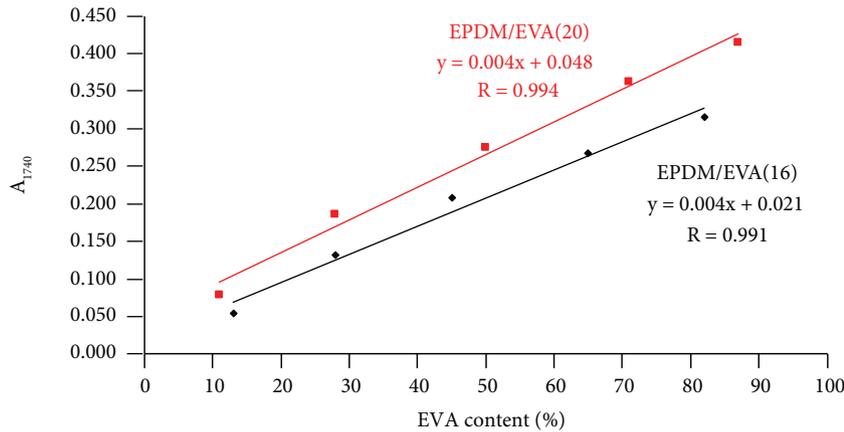Points with nominal EVA content in the blend and VA content determined by TGA.

Figure 7. Absorbance A_{1740} versus EVA content in EPDM/EVA blend.
Points with EVA content in the blend and VA content both determined by TGA.

VERIFICATION OF CALIBRATION CURVE

Four samples identified as Sample A, Sample B, Sample C, and Sample D were tested, two of EPDM/EVA(16) and two of EPDM/EVA(20). These samples were collected without the analyzer knowing about the VA content in the samples.

Each sample was analyzed five times (five aliquots) so that the median absorbance value A_{1740} (C=O band) of each sample was into the analytical curve equation.

These values were tested with the Eqs. 4 and 5:

$$\text{EPDM/EVA(16): } y = 0.003x + 0.031 \text{ (Fig. 6)} \tag{4}$$

$$\text{EPDM/EVA(20): } y = 0.004x + 0.051 \text{ (Fig. 6)} \tag{5}$$

where y represents the median absorbance value A_{1740}, and x represents EVA content (%).

The equations from Fig. 6 (nominal EVA values) were chosen, because they represent a simpler methodology than the equations from Fig. 7 (EVA values by TGA), besides, they have practically identical accuracies.

Initially, it was determined VA contents in EVA blends of the unknown samples by TGA, comparing the mass loss curves related to VA to know what blend are being analyzed and what equation must be applied.

Table 3. Analysis of Sample A.

A_{1740}	Parameters	EVA content – x [%]
0.052	$\mu = 0.052$	VA content by TGA: 16%
0.052	$R = 0.002$	
0.052	$\sigma = 0.001$	Applying Eq. 4: y = 0.052 → x = 7%
0.053	$\sigma_\mu \approx 0.001$	EVA content determined: 7%
0.054	$RD = 1.9\%$	EPDM content determined: 93%

In Sample A, with 16% VA obtained by TGA, it was noticed that the value of x applying Eq. 4 presented 7% as result, indicating that this sample should have EPDM/EVA(16) on 93/7 proportion, very close to that reported by the sample supplier, on 90/10 proportion.

Table 4. Analysis of Sample B.

A_{1740}	Parameters	EVA content – x [%]
0.180	$\mu = 0.180$	VA content by TGA: 20%
0.181	$R = 0.005$	
0.179	$\sigma = 0.002$	Applying Eq. 5: y = 0.180 → x = 32%
0.180	$\sigma_\mu = 0.001$	EVA content determined: 32%
0.176	$RD = 0.5\%$	EPDM content determined: 68%

In Sample B, applying Eq. 5 referring to EPDM blend with EVA(20), it was noted that the value of x was closer to 32%, indicating that this sample should have EPDM/EVA(20) on 68/32 proportion, very close to that reported by the sample supplier, on 70/30 proportion.

Table 5. Analysis of Sample C.

A_{1740}	Parameters	EVA content – x [%]
0.266	$\mu = 0.254$	VA content by TGA: 16%
0.254	$R = 0.019$	
0.260	$\sigma = 0.008$	Applying Eq. 4: y = 0.254 → x = 74%
0.247	$\sigma_\mu = 0.004$	EVA comtent determined: 74%
0.252	$RD = 1.6\%$	EPDM content determined: 26%

In this EPDM/EVA(16) sample, it was obtained 26/74 proportion by Eq. 4, which approach to the sample supplier information, EPDM/EVA(16) on 30/70 proportion.

In this last unknown sample analysis, the result presented using Eq. 5 was EPDM/EVA(20) sample on 27/73 proportion, also very close to that reported by the supplier, on 30/70 proportion, although in Sample D analysis the relative deviation was a little higher than 2%.

Table 6. Analysis of Sample D.

A$_{1740}$	Parameters	EVA content – x [%]
0.359	$\mu = 0.344$	VA content by TGA: 20%
0.351	$R = 0.063$	Applying Eq. 5: y = 0.344 → x = 73%
0.344	$\sigma = 0.027$	
0.296	$\sigma_{\mu} = 0.012$	EVA content determined: 73%
0.316	$RD = 3.5\%$	EPDM content determined: 27%

CONCLUSION

The methodology developed to determine EVA content in EPDM/EVA blend by UATR showed accurate results, because the relative errors were less than 2%, no higher than the FT-IR spectrometer limits of accuracy. In addition, it is important to mention that this methodology is non-destructive, it's fast (do not need sample treatment) and has lower cost, because it requires less investment in man-hours and equipment-hours. Therefore, if the quantity of samples and/or time of analysis were determinant for analyzes continuation, UATR without sample treatment would be chosen.

The analytical curves test revealed the need to know previously VA content in EVA to enable the continuity of the proposed methodology. Because of that, thermogravimetric analysis was used to VA content determination in EVA and to distinguish EPDM/EVA blends.

Finally, the methodology developed in this paper will provide an important contribution to the quality control of aerospace materials, besides being able to be applied with other VA contents, different from 16% and 20%.

AUTHOR'S CONTRIBUTION

Conceptualization, Rigoli PS, Mattos EC, Dutra RCL and Cassu SN; Methodology, Rigoli PS and Dutra RCL; Investigation, Rigoli PS and Diniz MF; Writing – Original Draft, Rigoli PS; Writing – Review and Editing, Rigoli PS, Mattos EC and Dutra RCL; Funding Acquisition, Dutra RCL; Resources, Murakami LMS, Diniz MF and Azevedo MFP; Supervision, Dutra RCL and Diniz MF.

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REFERENCES

Azevedo JB, Chavez MA, Junior RAC, Oliveira RGP, Rabello MS (2009) Influência da concentração de EPDM em compostos expansíveis de EVA: propriedades mecânicas e morfologia. Presented at: X Congresso Brasileiro de Polímeros. Anais do X Congresso Brasileiro de Polímeros; Foz do Iguaçu, Brazil.

Babbit RO, editor (1978) The Vanderbilt Rubber Handbook. 12th ed. Norwalk: R. T. Vanderbilt Company, INC.

Choi S-S, Kim Y-K (2011) Analysis of 5-ethylidene-2-norbornene in ethylene-propylene-diene terpolymer using pyrolysis-GC/MS. Polymer Testing 30(5):509-514. https://doi.org/10.1016/j.polymertesting.2011.04.005

Chowdhury SR, Sharma BK, Mahanwar P, Sarma KS (2016) Vinyl acetate content and electron beam irradiation directed alteration of structure, morphology, and associated properties of EVA/EPDM blends. Journal of Applied Polymer Science 13(321):43468. https://doi.org/10.1002/app.43468

D'Amelia RP, Gentile S, Nirode WF, Huang L (2016) Quantitative analysis of copolymers and blends of polyvinyl acetate (PVAc) using Fourier transform infrared spectroscopy (FTIR) and elemental analysis (EA). World Journal of Chemical Education 4(2):25-31.

Ding X, Wang J, Zhang S, Wang J, Li S (2015) Composites based on CB/CF/Ag filled EPDM/NBR rubber blends with high conductivity. Journal of Applied Polymer Science 132(4):41357. https://doi.org/10.1002/app.41357

Dutra RCL, Lourenço VL, Diniz MF, Azevedo MFP, Barbosa RV, Soares BG (1996) Poly(Ethylene-Co-Vinyl Acetate-Co-Vinyl Mercaptoacetate) (EVALSH)-determination of the vinyl mercaptoacetate content by thermogravimetric analysis and FTIR spectroscopy. Polymer Bulletin 36(5):593-600. https://doi.org/10.1007/BF00342451

Dutra RCL, Soares BG (1998) Determination of the vinyl mercaptoacetate content in poly(ethylene-co-vinyl acetate-co-vinyl mercaptoacetate) (EVASH) by TGA analysis and FTIR spectroscopy. Polymer Bulletin, 41(1):61-67. https://doi.org/10.1007/s002890050333

Dutra JCN, Sobrinho ASS, Homero H, Moraes JH, Massi M, Mello SAC (2006) Estudo e caracterização de uma faixa de aplicação segura da borracha vulcanizada EPDM previamente tratada com plasma de O2/Ar e N2/Ar. Presented at: IV Congresso Brasileiro de Engenharia Mecânica (conem); Recife, Brazil.

French AR, Benham JL, Pullukat TJ (1974) Quantitative determination of vinyl acetate content in ethylene vinyl acetate copolymers using multiple internal reflection spectroscopy. Applied Spectroscopy 28(5):477-479.

Fulin C, Lan C, Caihong L (2007) Study on the milling behavior of chloroprene rubber blends with ethylene-propylene-diene monomer rubber, polybutadiene rubber, and natural rubber. Polymer Composites 28(5):667-673. https://doi.org/10.1002/pc.20328

Hale A, Bair HE (1997) Polymer blends and block copolymers. In: Turi A, editor. Thermal characterization of polymeric materials. 2nd ed. New York: Academic Press. p. 745-886.

Higgins F, Rein A (2011) Quantitative analysis of copolymers using the Cary 630 FTIR spectrometer. Danbury: Agilent Technologies.

Hórak M, Vítek A (1978) Interpretation and processing of vibrational spectra. New York: John Wiley & Sons.

Lanxess Rubber (2012) Catalogo técnico: determinação do conteúdo de eteno, ENB e VNB no EP(D)M. São Paulo: Lanxess.

Luna CBB, Silva DF, Basílio SKT, Araújo EM, Silva AL, Bezerra AFC (2015) Desenvolvimento de blendas poliméricas visando a tenacificação dos polímeros: uma revisão. Semina: Ciências Exatas e Tecnológicas 36(1):67-80. https://doi.org/10.5433/1679-0375.2015v36n1p67

Mello TSD, Diniz MF, Dutra RCL (2018) UATR and NIRA evaluation in the quantification of ATBC in NC blends. Polímeros 28(3):239-245. https://doi.org/10.1590/0104-1428.16816

Rodrigues VC, Diniz MF, Mattos EC, Dutra RCL (2014) Quantificação por NIR/MIR de resina poliuretânica em misturas binárias com nitrocelulose, utilizadas em tintas. Polímeros, 24(3):367-372. https://doi.org/10.4322/polimeros.2014.027

Siqueira SHS, Dutra RCL, Diniz MF (2008) Determinação por espectroscopia nas regiões MIR/NIR do teor de NCO em adesivos poliuretânicos. Polímeros 18(1):57-62. https://doi.org/10.1590/S0104-14282008000100012

Smith AL (1979) Applied Infrared Spectroscopy. New York: John Wiley & Sons.