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ORIGINAL ARTICLES

Quantification of elastomers in CR/NR/BR blends

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Abstract

Using ternary blends is a technological solution to combine the best characteristics of different elastomers. Quantifying rubbers in a blend, in which each content influences the result, is a task complex and usually requires the coupling of techniques. Therefore, it is necessary to develop simple, fast and accurate methodologies for this purpose. This study presents the analysis of polychloroprene, poly-cis-isoprene and polybutadiene (CR/NR/BR) rubber, with the selection of bands A_{1116} (CR), A_{2960} (NR) and A_{738} (BR), by universal attenuated total reflection (UATR) infrared spectroscopy performed on the sample as received. The error found was 2%, with 98 to 99% of the data explained by the methodology. The methodology responds more adequately to CR and BR cis, but has the ability to detect up to 5% of NR and 10% of CR and BR. Acid-resistance data are used quantitatively in the determination of BR rubber, satisfactorily confirming the spectral data found.

Keywords: *acid-resistance, infrared spectroscopy, quantification, ternary rubber.*

Data Availability: Research data is only available upon request.

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1. Introduction

In recent decades, polymeric materials have achieved a vital position in all branches of science and technology. Rubbers are widely used as vibration absorbers to dissipate vibrational energy[1] and are also of paramount importance for the space sector, in which are used as flexible thermal protections and flexible joints in rocket engines[2], as well as for the aeronautical sector, in which are employed in aircraft tires[3]. Furthermore, this material is also applied in the footwear industry[4], and mainly in the automotive industry, in tires and other artifacts[5].

One type of rubber alone does not have the ability to provide all the desired properties for an elastomer artifact. It is necessary to use the strategy of mixing or blending rubbers, which are formulated to achieve the final properties required according to each project, the process capacity and the desired cost[6]. Such properties can be controlled by changing the morphology of the processing conditions and the composition of the blend[7].

Regarding the morphological characterization of elastomeric blends, Kaliyathan et al.[8] provide a review on blends of various binary and ternary rubbers, with different contents, including, for example, natural poly-cis-isoprene rubber and butadiene and styrene copolymer (NR/SBR) and ternary rubber containing NR, SBR and polybutadiene (NR/SBR/ BR). In the case of elastomeric blends, microscopy is an essential tool to understand the morphology, that is, the size, shape and distribution of phases and filler particles in the elastomeric blend. In the review, the authors address studies that use optical microscopy (OM), scanning and transmission electron microscopy (SEM, TEM) and atomic force microscopy (AFM). The conclusion is that the most suitable microscopy (OM, SEM, TEM or AFM) must be selected depending on the length scale (macro, micro and nano) of the heterogeneity. However, conducting a microscopy study is complex, particularly through TEM analysis, as several factors related to the characteristics of rubbers and microscopes must be considered before conducting an imaging process. Prior knowledge about the sensitivity of rubbers to irradiation, contrast enhancements for analyzing rubbers, the preparation of their surfaces, etc., is very important. Furthermore, the analysis of the morphology of each rubber constituent of the blend is necessary for the adequate interpretation of the image with corresponding physical and mechanical properties.

As future trend, Kaliyathan et al.[8] cite qualitative spectroscopy of the image obtained microscopically in conjunction with other spectroscopic techniques, such as Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, photoacoustic spectroscopy, atomic emission spectroscopy, electron spectroscopy and ions, magnetic resonance spectroscopy, and mass spectroscopy.

Although there are fewer qualitative infrared (IR) studies than quantitative studies of polymer blends, some research on the latter has been published recently of binary[9-11] and ternary[12,13] elastomeric systems for different technological purposes. However, for ternary rubbers, most of the time, the use of coupling techniques is necessary[14] online or offline, due to the possibility of overlapping thermal events or spectroscopic bands. Therefore, there are gaps in polymer characterization research through techniques and laboratory tests with lower complexity and analysis time, such as in the evaluation of samples as received, which can give rise to the development of new methodologies.

The ternary blend of chloroprene, NR and BR rubbers (CR/NR/BR), for example, stands out in ternary elastomeric systems because it is used for engineering applications in which high performance, chemical resistance and excellent tribological properties are required, i.e., friction, wear and lubrication that take place during contact between solid surfaces in relative movement, however there are few studies in the literature available on this ternary system. However, the qualitative study by Castaño-Rivera et al.[15] can be highlighted.

The qualitative FT-IR analysis of CR/NR/BR is cited by Castaño-Rivera et al.[15], among other techniques, such as X-ray diffraction (XRD), thermogravimetric analysis (TGA) and rheometric analysis, to study the effect of the type of filler on the mechanical properties of nanocomposites prepared with the ternary rubber, and the correlation with its structure, compatibility and curing properties. Qualitative analysis by FT-IR reflection, specifically by attenuated total reflection (ATR), appears in the study as an important technique to investigate the reinforcement interaction of nanoclays in rubber nanocomposites.

Simpler laboratory tests on rubbers containing one or more elastomers, such as the assessment of resistance to oxidative degradation or the acid-resistance test, in which the sample is subjected to a mixture of concentrated sulfuric and nitric acids at temperatures of 70 and 40 °C, have also been cited in the literature. These tests can indicate the chemical nature of the rubbers used in a formulation[16,17], which is of great practical use in the industry, as this is one of the challenges that the company encounters when it needs to replace rubber parts.

The study by Dutra and Diniz[16] investigated the methodology developed by Mano and Dutra[17] for the case of binary elastomer blends in vulcanized artifacts, including those that show similar IR spectra. The acid-resistance test was useful for differentiating saturated and unsaturated rubbers, thus constituting an alternative methodology for the characterization of rubbers. In the samples analyzed by Dutra and Diniz[16], the test provided a clear indication of the degradability of the polymer chains, even when there is a great predominance of less unsaturated structures in the mixture. The results indicate that it is possible to detect the component least resistant to the oxidizing mixture when its content is higher than 20% of the elastomeric total. The study can be considered as semi-quantitative for the binary rubbers analyzed.

Magalhães[13] evaluated the acid-resistance test quantitatively at 40 °C by subtraction, validating FT-IR data relating to the evaluation of BR content in the analysis of the ternary rubber NR/SBR/BR. Barros et al.[12] also evaluated quantitatively the BR content in mixture with the ethylene propylene diene monomer copolymer (EPDM/BR), by acid-resistance at 40 °C. The researchers recommend the methodology as an alternative to the FT-IR methodology developed for the binary blend.

The acid-resistance test was initially developed for the qualitative evaluation of saturated and unsaturated rubbers and was later applied in a semi-quantitative way to saturated and/or unsaturated binary blends that presented similar infrared spectra[16,17]. The method was then developed to the quantitative investigation[12,13] of ternary NR/SBR/BR rubbers. This study advances the aforementioned investigations, using the acid-resistance test to evaluate the influence of different BR contents on the degradation initiation time of another ternary rubber: the CR/NR/BR blend.

The development of fast, accurate, qualitative and quantitative methodologies to evaluate the composition of these systems becomes essential due to the commercial importance of elastomeric blends. These methodologies are important for industrial applications, in which the determination of a content range is sufficient for the evaluation of materials, and mainly in the aerospace sector, in which the costs of materials are extremely high and there is the critical factor of safety, which demands the detection of low elastomer content that would not be adequate to the project specifications.

Conventional determination of elastomer content in ternary systems are carried out using complex methodologies, which is time consuming and involve high costs, which often makes them impracticable for the industry. Therefore, there are opportunities for new developments in this area. Reinforcing the importance of the methodology developed in this study, no studies were found in the literature consulted that address the use of non-conventional FT-IR reflection techniques, not even in the most recent reviews[8,18], for determining the content of rubber components in ternary CR/NR/BR on samples as received, with data validation through test sample and acid-resistance tests. Therefore, it is clear that there is a gap in the scientific database on the characterization/quantification of this ternary elastomeric system. The importance of the contribution of this study lies in the development of accurate quantitative non-conventional FT-IR and fast, qualitative and quantitative acid-resistance methodologies for the analysis of CR/NR/BR.

2. Materials and Methods

2.1 Materials

CR/NR/BR vulcanized rubber samples, including test sample A_1, were prepared and kindly provided by the companies Zanaflex Borrachas and Tenneco Automotive Brazil, with

the following nominal content (wt. %): 10CR/40NR/50BR, 20CR/60NR/20BR, 30CR/5NR/65BR, 40CR/50NR/10BR and 50CR/10NR/40BR, according to the companies' internal procedures. It should be noted that the BR base elastomer used by Zanaflex has a higher cis C-C content than the one from Tenneco. The CR used in both companies has a cis chemical structure. The contents of the cis structure are not provided by companies due to internal policy.

2.2 Methodologies

2.2.1 FT-IR reflection (UATR) and acid-resistance test of CR/NR/BR

The conditions for the FT-IR analyses were: PERKINELMER IR spectrometer Frontier, 4000 to 400 cm^{-1} (mid-infrared _ MIR), resolution 4 cm^{-1}, gain 1, and 20 scans by universal attenuated total reflection (UATR). Samples were quantitatively analyzed as received. The samples were cut and the internal surface was analyzed, as the investigation of the surface could be interfered by the possible migration of additives from the formulation. The analytical bands used in this methodology were selected according to their variation in height (intensity) in relation to the content of each elastomer, in compliance with the Lambert-Beer law[19], at the following wavenumbers (cm^{-1}), measured by the following baselines (BL): for CR - 1659 (1778 to 1502), 1431 (1502 to 1388) and 1116 (1146 to 927); for NR - 2960 (3110 to 2744), 1376 (1388 to 1341) and 833 (880-790); for BR - 3006 (3110 to 2744), 966 (1146 to 927) and 738 (790 a 624). The assignment[19,20] is: $\mathbf{A}_{1659}$ (cis C=C), A_{1431} (CH_2), A_{1116} (C-C), A_{2960} (CH_3), A_{1376} (CH_3), A_{833} (vinylidene), A_{3006} (C-H), A_{966} (trans C=C) and A_{738} (cis C=C). Analyses were performed in quintuplicate. The calibration curves were constructed with the median[21] values of absorbance *versus* the elastomer content. The accuracy estimation is in accordance to the nonparametric statistical method used for spectroscopic data[21] (Equations 1 to 3) successfully used for IR spectroscopic data in different studies[9-11,22]. The methodology error is estimated by the median of the relative error[22].

Standard deviation:

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

where: R = higher absorbance value - lower absorbance value; K_R = 0.430 for 5 measurements[21].

Mean standard deviation:

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

where: n is the number of measurements.

Relative deviation (RD):

$$\boldsymbol{RD}_{(\%)} = \frac{\hat{\sigma}_{\hat{\mu}}}{\mu} \cdot \mathbf{100} \quad (3)$$

where: μ is the median value of absorbance.

The lowest methodology error and the highest linearity of the calibration curve (R^2) were the set of results used for selecting the best analytical band. The acid-resistance test was performed according to the methodology described in a previous study[16]. The test is performed as follows: small fragments of the sample are extracted in acetone and dried in an oven. 5 ml of a mixture 1:1 of concentrated sulfuric acid (density of 1.84 g/cm^3) and concentrated nitric acid (density of 1.42 g/cm^3) are placed in a test tube, which is then immersed in a water bath at 70 °C. After the contents of the test tube reach the bath temperature (around 5 min), the sample fragments are placed in the test tube and the time at which they begin to degrade is measured with a stopwatch. The degradation can be easily observed when small particles begin to appear on the surface of the sample, then dispersing in the mixture of concentrated acids. The authors[16,17] point out that if the attack is immediate and can't be measured in minutes, it is necessary to repeat the test in a bath at 40 °C, which is a milder condition and should result in a longer time until deterioration. As immediate degradation of CR/NR/BR occurred at 70 °C, the test was repeated at 40 °C to reduce the aggressiveness of the test conditions and allow measurements. The time measured in the acid-resistance test represents the onset time of degradation of the elastomeric material.

The tests were conducted in triplicate. The mean time was used for evaluating the relation between the onset time of degradation and the BR content. The CR/NR/BR sample coded "A_1" was analyzed by the same analysis conditions to verify the effectiveness of the developed FT-IR and acid-resistance methodologies.

3. Results and Discussions

3.1 FT-IR/UATR analysis of the CR/NR/BR blend

The content of each elastomer in the CR/NR/BR blend was determined separately, according to the methodology described in the experiment and discussed in the next topics.

3.1.1 FT-IR/UATR evaluation of analytical bands for determining CR, NR and BR content

Figure 1 presents the set of UATR spectra (sample as received) of the vulcanized ternary rubber CR/NR/BR, containing different levels, compared to the reference spectra of each elastomer. Spectra were organized in increasing order of BR content to facilitate the visualization of height/intensity variation of their analytical bands, which were chosen and evaluated in accordance with the Lambert-Beer law[19]. In this manner, the bands at 1659, 1431 and 1116 cm^{-1} were selected for the evaluation of CR determination. The first band evaluated at 1659 cm^{-1} is assigned to the C=C group[19], and was also considered in the study by Sathasivam et al.[20] on the FT-IR absorptions of cis-1,4-polychloroprene.

Table 1 shows the FT-IR/UATR data (sample as received) calculated for A_{1659}, for the determination of the CR content in the CR/NR/BR blend using a calibration curve, as well as the errors involved. The samples were organized in increasing order of nominal CR content to facilitate visualization of the increasing in absorbance value. This procedure was also carried out for each band and its corresponding elastomer to construct the other tables in the study.

Results from Table 1 were plotted in a calibration curve of the analytical band A_{1659} (median) (CR) *versus* the CR content (Figure 2). The methodology error was around 4%, in accordance with to Barros et al.[12] and lower than the reported in another study[14] (5%), for another ternary system containing NR and BR (NR/SBR/BR). This methodology error for CR/NR/BR (around 4%) could be considered satisfactory for the industry, because a specification range is routinely adopted for material acceptance. Even though the methodology showed some limitation for the 30% CR content, which can be attributed to this sample lower cis content informed by the suppliers, a tendency in linearity was observed in Figure 2, with 85% of the data explained by the developed methodology (R^2).

Figures 3 to 5 show the calibration curves of the other bands also evaluated for the determination of elastomer content in the CR/NR/BR blend: A_{1431} and A_{1116} (CR content), A_{2960}, A_{1376} and A_{833} (NR content), and A_{3006}, A_{966} and A_{738} (BR content).

All curves showed adequate linearity, varying between 84 and 99% of data explained by the developed methodologies. It should be noted that the sample 30CR/5NR/65BR was manufactured with a BR rubber with lower cis content and thus was discarded, so only four samples were used to determine the BR content. The lower cis content is confirmed by the difference in the intensity of the band around 740 cm^{-1} (marked with an asterisk) in the spectra of the two neat BR types (rubber as received from the suppliers) shown in Figure 6. Therefore, the Tenneco sample presented the band around 740 cm^{-1} with lower intensity (see Figure 1) due to the lower content of C=C cis, despite having a higher content of BR (30CR/5NR/65BR). This occurrence caused a deviation in the measurement of the most characteristic band of cis bonds. On the other hand, it was possible to measure a 5% NR content in CR/NR/BR using all samples of the NR curves, which constitutes a contribution of this research, as it is the minimum acceptable content for a material to be considered as a blend[23].

Regarding the calculations, this study adopted the criterion of showing only one table (i.e. Table 1, already mentioned) of one of the bands chosen for each elastomer and grouping all the results obtained in Table 2 (Equations 4 to 12) for the bands studied for CR, NR and BR, as the calculation mechanism is the same. The results most suitable for determining the aforementioned elastomers in the blend were marked in bold.

Table 2 shows that, in general, the selected bands presented satisfactory results. However, to define the most appropriate analytical band, it is necessary to consider other parameters such as the linearity of the calibration curve, the error of the

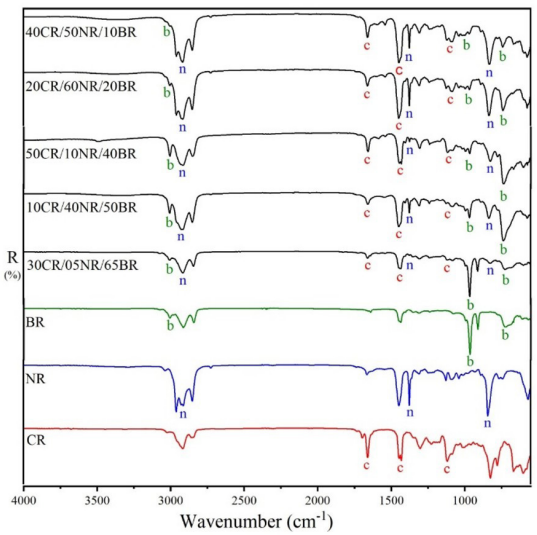

Figure 1. FT-MIR spectra/UATR reflection/ sample as received of the CR/NR/BR samples presented in increasing order of BR content, and of the neat rubbers. The bands evaluated for each elastomer are marked with the letters "c" for CR, "n" for NR, and "b" for BR.

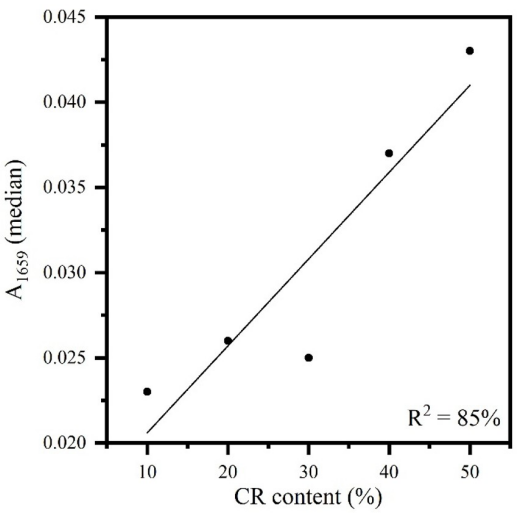

Figure 2. Calibration curve of FT-IR/UATR sample as received (A_{1659}) *versus* CR content in CR/NR/BR.

Table 1. FT-IR/UATR/sample as received (A_{1659}) results for the determination of CR in CR/NR/BR.

Sample (nominal content)	A_{1659} (median)	Mean standard deviation*	Relative deviation (%)	Methodology error (%)
10CR/40NR/50BR	0.023	0.001	4.35	
20CR/60NR/20BR	0.026	0.001	3.85	
30CR/5NR/65BR	0.025	0.001	4.00	3.85
40CR/50NR/10BR	0.037	0.001	2.70	
50CR/10NR/40BR	0.043	0.001	2.32	

*For mean standard deviation values close to zero, a value of 0.001 was assumed, in accordance with the decimal places of the absorbance value.

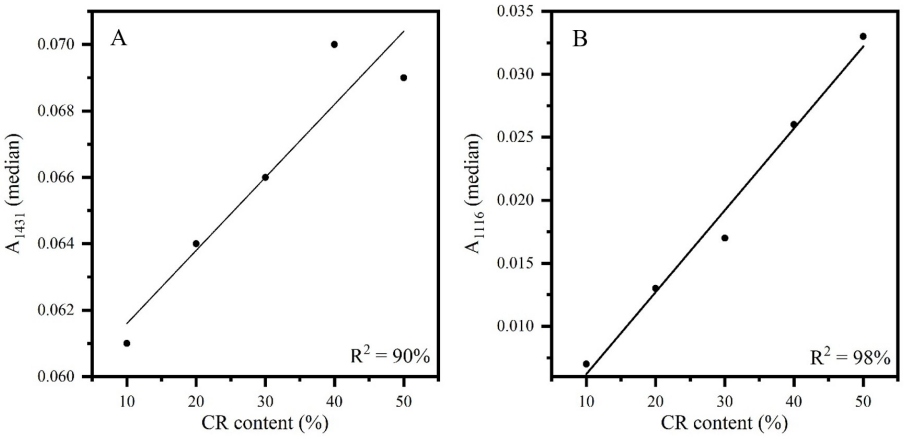

Figure 3. Calibration curves of FT-IR/UATR sample as received: (A) ($\mathbf{A_{1431}}$) *versus* CR content in CR/NR/BR; (B) ($\mathbf{A_{1116}}$) *versus* CR content in CR/NR/BR.

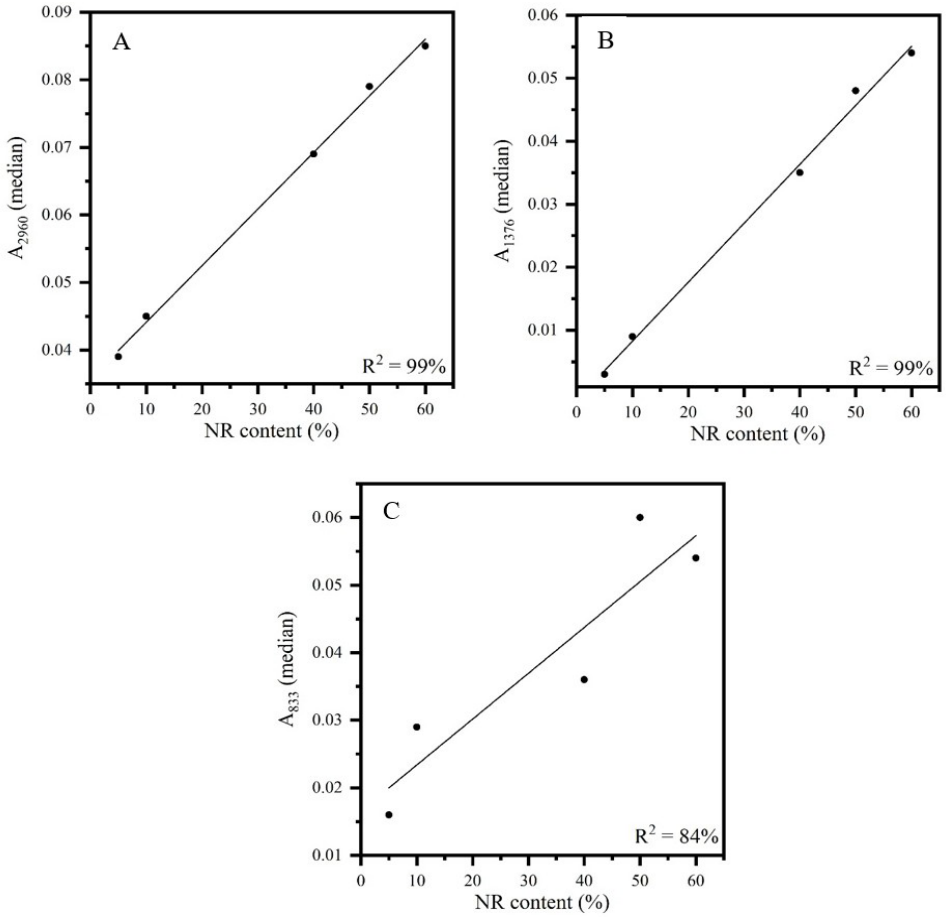

Figure 4. Calibration curves of FT-IR/UATR sample as received: (A) ($\mathbf{A_{2960}}$) *versus* NR content in CR/NR/BR; (B) ($\mathbf{A_{1376}}$) *versus* NR content in CR/NR/BR; (C) ($\mathbf{A_{833}}$) *versus* NR content in CR/NR/BR.

proposed methodology, the possibility of overlapping bands, and the characteristic intensity of the band that facilitates or makes the measurement of low contents difficult[19].

For the determination of CR content in the blend, the highest percentage of data explained by the methodology was mandatory for indicating the band at 1116 cm^{-1} as the

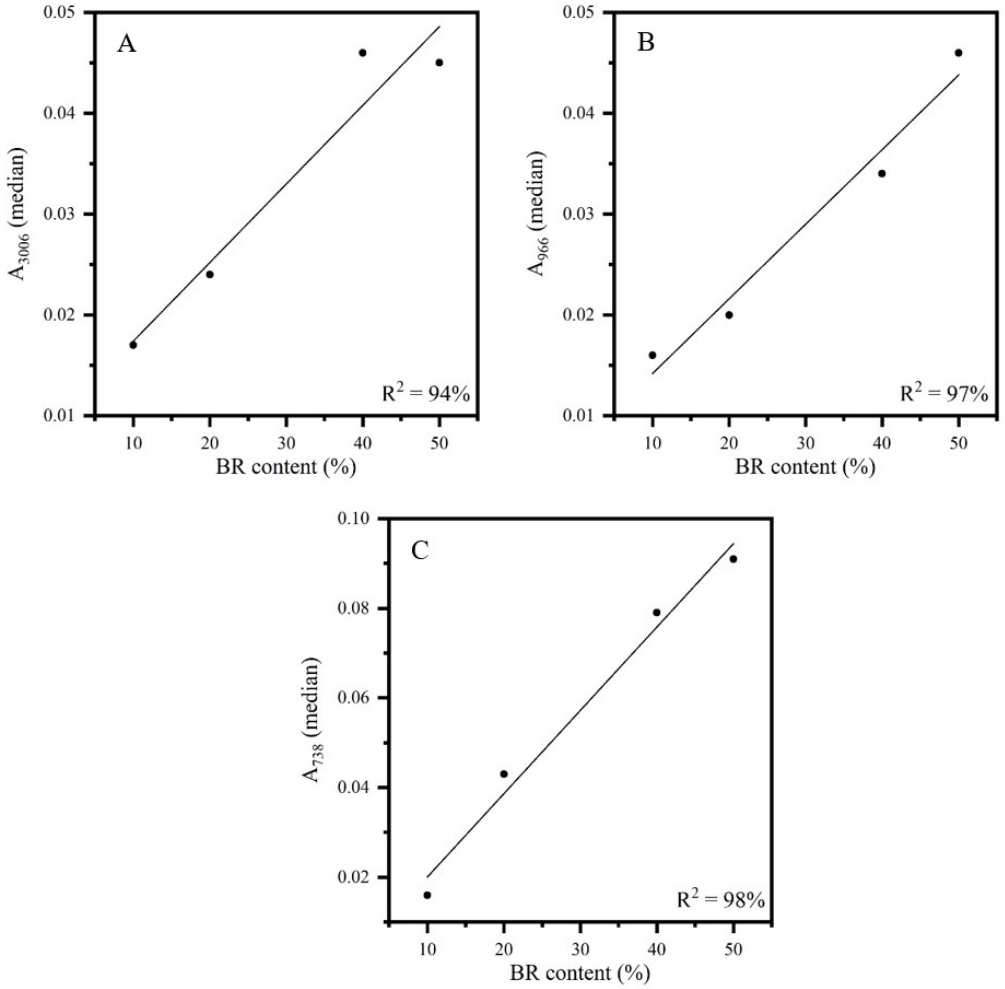

Figure 5. Calibration curves of FT-IR/UATR sample as received: (A) (**A_{3006}**) *versus* BR content in CR/NR/BR; (B) (**A_{966}**) *versus* BR content in CR/NR/BR; (C) (**A_{738}**) *versus* BR content in CR/NR/BR.

most appropriate, even though the error was around 6%. Errors of this order of magnitude are typically found in quantitative methodologies by reflection[12] or even through coupling techniques[14] for ternary rubbers.

In the case of NR, both the error and the percentage of data explained by the methodology indicated the band at 2960 cm^{-1} as the best option. This band is characteristic of CH_3[19] and has an intensity suitable for measuring low contents, as evidenced by the NR determination of 5% in the ternary blend. The band at 1376 cm^{-1}, also characteristic of CH_3[19], showed adequate results but with lower intensity, which can yield higher errors, as observed.

For the BR determination, the band that showed the most appropriate result in terms of methodology error and linearity was found at 738 cm^{-1}, which is characteristic of C=C cis[19,20].

3.2 Acid-resistance evaluation of the BR content

In addition to the qualitative FT-IR/UATR analysis of the sample as received, which confirmed the characteristic

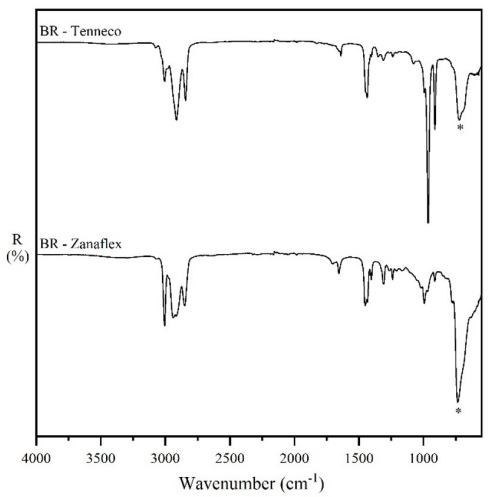

Figure 6. FT-IR/UATR spectra/sample as received of BR Tenneco and BR Zanaflex.

bands of CR/NR/BR (Figure 1 already shown), and the quantitative analysis that determined the levels of each elastomer, the acid-resistance test[16,17] was conducted to verify the quantitative relation between the increase in BR content and the degradation onset time of the CR/NR/BR blend. The test was carried out focusing on BR rubber because among the three elastomers, BR is the one with the longest degradation start time at a given temperature[16].

According to Dutra and Diniz[16], unsaturated NR, CR, and BR rubbers degrade within ≤ 1 minute at 70 °C. Therefore, the CR/NR/BR blend is expected to have a quick degradation at 70 °C, making it impossible to establish any relation between the BR content and the degradation time. Because of this occurrence, the test was conducted at 40 °C (Table 3).

The longer time required at 40 °C to start the degradation of each rubber in the blend permits a better individual visualization. Furthermore, according to the literature[16,17], the elastomers combined in the blend have different degradation onset time at 40 °C. NR and CR degrade in less than 3 minutes, while BR degrades between 10 and 30 minutes. Therefore, the expected behavior for the increase in BR content in the CR/NR/BR blend is an increase in the degradation start time for the blend, which is observed in the linear trend of Figure 7. Some deviation can be attributed to the different characteristics of some elastomers used from different suppliers, such as BR provided with higher content of trans or cis C=C vinyl. However, the results show that the presence of BR in CR/NR/BR is more noticeable from 20% onwards, which confirms what was observed by Dutra and Diniz[16] for binary blends. Due to the longer degradation initiation time (6 minutes) for BR compared to that observed for NR and CR (around 3 minutes) at 40 °C, BR, despite also being unsaturated, is the most resistant rubber to the oxidizing mixture in this analyzed system.

It was observed a correlation (Equation 13) with an adequate linearity (R^2 = 85%) between the data obtained through the acid-resistance tests and the BR content in the sample.

$$y=0.2242x+0.303 \quad y=0 \tag{13}$$

where: y is the degradation onset average time at 40 °C and x is the BR content in CR/NR/BR.

3.3 Assessment of the effectiveness of the methodologies developed

To evaluate the effectiveness of the methodologies developed, the UATR and acid-resistance was performed on test sample A_1 and results were presented in Tables 4 and 5. In the FT-IR analysis, the bands 1116 cm^{-1} for CR, 2960 cm^{-1} for NR and 738 cm^{-1} for BR were analyzed, which were, according to the methodology developed, the most suitable for determining the levels of these elastomers in the CR/NR/BR blend. The corresponding equations previously shown were used (Equations 6, 7 and 12). For the calculated values, whole numbers were considered for comparison with the nominal values.

The results of the FT-IR/UATR/sample methodology as received can be considered with adequate precision, as the methodology error is 1.80% (median of the 3 relative errors), considering the 3 bands selected (Table 2). Furthermore, considering the technological aspect[24] of rubber industries, which use specification ranges for the acceptance of their products, the calculated accuracy meets the requirements.

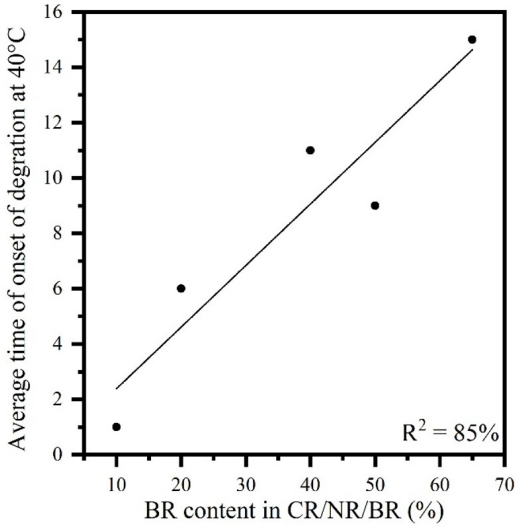

Figure 7. Initial degradation time (min) at 40 °C *versus* BR content (%) in CR/NR/BR.

Table 2. Comparison of FT-IR UATR data (as received) for each CR/NR/BR band analyzed, including methodological errors and data from the respective calibration curves.

Elastomer in CR/NR/BR	Band (cm^{-1})	Methodology error (%)	(Equation Number) Calibration curve equation*	% of data explained by the method. R^2
CR	A_{1659}	3.85	(4) y= 0.0005x + 0.0155	85
	A_{1431}	1.51	(5) y= 0.0002x + 0.0594	90
	A_{1116}	**5.88**	**(6) y= 0.0007x + 0.0003**	**98**
NR	**A_{2960}**	**1.45**	**(7) y= 0.0008x + 0.0358**	**99**
	A_{1376}	2.86	(8) y= 0.0009x + 0.0011	99
	A_{833}	2.78	(9) y= 0.0007x + 0.0166	84
BR	A_{3006}	3.19	(10) y= 0.0008x + 0.0096	94
	A_{966}	3.97	(11) y= 0.0007x + 0.0068	97
	A_{738}	**1.80**	**(12) y= 0.0019x + 0.0014**	**98**

*y= median absorbance value of the analytical band and x= elastomer content.

Table 3. Results of acid-resistance (40 °C) for the CR/NR/BR blend.

Sample	Time (min)	Average (min)
40CR/50NR/10BR	1/2/1	1
20CR/60NR/20BR	4/7/8	6
50CR/10NR/40BR	12/10/12	11
10CR/40NR/50BR	10/9/9	9
30CR/5/NR/65BR	14/15/16	15

Table 4. FT-IR/UATR data/sample as received for test sample A_1 from CR/NR/BR.

Sample	A1116 (CR) median	A2960 (NR) median	A738 (BR) median	Calculated content (%)	Nominal content (%)
A1	0.027	0.077	0.016	38/52/8	40/50/10

Table 5. Acid-resistance data (40 °C) for test sample A_1 of CR/NR/BR.

Sample	Time (min)	Mean (min)	Calculated BR content (%)	Nominal BR content (%)
A_1	4	4	16	10
	4			
	4			

The BR content calculated for sample A_1 with Equation 13 (16%) in the acid-resistance test can also be considered satisfactory from an industrial point of view, even considering its lower precision, as long as the nominal BR content is not higher than 20%. In this condition, results from the acid-resistance test validate the FT-IR data, and are able to distinguish the content in which the influence of this elastomer on the beginning of degradation in the blend start to be noted[16].

4. Conclusions

The objective of this study was to develop a simple, fast and accurate methodology for quantifying the elastomer content in the CR/NR/BR blend. The purpose was achieved, which contributes to the state of the art of research in the determination of elastomer contents in ternary elastomeric systems. It is noteworthy that the proposed methodology is the FT-IR/UATR analysis with the sample as received, that is, without sample preparation. Therefore, time spent is reduced and accurate values are found without major complexities, especially for samples containing CR and BR cis. The methodology can also be applied to different CR/NR/BR blends, even detecting the lowest possible content in a blend (5%). Results were validated through a test sample, both for the FT-IR analysis and for the acid resistance test, which is a simple and quick laboratory examination. The applicability of the acid resistance test was expanded in this study for the determination of BR in the CR/NR/BR blend.

5. Author's Contribution

- **Conceptualization** –Taynara Alves de Carvalho; Natália Beck Sanches; Rita de Cássia Lazzarini Dutra.
- **Data curation** – NA.
- **Formal analysis** – NA.
- **Funding acquisition** - Rita de Cássia Lazzarini Dutra.
- **Investigation** – Milton Faria Diniz; Taynara Alves de Carvalho; Alexandra Helena de Barros; Rachel Farias Magalhães.
- **Methodology** –Taynara Alves de Carvalho; Alexandra Helena de Barros; Rachel Farias Magalhães; Milton Faria Diniz; Rita de Cássia Lazzarini Dutra.
- **Project administration** – Rita de Cássia Lazzarini Dutra.
- **Resources** – Lídia Mattos Silva Murakami.
- **Software** – NA.
- **Supervision** – Natália Beck Sanches; Jorge Carlos Narciso Dutra; Rita de Cássia Lazzarini Dutra
- **Validation** –Taynara Alves de Carvalho; Alexandra Helena de Barros; Rachel Farias Magalhães; Milton Faria Diniz; Rita de Cássia Lazzarini Dutra.
- **Visualization** – Taynara Alves de Carvalho; Natália Beck Sanches; Rita de Cássia Lazzarini Dutra.
- **Writing – original draft** – Taynara Alves de Carvalho; Rita de Cássia Lazzarini Dutra.
- **Writing – review & editing** – Taynara Alves de Carvalho; Alexandra Helena de Barros; Rachel Farias Magalhães; Natália Beck Sanches; Rita de Cássia Lazzarini Dutra.

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