FT-IR methodology (transmission and UATR) to quantify automotive systems

Ana Carolina Ferreira[1], Milton Faria Diniz[2] and Elizabeth da Costa Mattos[1,2]*

[1]Departamento de Química, Instituto Tecnológico de Aeronáutica – ITA, São José dos Campos, SP, Brazil
[2]Divisão de Química – AQI, Instituto de Aeronáutica e Espaço – IAE, São José dos Campos, SP, Brazil
beth1.mattos@gmail.com

Abstract

When using Fourier transform infrared spectroscopy (FT-IR) under the qualitative aspect for characterization of polymer blends, often a simple identification of each one of the existing polymers in the blend does not justify the material failure since different amounts of each component may result in different mechanical properties, which should be a possible cause for of material failure when applied to an automotive part. Thus, seeking for a better justification in the understanding of material failure analysis, a new quantitative FT-IR methodology was developed in the mid-infrared region (MIR), using the transmission techniques and universal attenuated reflectance for the determination of Acrylonitrile Butadiene Styrene (ABS) and polycarbonate (PC). Transmission mode was more suitable. The relative band (A_{831}/A_{2237}) was chosen for the preparation of the calibration curve that showed a 0.99% error methodology, which is within the FT-IR spectrometer accuracy limit ($\leq 2\%$); therefore, it is accurate for the analysis of the system.

Keywords: *automotive systems, MIR, polymer blends, quantification, transmission.*

1. Introduction

As known, the polymers exhibit thermal stability, resistance to chemical action, mechanical properties, among others, and are currently one of the most used materials, as external and internal components, in the automotive industry. Plastics have high reliability index and many advantages over traditional materials such as steel, aluminum and glass. About 100 kg of plastics are used inside and/or outside the vehicle[1].

In the European automotive industry, the plastics or thermoplastics materials contribute to 10% of the total weight of the vehicle, and about 41% of this material are made up of polypropylene (PP), 20% polyamide or nylon (PA), 14% ABS, 6% PC, 6% polyacetal (POM), 5% poly (butylene terephthalate) (PBT), 2% poly (methyl methacrylate) (PMMA), and other materials. In the American vehicle industry, 38% of plastic materials are inside the car, 29% in the body, 10% in the hood and 23% in the powertrain system and chassis. The choice of polymer materials is at 47% PVC, 20% PP, 5% polyurethane, and other materials; the non-plastic ones correspond to 28%[2].

The advantages obtained from the use of plastics are related to the economy of fuel and production investments. Furthermore, the possibility of design sophistication, the use of ways of less traditional solutions and increased safety drive the application of polymeric materials in automotive solutions. The disadvantages are: flammability, low impact resistance, deterioration by thermal and environmental action, etc. However, in accordance with the required specification of the material to be used, there may be a type of polymer specially produced to meet the requirements of use, overcoming a disadvantage found in a common plastic[1].

There are several types of polymers applied to the component parts of vehicles, such as the instrument panel,

the bumpers, the upholstery, the carpets, the head and tail lamps, as well as in the door trim panels and in the roof. Probably, in the future, polymers will be used in other places of such automotive systems[3].

In the automotive industry, some polymers are "enriched" by incorporation of loads and changes in mechanical and thermal properties by the "healing" process, making them engineering plastics[4].

Engineering plastics are stable materials for certain periods. Therefore, they are used in applications where they can suffer mechanical, thermal, electrical, chemical or environmental stress. In general, these are more expensive than plastic "commodities", due to a more elaborate manufacturing. They are preferably chosen for their easy processability and flexibility in providing more complex designs with good dimensional stability and excellent resistance to chemical corrosion in hostile environments. The most commonly used polymers are: high molar mass polyethylene (UHMWPE), poly (methylene oxide) (POM), poly (ethylene terephthalate) (PET), PBT, PC, PA, and others[4].

The increasing use of polymeric materials by industries, aiming to replace several traditional materials, has attracted the attention of researchers in the discovery of new materials achieved through blends or polymer blends, in order to obtain better performance of the mechanical properties, lower cost/benefit and environmental impact. An alternative that meets these requirements is the preparation of blends, consisting of compatibilization of polymers with different characteristics. The major advantages of these materials are the range and versatility of their applications coupled with the ease of processing, enabling the production of diverse devices and making them incomparable with other materials[5].

One of the most important is the blend PC/ABS. This importance is due not only to the acquired characteristics, such as impact resistance and temperature, but also to good dimensional stability. It is widely used in the automotive industry as items of the panel, steering columns covers, chrome logos, internal housings etc.[5].

The virgin ABS, with an amorphous thermoplastic origin, is composed of acrylonitrile (AN) (20 to 30%), styrene (20 to 60%), the elastomeric phase consists of butadiene (20 to 30%). As described by Carvalho[6], it consists of two phases in which the SAN copolymer, composed of acrylonitrile and styrene, is the continuous phase (matrix), wherein the dispersed elastomeric phase is butadiene. The butadiene rubber phase has grafted SAN (grafting) on its surface, which ensures compatibility between the two phases. The acrylonitrile provides thermal and chemical resistance, fatigue resistance, strength and stiffness; styrene provides ease of processing, gloss, hardness and rigidity; and butadiene provides ductility at low temperature, impact resistance, thermal stability and good surface finish.

The PC, a thermoplastic of amorphous origin, consists of long linear chains of polyesters of carbonic acid and phenols (phenyl) such as bisphenol A. The presence of phenyl group in the molecular chain and two methyl groups contributes to the rigidity of molecular PC. This rigidity has a large effect on the properties of PC, which contributes to the lack of mobility of the individual molecules, thus resulting in a good heat resistance and excellent impact resistance. For blends of PC/ABS, it is expected that the impact resistance is higher than that of the matrix component[7].

Typically the blend PC/ABS for vehicle applications has about 60 to 70% PC, since it is from this content that it is possible to perceive the earned properties in the blend. Due to economic and technical reasons, the blend used is the one that has intermediate cost and properties. There are specific applications where the properties of the PC/ABS blends are enough to achieve the necessary features for a specific piece.

The properties of different PC/ABS blends are determined mainly by the type of PC content as well as the proportion of the acrylonitrile butadiene and styrene monomers present in the ABS, as shown in Figure 1.
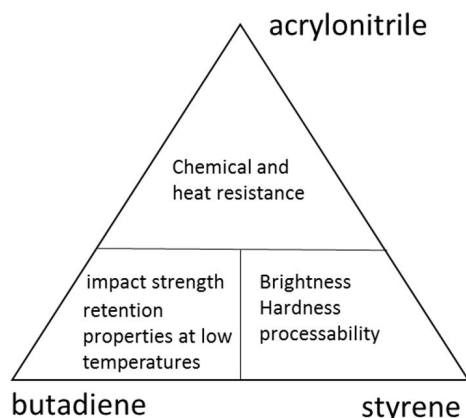

Figure 1. Influence of co-monomers in ABS properties[8].

The impact resistance of PC/ABS is one of its main properties, and the type used ABS and PC content exerts a strong influence on this property[8].

Blends produced with high value materials, such as ABS and PC, allow to obtain products with a wide range of physical, chemical and mechanical properties. Thus ABS contributes to a better processability and lower cost of the blend basically due to its cost per kilogram being less than the cost of PC. However, PC provides good mechanical and thermal properties to the blend, which justifies its use. These two materials have a strong chemical interaction, and are dependent on the percentage of the mixture of each component[7].

With the development of various polymers, there is also the need for the advancement of instrumental analysis techniques in order to determine the chemical structure of new materials and/or quantify them. As known, the FT-IR spectroscopy is one of the techniques that has merit for this purpose and has been successfully applied to various polymer systems in the group's laboratories of the *Divisão de Química* (AQI) of the *Instituto de Aeronáutica e Espaço* (IAE), including the use of last-edge techniques with surface analysis (universal attenuated total reflectance - UATR) in wide spectral range (mid-infrared, MIR, near-infrared, NIR, and others)[9-11].

The opportunity to develop a methodology applied to polymer blends, used in the automotive sector, is still not very explored; therefore, in the literature, FT-IR studies could be found for other types of materials for this sector, but not for the proposition of the present research.

Ruschel et al. reported it was possible to confirm the usefulness of this conventional technique, in combination with the chemometric tools HCA and PCA for diesel and biodiesel oil blends classification differentiating them from their infrared spectra even though these mixtures are composed of various types of biodiesel from three different raw materials soybean oil, residual oil and hydrogenated vegetable fat for frying and two alcoholic routes: methyl and ethyl[12]. In the study of Tahmassebi et al., it was analyzed the performance of automotive coatings, using different techniques, among which the infrared spectroscopy for monitoring the oxidation, applying the characteristic functional groups, when the ink is exposed to weathering test[13].

Therefore, given the presented scenario, the interest of the automobile company in the development of methodologies to assist in solving problems occurring in the field to manufactured using blends and the fact that studies including quantitative analysis by means of FT-IR technique transmission and reflection are mentioned in smaller numbers in the literature, there has been a great interest in the development of a quantitative method for blends of the type PC/ABS, which should lead to troubleshooting in the field, when the blend is applied to the workpiece, but not in the appropriate proportions of each material.

To achieve this purpose, the present study evaluates the applicability of FT-IR transmission and reflection (latest generation, as UATR) absorption spectroscopy, with existing laboratory facilities in AQI-IAE, for the identification and quantification of the polymer base, used in different automotive industrial formulations.

2. Materials and Methods

2.1 Samples

Different polymer blends PC/ABS were kindly prepared and provided by SABIC company. The donated samples were named: 100% PC resin LEXAN™ 123R-112, 100% ABS resin CYCOLAC™ MG37 EPX NA100, 30% PC/70% ABS, 50% PC/50% ABS, 70% PC/30% ABS. In addition, using the pure samples, 100% PC resin LEXAN™, 100% ABS resin CYCOLAC™ MG37 EPX NA 100, Mackenzie gently prepared the blends 40% PC /60% ABS, 80% PC /20% ABS.

For the preparation of the blends 40% PC/60% ABS and 80% PC/20% ABS, the previously weighed pure materials in their concentrations were mixed using the equipment Mix - MH Equipamentos Ltda., with subsequent extrusion of the material.

2.2 Methodology

The samples were analyzed in PERKINELMER SPECTRUM ONE FT-IR spectrometer (resolution 4 cm^{-1}, gain 1, range 4000 to 550 cm^{-1}, 20 scans) by means of reflection techniques, using accessory UATR and transmission (resolution 4 cm^{-1}, gain 1, range 4000 to 400 cm^{-1}, 20 scans).

Using previously prepared mixtures in the following concentrations: 30% PC/70% ABS, 40% PC/ 60% ABS, 50% PC/50% ABS, 70% PC/30% ABS, 80% PC/20% ABS, the calibration or analytical curve was built.

The films were prepared by dissolving in chloroform (five aliquots) being called cast films in accordance with the sample preparation techniques for IR analysis.

The preparation procedure of cast films of concentrations of 30% PC/70% ABS, 40% PC/60% ABS, 50% PC/50% ABS, 70% PC/30% ABS, and 80% PC/20% ABS was as follows: each of the above blends was weighed in an amount equal to the total weight 0.05g. We dissolved each of the blends in 15 mL of chloroform under stirring and heating. After the total dissolution of the material, samples were placed in Petri dishes, and 5 mL of chloroform were used to the beaker wash to ensure all the material was transferred to the Petri dishes and these were placed on a flat surface, waiting to complete evaporation of the chloroform in order to obtain a

cast film. For each sample, five aliquots were analyzed at the locations marked as 1, 2, 3, 4 and 5, as shown in Figure 2.

Analysis by UATR, the samples were analyzed by placing them in contact with the surface of the ZnSe diamond crystal, with application of torque (120 N). For analysis by transmission, the cast film was placed in the beam path, in marked areas.

The data were calculated according to Hórak and Vítek[14] form adopted in earlier work of the group and it was successfully carried out involving quantitative IR analysis[15-18]. For each sample, five aliquots were analyzed and, from the absorbance values, the median was calculated (μ). The standard deviation ($\hat{\sigma}_{\hat{\mu}}$) of the median absorbance is calculated according to Equation 1:

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

Where $\hat{\sigma}$ is the standard deviation and n is the number of measures. $\hat{\sigma}$ is given by Equation 2:

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

Where K_R is the coefficient for the calculation of the average standard deviation from the variation range of values (for 5 experiments, $K_R = 0.430$); and R is the difference between the largest and the lowest value of absorbance ($X_n - X_1$).

The relative error for each sample analyzed was determined using Equation 3:

$$Relative\,error\,(\%) = \left(\frac{\hat{\sigma}_{\hat{\mu}}}{\mu}\right) \times 100 \tag{3}$$

For the methodology of the calculation of error, it was adopted the median value[14] of the errors, as performed in previous studies[15-18].

The choice of the baseline, analytical and reference peak was made according to the lowest relative error and the largest correlation coefficient (R) in the calibration curves, as in previous work[15].
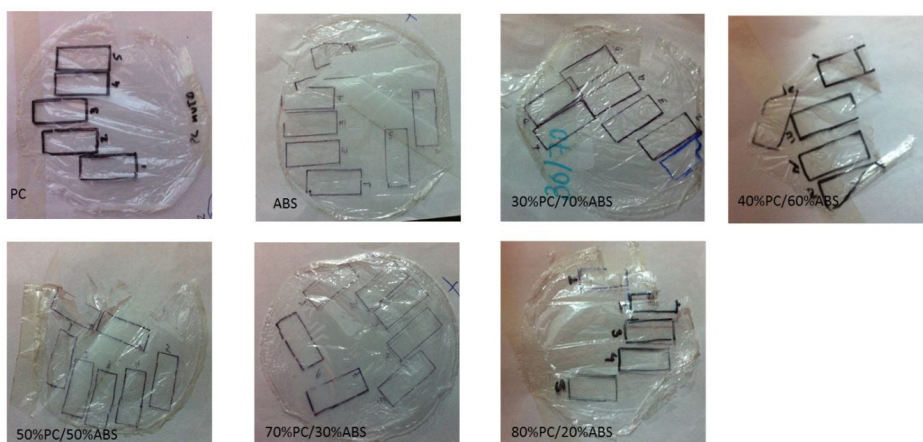

Figure 2. Cast films obtained after solvent evaporation (marked locations were analyzed by IR transmission and UATR).

3. Results and Discussion

3.1 FT-IR characterization by transmission of the main bands observed in the blend of ABS and PC

As the transmission method has a higher intensity of each characteristic band of each polymer, it was decided to place each of these for subsequent choice of analytical bands for the study. The absorption characteristics of the ABS polymer are (cm⁻¹): 3010-3110: axial deformation or aromatic C-H stretch, 2237: axial deformation C≡N, 1602: axial strain C═N and angular deflection of C−C of the aromatic ring, 1506: angular deformation ArCH, 1453: asymmetric angular deformation CH_3, 1365: symmetrical angular deformation CH_3, 966: angular deformation C═C, 735-765: angular deformation, ArCH (mono-substituted) and 697: aromatic C-H out of plane angular deformation[19].

The PC characteristics are absorptions at (cm⁻¹): 3010-3110: axial deformation aromatic C-H, 1775: axial deformation C═O, 1230, 1164, 1081 and 1015: axial deformation in C-O-C, 831: angular deformation aromatic C-H (para replacement)[19]. Figure 3 includes the FT-IR spectra in the MIR region of the pure polymers studied.

It can be observed through the bands indicated in Figure 4 that as there are increasing PC concentrations, the intensities of the bands at 1775 and 831 cm⁻¹ increase and the absorption found at 2237cm⁻¹ decreases associated with the corresponding decrease in acrylonitrile content, suggesting that it is possible to perform the determination of the levels of the blend by FT-IR because the analyzed system obeys the Lambert-Beer law[19], namely:

$$A = a \times b \times c \tag{4}$$

where A = absorbance, or absorption; a = molar absorptivity or molar extinction coefficient (characteristic band), the capacity of one mole of substance for absorbing light at a given wavelength or wavenumber or, in other words, how strongly a substance absorbs radiation at a specific frequency; b = thickness; c = concentration[19].

Therefore, for this study, based on the intensities and different positions of wave number for each polymer, the mentioned bands are chosen for the determination of contents of PC and ABS in the blend.

One of the causes of errors in IR quantitative analysis is the variation of intensity of the same concentration samples, due to thickness variations of these materials analyzed, and a mathematical artifice used in IR spectroscopy is to divide the values of the intensities of absorptions constituting the band on (A1/A2) as:

$$\frac{A1}{A2} = \frac{a1 \times b \times c1}{a2 \times b \times c2} \tag{5}$$
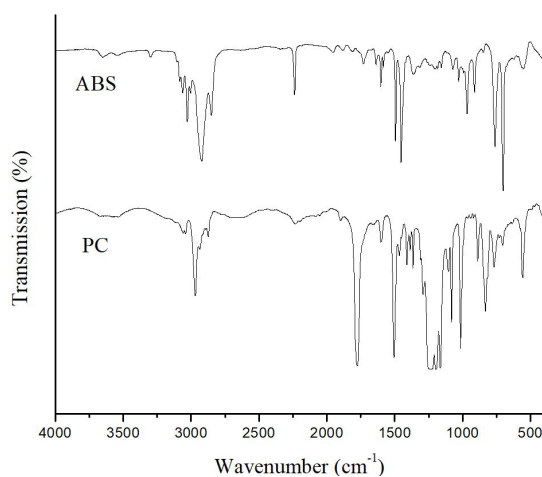

Figure 3. Spectra FT-IR (MIR - Transmission) of pure polymers.
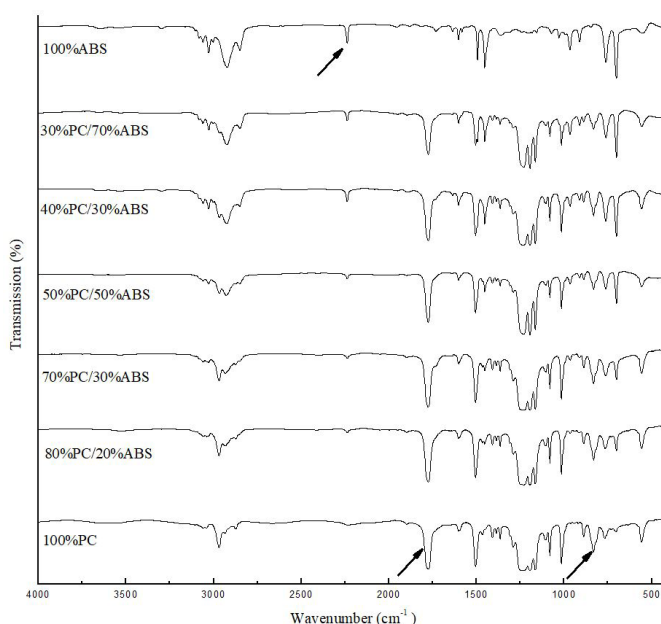

Figure 4. Spectra FT-IR (MIR - Transmission) of the polymer blend film.

Therefore, to eliminate the effect of the thickness in the calculation of the intensity of absorption of this determination, the analytical bands were used (A1 and A2) of each polymer as reference bands from one another, thereby composing a relative band PC/ABS. For the application of the Lambert-Beer law, the absorbance data obtained were placed on a function of the relative concentration[20].

3.2 Choice of analytical bands of ABS and PC, UATR method

Just as was done in the transmission method, we studied the determination by the reflection method, with UATR accessory. Remember that a slight difference may occur in the position of each of the analytical bands in these different methods for collecting the infrared spectra.

The absorption at 697 cm⁻¹ was chosen as the analytical band for determining the content of ABS, and those found at 1770 and 829 cm⁻¹ for determining the content of PC in the blend, all indicated in Figure 5. These bands were chosen as analytical, therefore, it can be seen that the increase in the intensity of the band at 697 cm⁻¹ is related to the increase in the ABS content, as well as at the bands of 1770 and 829 cm⁻¹, with the increase in PC content in the blend. The band of 2237 cm⁻¹, referring to the ABS, did not show good response to this method, because of its low intensity, so it was not chosen as analytical band.

3.3 Choice of the reference band, UATR method

Table 1 shows the analytical bands adopted and their respective baselines. The absorption at 697 cm⁻¹ was at baseline 718-660 cm⁻¹, 1840-1694 cm⁻¹ for the band 1770 cm⁻¹, and

864-793 cm⁻¹ for the band at 829 cm⁻¹, with similar methodology for baseline evaluation used by Rodrigues et al.[17]. As for eliminating the effect of the thickness, the reference band used in this case was the analytical band of ABS, the band at 697 cm⁻¹. The use of reference band, to compose a relative band, improves accuracy of the methodology[17].

Table 2 shows the analytical bands, the chosen baselines and results as relative error in the methodology and correlation coefficients R.

Evaluating Table 2, the bands at 829 and 697 cm⁻¹, respectively, for PC and ABS, show the set of lower data error (3.20%) and the correlation coefficient (0.99).

3.4 Choice of analytical bands of ABS and PC, transmission method

As previously mentioned, for this study, based on the intensities and different positions of wave number for each polymer, the absorption at 2237 cm⁻¹ was chosen as the analytical band to determine the ABS content, and two possibilities of analytical bands, 1775 and 831 cm⁻¹, to determine the content of PC in the blend, all already mentioned in Figure 4. The baselines adopted for the measurements are shown in Table 3. Likewise, as has been previously reported for

Table 1. Baselines for analytical band ABS and PC.

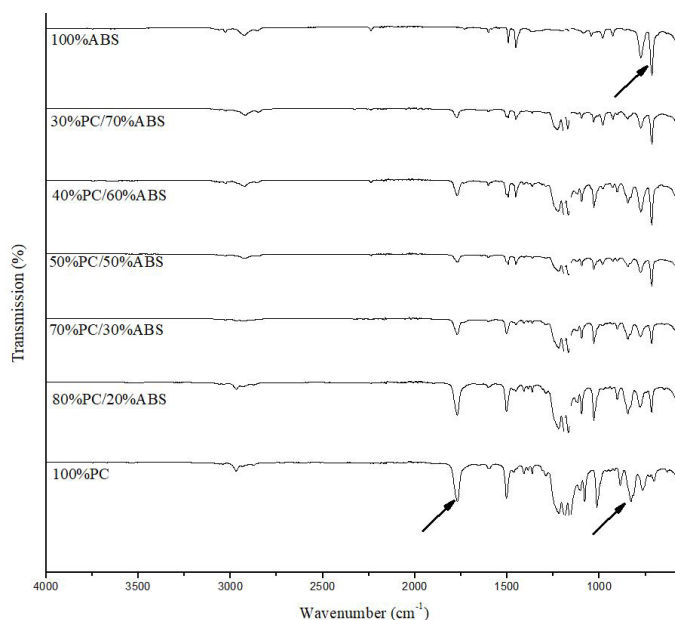| Polymer type	Analytical band (baseline) cm⁻¹
ABS	697 (718-660)
PC	1770 (1840-1694)
	829 (864-793)

Figure 5. Spectra FT-IR (MIR - Reflection - UATR) of the polymer blend film.

Table 2. FT-IR data errors in the methodology and correlation coefficient of different analytical bands analyzed for the blend PC/ABS.

Analytical band (baseline) cm⁻¹	Analytical band (baseline) cm⁻¹	Relative error in the methodology	Correlation coefficients R
1770 (1840-1694) C=O	697 (718-660) ArCH	7.10	0.99
829 (864-795) ArCH (para replacement)	697 (718-660) ArCH	3.20	0.99

the UATR method, these bands were chosen as analytical, therefore, it can be seen that the increase in the intensity of the band at 2237 cm⁻¹ is related to the increase in the ABS content, as well as in the bands 1775 and 831 cm⁻¹, with the increase in PC content in the blend.

3.5 Choice of the reference band transmission method

Table 3 refers to the adopted analytical bands and their respective baselines. The choice of the best set of analytical bands occurred after evaluating the accuracy in measuring the intensity of the band.

Table 4 shows the analytical bands analyzed, chosen baselines and results as relative error in the methodology and correlation coefficient R. Bands at 831 and 2237 cm⁻¹, respectively, for PC and ABS, showed the lowest error (0.99%), the and highest correlation coefficient (0.96). Considered a best result compared to other pairs of bands of the analytical methods previously assessed, these absorptions were adopted as relative band (A_{831}/A_{2237}) to study transmission.

Table 5 shows the results obtained by applying Equations 1, 2 and 3 for the relative band (A_{831}/A_{2237}) taking into account the relative concentration, in an attempt to achieve higher precision. The error methodology, which is the median of the relative error, is 0.99, within the limits of measurement accuracy ($\leq 2\%$).

3.6 Calibration curve obtained by transmission

Figure 6 shows the analytical transmission curve (A_{831}/A_{2237}) *versus* relative concentration (PC concentration/ABS concentration). From the analytical curve, Equation 6, the following correlation (R = 0.96) is proposed:

$$y = 2.451x + 1.260 \tag{6}$$

Table 3. Baselines for analytical bands of ABS and PC.

Polymer type	Analytical band (baseline) cm⁻¹
ABS	2237 (2280-2184)
PC	1775 (1840-1690)
	831 (864-791)

Where y is the median value of A_{831}/A_{2237} example, the relative concentration (PC concentration/ABS concentration) in the polymer blend.

3.7 Choice of analytical band ABS and PC, transmission method, evaluation of polycarbonate concentration

Until then, it was considered the correlation coefficient R with respect to the relative concentration, aiming to find a more precise methodology according to the analyzed system. In the next paragraph, the concentration of polycarbonate will be taken into account and not the relative concentration.

The idea is based on the fact that there are several types of ABS polymers with different concentrations of each of the monomers present in the blend, and the content of each monomer will vary according to the application. It is important to note that the polymer ABS, which was kindly supplied by SABIC, presents 100% of ABS resin of the type CYCOLAC™ MG37 EPX NA 100, wherein the amount of each monomer is considered confidential information for supplier.

Therefore, for this method to be applied in any type of ABS, it was decided to develop the construction of a calibration curve taking into account the concentration
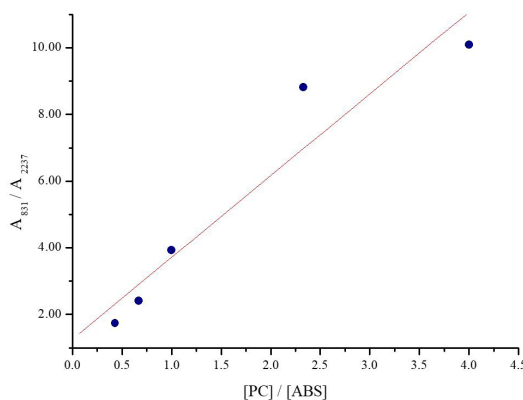
Figure 6. Relative absorbance values (A_{831}/A_{2237}) obtained by transmission *versus* relative concentration.

Table 4. FT-IR data relative errors in the methodology and correlation coefficient of different analytical bands analyzed for the blend PC/ABS by evaluating the relative concentration.

Analytical band (baseline) cm⁻¹	Analytical band (baseline) cm⁻¹	Relative error in the methodology %	Correlation coefficient R
1775 (1840-1690) C=O	2237 (2280-2184) C≡N	1.57	0.94
831 (864-791) ArCH (para replacement)	2237 (2280-2184) C≡N	0.99	0.96

Table 5. FT-IR data of the median, standard deviations average, relative errors and error in the chosen relative band A_{831}/A_{2237}.

[ ] PC	[ ] Relative [PC]/[ABS]	Median μ	Standard deviation ($\hat{\sigma}_{\hat{\mu}}$)	Relative error %	Error in the methodology %
30	0.43	1.739	0.017	0.99	
40	0.67	2.204	0.022	0.92	
50	1.00	3.921	0.061	1.55	0.99
70	2.33	8.808	0.141	1.60	
80	4.00	10.089	0.099	0.98	

of the PC, and not the relative concentration (PC/ABS). As the best results were already cited in Table 4, these are the values used for the development of this methodology.

Table 6 shows the analyzed analytical bands, chosen baselines, results of relative errors in the methodology and correlation coefficients R. Bands at 831 and 2237 cm⁻¹, respectively, for PC and ABS are also those with the lowest error (0.99%) and the highest correlation coefficient (0.99). Considered a best result compared to other pairs of bands of the analytical methods previously assessed, these absorptions were adopted as relative band (A_{831}/A_{2237}) to study transmission.

Table 7 contains the results obtained by applying Equations 1, 2 and 3 for the relative band (A831/A2237), taking into account the PC concentration. Remember that the values of the median, average standard deviation and relative error are the same as already calculated and shown in Table 5. The error methodology, which is the median of the relative error, is 0.99, within the limits of precision instrument ($\leq 2\%$).

3.8 Calibration curve obtained by transmission, evaluation of polycarbonate concentration

Figure 7 shows the analytical transmission curve (A_{831}/A_{2237}) *versus* PC concentration. From the analytical curve, Equation 7, the following correlation (R = 0.99) is proposed:

$$y = 18.149x + 4.408 \tag{7}$$

Where *y* is the median value of A_{831}/A_{2237} and *x* is the PC concentration in the polymer blend.

3.9 Calibration curve test for transmission technique

According to what has been stated above, the bands at 831 and 2237 cm⁻¹, respectively, for PC and ABS, present the lowest error and showed the highest correlation coefficient, using the relative concentration and PC concentration. Therefore, the two showed methods will be used to assess the test sample. This is a verification procedure of the methodology, where two samples were analyzed with the following concentrations: 70% PC/30% ABS for sample

A and 50% PC/50% ABS for sample B. These samples were prepared using the same materials applied to construct the calibration curve. Another test sample, sample C, was prepared with the following concentration: 50% PC/50% ABS, this ABS is of the type Novodur™ P2MC, material kindly donated by Styrolution company and the PC is of the same type used above (Resin LEXAN™). With Equations 6 and 7, the amount of PC concentrations was calculated using the methodology of relative concentration and PC concentration.

Using Equation 6, it was calculated the value of the PC concentration, being y the median relative analytical band (A_{831}/A_{2237}) obtained in the analysis, and x is the value (%) of relative concentration (PC concentration/ABS concentration).

For the calculation of ABS and PC concentrations, it was used Equation 8:

$$X = \frac{[PC]}{[ABS]} \Rightarrow [PC] = X[ABS] \tag{8}$$

Substituting Equation 8 into Equation 9, it is calculated the value of the ABS concentration. The percentage (%) of PC was calculated by difference for a total of 100%. The values found are shown in Table 8.
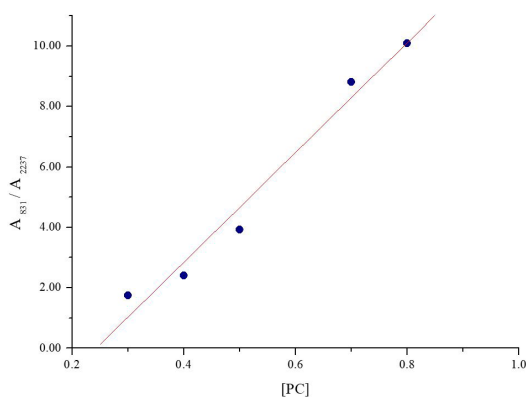

Figure 7. Relative absorbance values (A_{831}/A_{2237}) obtained by transmission *versus* PC concentration.

Table 6. FT-IR data errors in the methodology and correlation coefficient of different analytical bands analyzed for the blend PC/ABS, evaluation of polycarbonate concentration.

Analytical band (baseline) cm⁻¹	Analytical band (baseline) cm⁻¹	Relative error in the methodology %	Correlation coefficient R
1775 (1840-1690) C=O	2237 (2280-2184) C≡N	1.57	0.98
831 (864-791) ArCH (para replacement)	2237 (2280-2184) C≡N	0.99	0.99

Table 7. FT-IR data of the average deviations and errors in the chosen relative band A_{831}/A_{2237}.

[PC]	Standard deviation ($\hat{\sigma}_{\hat{\mu}}$)	Relative error %	Error in the methodology %
30	0.017	0.99	
40	0.022	0.92	
50	0.061	1.55	0.99
70	0.141	1.60	
80	0.099	0.98	

Table 8. Calculation of the concentrations of PC/ABS of the samples from tests A, B and C by using a relative concentration.

Sample	Concentration	PC concentration	ABS concentration
A	70% PC/30% ABS	75.5	24.5
B	50% PC/50% ABS	52.3	47.7
C	50% PC/50% ABS	51.1	48.9

Table 9. Calculation of the concentrations of the PC/ABS of the samples from tests A, B and C by using the PC concentration.

Sample	Concentration	PC concentration	ABS concentration
A	70% PC/30% ABS	72.8	27.2
B	50% PC/50% ABS	46.0	54.0
C	50% PC/50% ABS	45.3	54.7

$$[PC] + [ABS] = 100\% \tag{9}$$

Using Equation 7, it was calculated the value of the PC concentration, being y the median relative analytical band (A_{831}/A_{2237}) obtained in the analysis, and x is the value (%) of PC concentration. The percentage (%) of ABS was calculated by difference for a total of 100%. The values found are shown in Table 9.

Although both methods have shown good accuracy, the one which takes into account the relative concentration showed better results in comparison with PC concentration when applied to the calibration curve of the test, even with a different type of ABS used.

4. Conclusion

This study demonstrated the application of FT-IR spectroscopy in the MIR region for the characterization and quantification of automotive blends of PC/ABS using two methodologies: UATR and transmission. Some relative bands were evaluated using both methods, while the A_{831}/A_{2237} showed better results, that is, the lowest relative error and the highest correlation coefficient, when applied to the transmission method. As there are many types of ABS polymers with different concentrations of each of the monomers present in the blend, two calibration curves were constructed using the relative concentration and also the PC concentration. Both curves proved useful to characterize and quantify the content of each polymer present in the polymer blend PC/ABS, with a better accuracy for the observed found in the relative concentration.

The methodological error found in MIR methodology - Transmission (0.99%) for the two calibration curves used is within the accuracy limit of FT-IR spectrometer ($\leq$2%), so the methodology is accurate.

5. References

1. Hemais, C. A. (2003). Polímeros e a indústria automobilística. *Polímeros: Ciência e Tecnologia*, *13*(2), 107-114. http://dx.doi.org/10.1590/S0104-14282003000200008.

2. Cordebello, F. S. (2003). Polímeros do futuro – tendências e oportunidades: palestras técnicas (II). *Polímeros: Ciência e Tecnologia*, *13*(1), e4-e43. http://dx.doi.org/10.1590/S0104-14282003000100003.

3. Neto, N. J. R. (2012). *A evolução dos polímeros na indústria automobilística* (Term paper). Sorocaba: Faculdade de Tecnologia do Estado de São Paulo – FATEC. Retrieved in 2014, April 16, from //fatecsorocaba.edu.br/principal/pesquisas/nuplas/dissertacoes/TCCs1sem2012/TCC_Nelson_Joao.pdf

4. Dornelles, A. M. L. F., & Atolino, W. J. T. (2009). *Plásticos de engenharia: seleção eletrônica no caso automotivo*. São Paulo: Artliber Editora.

5. Novaes, I. C. (2010). *Estudo das propriedades físico-mecânicas da blenda ABS/PC* (Term paper). São Paulo: Faculdade de Tecnologia do Estado de São Paulo – FATEC. Retrieved in 2014, March 11, from http://www.scribd.com/doc/221425914/Acrilonitrila-Butadieno-Estireno-Estudo-Propriedas Fisico-Mecanica

6. Carvalho, C. (2009). *Reciclagem primária de ABS: propriedades mecânicas, térmicas e reológicas* (Master's dissertation). Universidade do Estado de Santa Catarina, Joinville.

7. Candido, L. H. A. (2011). *Estudo do ciclo de reciclagem de materiais em blendas acrilonitrila butadieno estireno/policarbonato* (Doctoral thesis). Universidade Federal do Rio Grande do Sul, Porto Alegre.

8. Simielli, E. R., & Santos, P. R. (2010). *Plástico de engenharia, principais tipo e sua moldagem por injeção*. São Paulo: Artiliber.

9. Santos, R. P., Oliveira, M. S., Mattos, E. C., Diniz, M. F., & Dutra, R. C. L. (2013). Study by FT-IR technique and adhesive properties of vulcanized EPDM modified with plasma. *Journal of Aerospace Technology and Management*, *5*(1), 65-74. http://dx.doi.org/10.5028/jatm.v5i1.162.

10. Sanches, N. B., Diniz, M. F., Alves, L. C., Dutra, J. C. N., Cassu, S. N., Azevedo, M. F. P., & Dutra, R. C. L. (2008). Avaliação da aplicabilidade de técnicas FT-IR de reflexão (UATR) e de transmissão para a determinação do teor de acrilonitrila (AN) em NBR. Polímeros. *Ciência e Tecnologia*, *18*(3), 249-255. http://dx.doi.org/10.1590/S0104-14282008000300011.

11. Nogueira, L. M., Dutra, R. C. L., Diniz, M. F., Pires, M., Evangelista, M., Santana, F. A., Tomasi, L., Santos, P., & Nonemacher, R. (2007). Avaliação da aplicabilidade de técnicas MIC/FT-IR/DSC para caracterização de filmes multicamadas. *Polímeros: Ciência e Tecnologia*, *17*(2), 158-165. http://dx.doi.org/10.1590/S0104-14282007000200015.

12. Ruschel, C. F. C., Huang, C. T., Samios, D., & Ferrão, M.F. (2014). Análise exploratória aplicada a espectros de reflexão total atenuada no infravermelho com transformada de Fourier (ATR-FTIR) de blendas de biodiesel/diesel. *Quimica Nova*, *37*(5), 810-815. http://dx.doi.org/10.5935/0100-4042.20140130.

13. Tahmassebi, N., & Moradian, S. (2004). Predicting the performances of basecoat/clearcoat automotive paint system by the use of adhesion, scratch and mar resistance measurements. *Polymer Degradation & Stability*, *83*(3), 405-410. http://dx.doi.org/10.1016/j.polymdegradstab.2003.09.002.

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

15. Mattos, E. C., Moreira, E. D., Dutra, R. C. L., Diniz, M. F., Ribeiro, A. P., & Iha, K. (2004). Determination of the HMX and RDX content in synthesized energetic material by HPLC, FT-MIR, and FT-NIR spectroscopies. *Quimica Nova*, *27*(4), 540-544. http://dx.doi.org/10.1590/S0100-40422004000400005.

16. Siqueira, S. H. S., Diniz, M. F., & Dutra, R. C. L. (2008). Determinação por espectroscopia nas regiões MIR/NIR do teor de NCO em adesivos poliuretânicos. *Polímeros: Ciência e Tecnologia*, *18*(1), 57-62. http://dx.doi.org/10.1590/S0104-14282008000100012.

17. Rodrigues, V. C., Diniz, M. F., Mattos, E. C. & Dutra, R. C. L. (2014). Quantificação por NIR/MIR de resina poliuretânica em misturas binárias com nitrocelulose, utilizadas em tintas. *Polímeros: Ciência e Tecnologia*, *24*(3), 367-372. http://dx.doi.org/10.4322/polimeros.2014.027.

18. Damazio, D., Diniz, M. F., Mattos, E. C., & Dutra, R. C. L. (2014). Determinação por FT-IR de transmissão e reflexão (UATR) de etileno e propileno em EPDM. *Polímeros: Ciência e Tecnologia*, *24*(6), 703-710. http://dx.doi.org/10.1590/0104-1428.1536.

19. Smith, A. L. (1979). *Applied infrared spectroscopy*. New York: John Wiley & Sons.

20. Mattos, E. C. (2007). *Caracterização e quantificação por meio de técnicas FT-IR, HPLC e TG de polímeros utilizados em composições de explosivos plásticos* (Doctoral thesis). Instituto Tecnológico de Aeronáutica, São José dos Campos.