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Infrared Spectroscopy Applied to Materials Used as Thermal Insulation and Coatings

Natália Beck Sanches¹, Ricardo Pedro¹, Milton Faria Diniz², Elizabeth da Costa Mattos², Silvana Navarro Cassu², Rita de Cássia Lazzarini Dutra²

ABSTRACT: It is very important to control the characteristics of a polymer used in rubber compositions and paints in aerospace applications. Hence, the development of simple and fast methodologies that allow the identification of these compositions becomes attractive to researches carried out in this area. This study has evaluated infrared (IR) techniques, such as transmission, universal attenuated total reflection (UATR), and attenuated total reflection (ATR), for the characterization of elastomers and paints. It takes into consideration the characteristics of surface techniques, such as the depth of penetration of the IR beam into the sample. The presence of additives in low concentrations on paints was only detected by UATR after grinding the components. Results show that it is possible to differentiate rubber mixtures with similar IR spectra and to detect small amounts of additives in the surface of coatings.

KEYWORDS: Rubbers, paints, infrared, FT-IR, ATR, UATR.

INTRODUCTION

Polymers are used in many industrial areas, such as the aerospace (Dutra *et al.*, 2002; Oliveira *et al.*, 2011). Their different types, with specific characteristics, are used in propellant (Sciamareli *et al.*, 2012), composites, rubbers (Ferrari *et al.*, 2012; Santos *et al.*, 2013), and coatings (Blackford, 1999).

The resin most often utilized in aerospace applications is hydroxyl terminated polybutadiene (HTPB), which is used in propellants and flexible insulation protection (Lourenço *et al.*, 2006; Crespim *et al.*, 2007). It is known that phenolic resins are employed in composites for rigid thermal insulation, while epoxy are used in adhesive compositions for these same protections and in polymer arrays for the aeronautical sector (Pardini, 2000). Rubbers are used in flexible thermal insulation, and the most cited ones in literature for using in aerospace applications are copolymers of acrylonitrile and butadiene (NBR) and ethylene-propylene-diene rubber (EPDM) (Moraes *et al.*, 2007).

Traditionally, aircraft paints are coatings with specific characteristics and requirements, because in extreme cases the use of a defective one may contribute to injuries in a catastrophic scale (Blackford, 1999). The requirements are associated with the environment in which modern aircrafts are used and how they are painted, among other factors. Thus, there are significant differences in formulations used for the aerospace sector compared to other industrial areas, allowing the use of products that can cause damage to people's health, such as chromate pigments, or to the environment, like large amounts of solvents.

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Generally, solvents are used to decrease viscosity and facilitate the application of paints. The vehicle or binder is the chemical component that will generate a film on the surface, besides being responsible for keeping the other constituents scattered and clumped. Fillers are materials that provide specific properties to paints, for example, the magnetic nanoparticles that turn aircrafts non-detectable to radars. The additives are compounds used from storage to product application. For example, microbicides preserve the paint during its storage and catalysts reduce the time of film formation during product application (Mello *et al.*, 2012).

With regard to the analysis of polymers used in the aerospace industry, there are studies in the literature (Sanches *et al.*, 2006; ASTM D3677-10, 2010; Romão *et al.*, 2006; Hori *et al.*, 1990) that employ mid infrared (MIR) spectroscopy for identification, characterization, and quantification of materials. In these investigations, analyses of materials using Fourier transform infrared (FT-IR) techniques with variation of the parameters, in different layers of the surface, were not explored.

It is also known that some components present in paints cannot be directly analyzed by using conventional FT-IR techniques, because the characteristic bands overlap with absorptions of other components often seen in high concentrations. Although the study of bands overlapping could be done by using mathematical methods, such as derivatives and deconvolution to quantify components, these ones, in some cases, are complex and depend on the thickness of the analyzed samples. This limitation becomes even more relevant when additives are present in extremely low concentrations. A specific methodology must then be studied.

The FT-IR literature emphasizes that, in the analysis of multiple components systems, there are factors to be considered: influence of sample preparation, total or partial analyses of composition (Allen, 1992; Dutra *et al.*, 1995), and the technique used to obtain the spectrum, single or coupled (Mattos *et al.*, 2004; Almeida *et al.*, 2002; Mateo *et al.*, 2009). In these cases, it is helpful to perform the evaluation of characteristic functional groups, the query to the database of reference spectra (Smith, 1979) using spectra software (Szafarska *et al.*, 2009), and the interpretation of similar studies to highlight the limitations and potential of techniques (Miliani *et al.*, 2002).

Different FT-IR techniques may be suitable for the study of many kinds of materials, according to their characteristics. The most common surface technique is the attenuated total reflection (ATR), which can be used for the analysis of liquid and dried paint films (Mazzeo *et al.*, 2007; Zhang *et al.*, 2009). In the ATR spectroscopy, the radiation passing through the crystal reflects totally on its internal surface (Waltham, 2005). When a radiation absorbing material is placed in contact with a crystal, the infrared (IR) beam penetrates the thin layer of the sample surface and loses energy, causing the attenuated total reflectance. In this technique, good contact between the sample and the crystal is essential (Pandey and Kulshreshtha, 1993).

The penetration depth of the IR beam into the sample depends on the IR radiation angle of incidence, the radiation wavelength, and the refractive indices of the crystal and sample. Ge crystals are able to analyze thinner surfaces (Pandey and Kulshreshtha, 1993). In the ATR technique, different species of the sample surface and interior can be revealed depending on the analysis procedure. The literature reports (Pandey and Kulshreshtha, 1993; PerkinElmer, 2005) and experiences indicate that this aspect must be considered if the study requires selective analysis of the very superficial layer.

Ultimate FT-IR techniques, such as the universal ATR (UATR), have found prominence in the analysis of different materials (PerkinElmer, 2005; Abidi and Hequet, 2005). This technique of internal reflection is able to perform nondestructive analysis of solids, powders, liquids, and gels. In it, the IR beam passes through an ATR element composed of ZnSe (refractive index 2.67) or diamond-KRS-5 (refractive index 2.42), with high refractive index, and reaches the surface of the sample.

One of the prerequisites of the UATR technique is good contact between the crystal and the sample surface. The probe strength can be adjusted to obtain the most suitable contact, since different pressure levels influence directly on the intensities of the obtained spectra. Because the IR beam does not penetrate deeply into the sample, this technique is suitable for analyzing surfaces with thickness of only a few microns (Pandey and Kulshreshtha, 1993).

It was observed in the literature some gaps related to the use of surface FT-IR techniques, varying the degree of sampling depth. Hence, it was concluded that it is essential the development of new characterization methodologies that

enable rapid identification of the different materials used in the aerospace industry. The aim of this work was to show the new results obtained by the Chemical Department of the *Instituto de Aeronáutica e Espaço* (AQI/IAE), in the characterization of different types of materials by using FT-IR reflection techniques, such as ATR and UATR. In addition, the transmission FT-IR technique was applied to identify rubber mixtures.

EXPERIMENTAL

The nitrile rubber (NBR) and rubber mixtures used in this study were prepared in AQI/IAE. The paint and additives were provided by Rohm and Haas. The chemical structure of the additives carbendazim (2-methoxycarbonylamino-benzimidazole), Diuron (N'-(3,4-dichlorophenyl)-N, N-dimethylurea) and OIT (2-N-octyl-4-isothiazolin-3-one) is shown in the text. Portions of the samples, before and after extraction with acetone, were also subjected to Beilstein and acid-resistance tests (Dutra and Diniz, 1993). A treatment with heated ortho-dichlorobenzene was performed as well.

EVALUATION OF TRANSMISSION AND REFLECTION FT-IR TECHNIQUES FOR CHARACTERIZATION OF RUBBERS

NBR was analyzed qualitatively by transmission, preparing the sample by pyrolysis (Smith, 1979) after extraction in methanol for eight hours, using the liquid film technique. For the UATR analysis, the NBR sample was placed in contact with the surface of the crystal and a force of 80 N was applied with the aid of an articulated arm. For ATR (KRS-5 or Ge) analysis, the NBR sample was placed on both sides of the crystal. In this study, KRS-5 (TlBr-crystal mixture TII) with refractive index 2.4 and Ge with refractive index 4.0 crystals were utilized. The filler was analyzed by transmission, preparing the specimen with the KBr disc technique.

EVALUATION OF TRANSMISSION FT-IR TECHNIQUES FOR CHARACTERIZATION OF RUBBERS AND THEIR MIXTURES

An unknown mixture of rubbers was analyzed qualitatively by transmission, preparing the sample by pyrolysis after extraction for eight hours in acetone, using

the liquid film technique (Smith, 1979). All analysis were performed using the spectrometer Spectrum One PerkinElmer (resolution 4 cm⁻¹, gain 1, spectral range 4000–400 cm⁻¹, 40 scans).

UATR ANALYSIS OF PAINTED SURFACE

A paint film was applied on a flat glass substrate. After drying, the film was removed by scraping and then analyzed. The paints additives were analyzed directly, without the need of sample preparation. UATR analysis was performed using the spectrometer Spectrum One, PerkinElmer, DTGS detector (resolution 4 cm⁻¹, spectral range 4000–550 cm⁻¹, gain 1, 20 scans). Spectra were obtained using the accessory UATR and applying a force of 80 N.

RESULTS AND DISCUSSION

This section presents the evaluation of FT-IR techniques for the analysis of elastomers and paints, using methods traditionally applied and developed in AQI/IAE laboratories.

APPLICABILITY OF TRANSMISSION AND REFLECTION FT-IR TECHNIQUES FOR CHARACTERIZATION OF RUBBERS

It is known that conventional FT-IR techniques can be applied to the characterization of rubbers (Matheson *et al.*, 1994; Wake *et al.*, 1983; Williams and Besler, 1995). In this work, different information is obtained by using independently transmission (liquid phase of pyrolyzate) and reflection (ATR and UATR) techniques. These were used for the characterization of the polymer and the filler, respectively.

Figure 1 shows the FT-IR spectra obtained from NBR analysis by using different techniques. It is observed that the analysis of the liquid phase of the pyrolyzate resulted in a spectrum (Fig. 1a) with the base polymer characteristic absorptions. The band observed at 2237 cm⁻¹ is assigned to the stretching of the C-N group, and the peaks in the region of 1000–900 cm⁻¹ are assigned to the wagging bending vibration of vinyl and trans C=C groups. In the spectra obtained by reflection using different crystals (Figs. 1b, 1c and 1d), the band at 2237 cm⁻¹ showed lower intensity and there was a contribution of Si-O groups in the region of 1100–900 cm⁻¹,

the latter related to the load used in the formulation (Smith, 1979). Figure 1e shows these load-related bands, analyzed by transmission (KBr pellet), after rubber calcination.

Although the spectra obtained by using reflection techniques did not clearly evidence the absorptions of NBR, they were able to indicate the filler used in the formulation. In order to obtain the same filler related information by using transmission techniques, it is necessary to apply supplementary sample preparation techniques, such as KBr pellet after rubber calcination.

The use of reflection techniques can also be applied to the detection of silica filler in silicone rubbers, instead of using a large number of techniques to achieve the same goal. This is important because applying some sample preparation techniques for transmission analysis, such as calcination, can induce the formation of silicon oxide in this type of rubber.

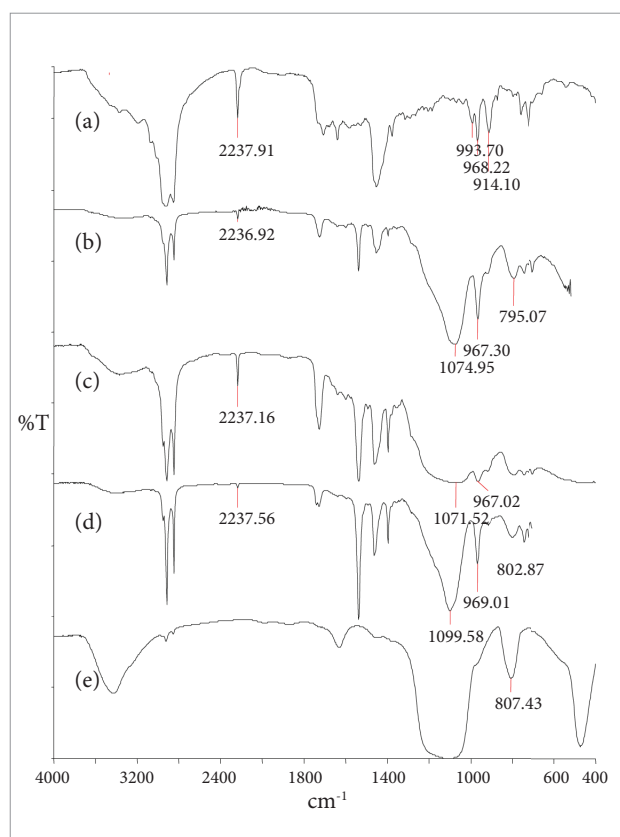


Figure 1. FT-IR spectra obtained from analysis of the nitrile rubber through different techniques: (a) Nitrile rubber transmission pyrolyzed (liquid film), (b) Nitrile rubber – UATR, force 80, (c) Nitrile rubber – ATR/KRS-5, (d) Nitrile rubber – ATR/Ge, and (e) residue obtained after calcination of rubber on Bunsen burner – transmission, KBr pellet.

It might lead to misinterpretation, since not all silicone rubbers have silica as filler.

APPLICABILITY OF FT-IR TRANSMISSION TECHNIQUES FOR THE CHARACTERIZATION OF RUBBERS AND THEIR MIXTURES

As it is known, pyrolysis of rubbers without solvent extraction is performed only to determine the base polymer and the best solvent for its extraction. Because additives bands are also observed, it is necessary to extract the rubber sample in order to obtain a spectrum that shows only characteristic bands of the polymer (Smith, 1979; Wake *et al.*, 1983). The identification of rubber mixtures by using FT-IR is possible, providing that their characteristic bands are different, without the occurrence of overlapping.

Figure 2 illustrates the application of the FT-IR transmission technique (pyrolysis without control of temperature) to an unknown mixture of rubbers, with and without extraction.

The main absorptions observed in the spectrum of the pyrolyzed rubber without extraction (Fig. 2a) and their attributions (Smith, 1979) are: 1376 cm^{-1} , angular bending vibration (δ) of CH_3 groups; 991 and 909 cm^{-1} , wagging bending vibration (ω) of vinyl group; 964 cm^{-1} , wagging bending vibration of trans groups; and 887 cm^{-1} , wagging bending vibration of vinylidene groups. These absorptions positions, shapes, and intensities suggest the presence of EPDM and/or NR (poly cis-isoprene or natural rubber) elastomers, which requires the use of acetone solvent for removal of the plasticizer and other additives (Wake *et al.*, 1983).

The sample was extracted for eight hours in Soxhlet apparatus, using acetone as the solvent. Then, it was pyrolyzed and analyzed as a liquid film (Fig. 2b). The same main bands were observed, as expected, because plasticizers used in EPDM and NR formulations are apolar and their groups do not contribute with different absorptions in the spectrum of the pyrolyzates without extraction. The band at 887 cm^{-1} is characteristic of NR rubber, but it is also present in the EPDM rubber. To further elucidate the chemical structure of the sample, a comparison was made between the IR spectrum of this sample and that of known EPDM and NR rubbers, pyrolyzed after extraction in acetone (Figs. 2b and 2c).

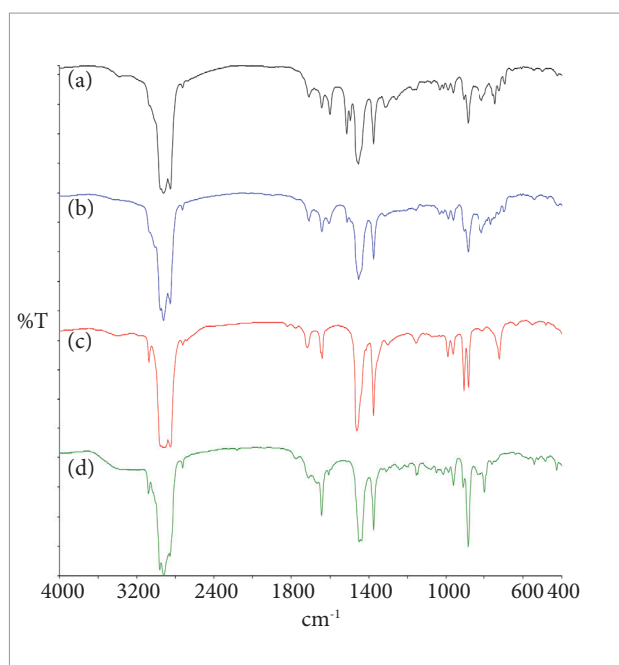


Figure 2. FT-IR spectra of (a) sample pyrolyzed without extraction, (b) sample pyrolyzate after extraction with acetone, (c) spectrum of known EPDM, pyrolyzed after extraction with acetone, and (d) spectrum of known NR, pyrolyzed after extraction with acetone.

To better identify the EPDM bands, it was also applied a treatment with hot ortho-dichlorobenzene to the sample, which was then pyrolyzed to obtain the IR spectrum. The resultant IR spectrum (Fig. 3a) showed more clearly the presence of EPDM rubber (bands marked with an asterisk), as can be visualized in Fig. 3b.

The Beilstein test was performed before and after extraction in acetone to confirm the absence of halogen compounds, expected because EPDM and NR do not present halogens in their compositions. The negative result corroborates the hypothesis of the presence of these elastomers.

The acid-resistance test, which basically classifies the rubber resistance when treated with an acid mixture at 40°C and 70°C, was also performed in the sample to elucidate the mixture composition. The sample did not show degradation at 40°C in the time established for the test, i.e. 15 minutes (Dutra and Diniz, 1993). At 70°C, it was observed degradation in around three minutes, confirming that the rubber has a certain content of EPDM. If the sample contained only NR, it would resist for only a few seconds, for less than one minute.

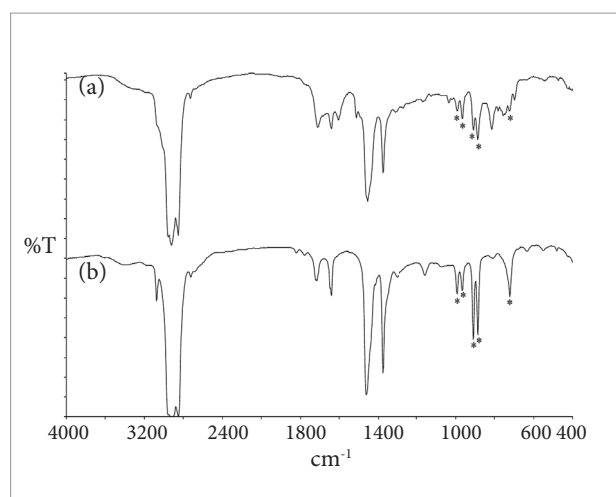


Figure 3. FT-IR spectra of (a) pyrolyzed insoluble portion, after ortho dichloro benzene treatment (previously extracted in acetone for eight hours), and (b) pyrolysed EPDM (reference).

Basically, FT-IR analysis of the liquid pyrolysis products, associated with Beilstein and acid resistance tests (Dutra and Diniz, 1993), within the detection limits of the FT-IR technique, indicated that the unknown rubber consists of NR and EPDM.

The utilization of acid-resistance test to characterize rubber mixtures (Dutra and Diniz, 1993), also developed in IAE/AQI, is important especially in EPDM mixtures. This elastomer is considered as a replacement for NBR in the aerospace industry. The addition of NR in a rubber mixture may be intended to lower the cost, but it certainly affects properties. Hence, we can conclude that appropriate methodologies for the quality control of materials, contemplating the application of different tests and analyses, are fundamental to achieve the outlined goals, essentially in the aerospace industry, where materials require specific properties.

APPLICABILITY OF TRANSMISSION AND REFLECTION FT-IR TECHNIQUES FOR CHARACTERIZATION OF PAINTS

As mentioned, aeronautical coatings may contain hazardous products, such as chromate pigments (Blackford, 1999). The identification of chromate anions (CrO_4^{2-}) can be performed by IR spectroscopy in the region of 800 to 900 cm^{-1} (Smith, 1979).

Copper chromite is used in the aerospace industry as a catalyst precursor (Faillace *et al.*, 1999). It was characterized by transmission (KBr disc), reflection, and

photoacoustic detection (PAS) FT-IR techniques in an article published by the IAE/AQI group (Campos *et al.*, 2003). It was observed that FT-IR techniques are able to indicate the catalyst method of synthesis. This is possible by using surface analysis techniques, with different degrees of sampling depth, without the need for other characterization methods. Therefore, the techniques used in this study (Campos *et al.*, 2003) have emerged as new alternatives for characterizing other types of catalysts or materials containing these kinds of compounds, such as chromium-based anions.

Certain additives, as OIT, diuron, and carbendazim, are added in small contents to preserve coatings during storage (Mello and Suarez, 2012). In this study, the methodology of chromium-based compounds (Campos *et al.*, 2003) was applied to the analysis of paints, with different degrees of sampling depth.

ANALYSIS OF PAINTS BY UATR

Figure 4 shows the UATR spectra of additives OIT, carbendazim, and diuron, painted with and without preservatives, dried resin, and filler.

The main bands observed in the FT-IR spectrum of OIT (Fig. 4a) are: 2924, 2855 and 722 cm^{-1} (stretching and rocking bending vibration of the CH_2 aliphatic group), 1618 cm^{-1} (stretching of the $\text{C}=\text{O}$ group), as well as at 1263 and 781 cm^{-1} (vibration of five-membered heterocyclic ring). The spectrum of carbendazim (Fig. 4b) showed bands at: 3320 cm^{-1} (stretching of N-H secondary group), 1710 cm^{-1} (stretching of $\text{C}=\text{O}$ group), 1627 cm^{-1} (stretching of the $\text{C}=\text{O}$ group and of the $\text{C}=\text{N}$ 5-membered heterocyclic ring), 1591 cm^{-1} (stretching of the C-C aromatic and $\text{C}=\text{N}$ groups), 1266 and 1093 cm^{-1} (stretching of the C-O group), and 726 cm^{-1} (vibration of five-membered heterocyclic ring and of the C-H aromatic substitution group).

The spectrum of the additive Diuron (Fig. 4c) shows bands at: 3280 cm^{-1} (stretching of the N-H group), 1651 cm^{-1} (stretching of $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups), 1584 cm^{-1} (stretching of the C-C aromatic group), 1473, 1298 and 1186 cm^{-1} (stretching of the C-N group), 1132 cm^{-1} (wagging of C-Cl aromatic group), as well as 864 and 813 cm^{-1} (bending vibration of the CH-tri-aromatic substitution group) (Smith, 1979; Silverstein *et al.*, 2005).

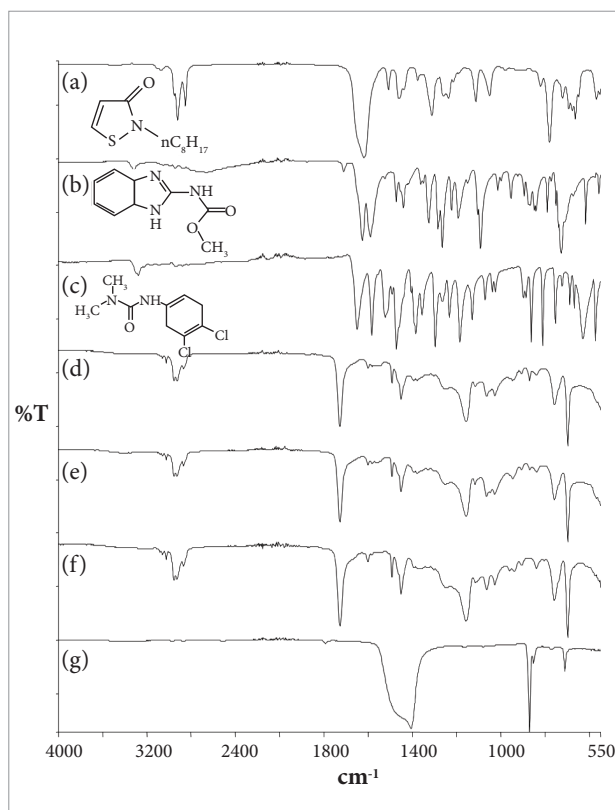


Figure 4. UATR spectra of: (a) OIT, (b) carbendazim, (c) diuron, (d) paint without preservatives, (e) paint with preservatives, (f) dry resin, and (g) calcium carbonate.

The additives OIT, carbendazim and diuron presented intense peaks that could be potentially used as analytical bands. However, the direct analysis of these compounds in the paint, by using UATR, was not possible because spectra of the paint, without (Fig. 4d) and with (Fig. 4e) preservatives are virtually identical. The resin (Fig. 4f) and filler (Fig. 4g) are present in high concentrations, so these ingredients could be the major interferences to the direct analysis. In fact, the main bands observed are associated with the resin (Fig. 4f): 1728 cm^{-1} (stretching of the $\text{C}=\text{O}$ group), 1159 cm^{-1} (stretching of the C-O group), and 698 cm^{-1} (bending vibration of C-H aromatic substitution group).

Although the characterization of preservatives in the surface of paints by UATR was not possible in the studied conditions, it is known that they are added to the compound to control proliferation of microorganisms (Lindner, 2005). Thus, we can suppose that some content of preservatives is present on the film surface.

It is known that the diffusion phenomenon is a process that depends on the size of the involved particles. The rate of diffusion is inversely proportional to the size of the particle. Hence, a smaller particle will diffuse faster and migrate easier to the surface. Preservatives were grinded to obtain different particle sizes. These samples were studied to investigate the effect of particle size on surface analysis results.

EVALUATION OF THE INFLUENCE OF PARTICLE SIZE IN THE DETECTION OF PRESERVATIVES AT THE PAINTED SURFACE BY UATR

Results of grinded preservatives are presented in Table 1 and show that preservatives reduce their size up to one fifth, when grinded for six minutes. The values represent the average of two determinations. Stabilizers (wetting agents and dispersants) were added to the samples to prevent agglomeration of crystals. Although the resulting particle sizes are very close, there seems to be a tendency of increasing the particle size with time, indicating agglomeration of particles (Welin-Berger and Bergenstahl, 2000). This increasing is negligible compared to the magnitude and extent of the uncertainty in its determination, and therefore it was neglected.

The smaller the particle size, the most effective the preservative should be in the microbiological control.

The explanation for this is that with smaller particle sizes, preservatives cover a larger surface area and can be used in lower concentrations. In smaller sizes, these additives also migrate more easily to the surface, becoming more bio-available to control microbes.

UATR ANALYSIS AFTER GRINDING OF PRESERVATIVES

The UATR paint spectra, with and without preservatives and grinding, compared to UATR reference spectra of the additives (OIT, diuron, and carbendazim), are shown in Fig. 5. The band with low intensity around 3320 cm^{-1} (N-H group), detected in the spectra of paints containing grinded preservatives (specially the six-minute grinded sample), and the peaks at 1625 cm^{-1} (C=O group and C=N 5-membered heterocyclic ring), and around 1330 cm^{-1} (C-N group), may indicate the presence of carbendazim. The absorption around 1625 cm^{-1} might have also contributed to the OIT bands around 1620 cm^{-1} (C=O group). The band around 870 cm^{-1} (C-H aromatic substitution group) might be from the additives diuron and/or carbendazim, and the absorption observed at 782 cm^{-1} (vibration of five-membered heterocyclic ring), from the additive OIT.

Table 1. Particle sizes of preservatives.

Sample	Particle size (μm)					
	Without grinding		Grinding for 1 minute		Grinding for 6 minutes	
	Zero time	3 months	Zero time	3 months	Zero time	3 months
1	32.073 \pm 0.422	33.148 \pm 0.234	14.711 \pm 0.102	14.900 \pm 0.101	4.963 \pm 0.023	5.234 \pm 0.036
2	31.834 \pm 0.357	35.133 \pm 0.289	16.529 \pm 0.115	16.987 \pm 0.078	6.487 \pm 0.109	6.610 \pm 0.101
3	32.189 \pm 0.309	33.390 \pm 0.415	11.870 \pm 0.111	13.041 \pm 0.099	5.992 \pm 0.197	6.123 \pm 0.099
4	32.558 \pm 0.178	32.098 \pm 0.238	4.570 \pm 0.098	15.067 \pm 0.121	5.336 \pm 0.136	5.897 \pm 0.020
5	31.845 \pm 0.310	33.022 \pm 0.102	15.460 \pm 0.201	16.001 \pm 0.309	4.196 \pm 0.099	4.223 \pm 0.021
6	32.012 \pm 0.284	32.917 \pm 0.287	15.649 \pm 0.193	16.122 \pm 0.235	5.971 \pm 0.099	5.992 \pm 0.113

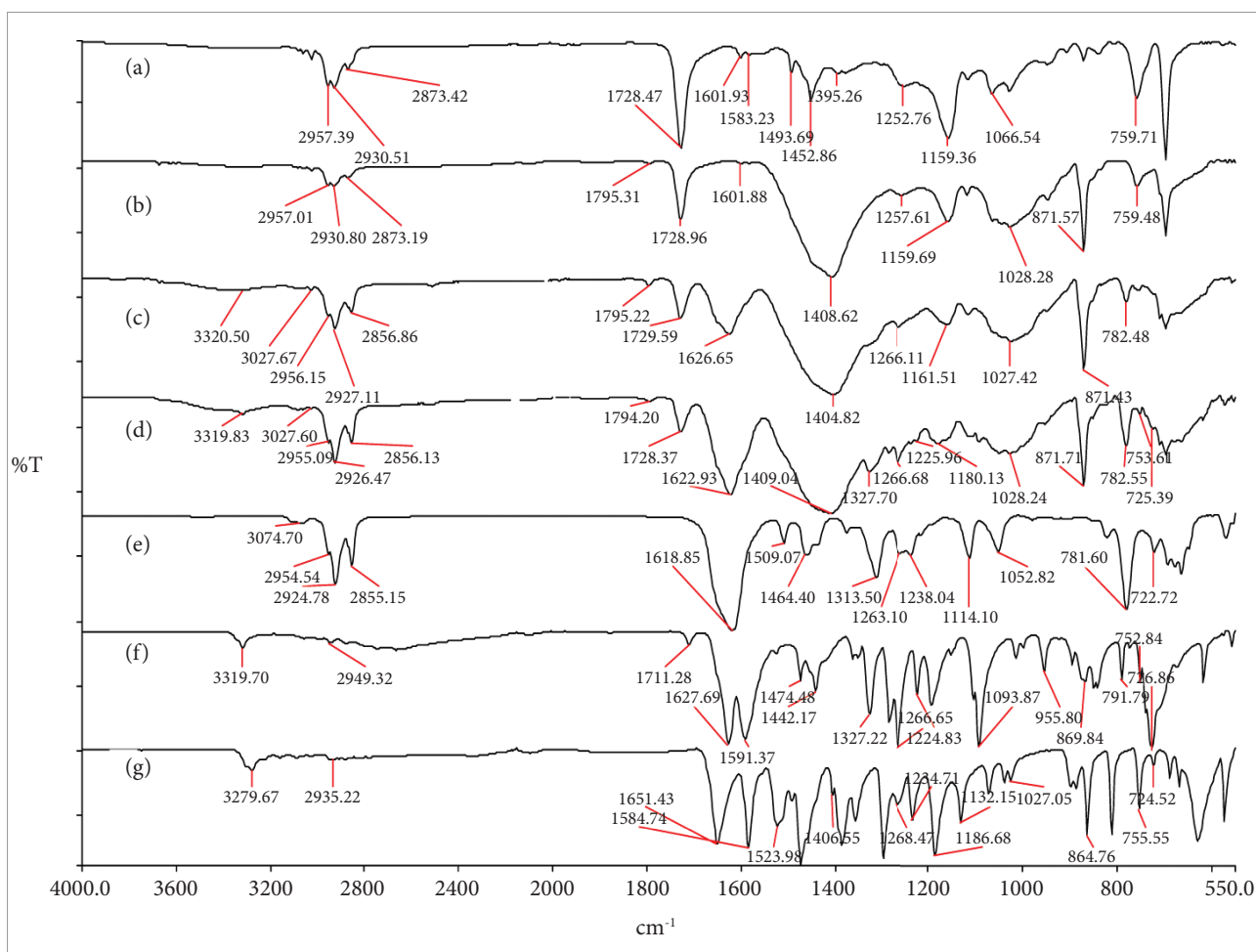


Figure 5. Spectra of UATR – (a) paint without preservatives, (b) paint with preservatives, without grinding, (c) paint with preservatives, grinded during one minute, (d) paint with preservatives, grinded during six minutes, (e) OIT, (f) carbendazim, and (g) diuron.

CONCLUSIONS

The evaluation of IR techniques for the characterization of elastomers and coatings indicated that:

- Transmission and reflection techniques applied to the same rubber sample, NBR in this study, can provide different information, highlighting only the base polymer characteristic absorptions (by pyrolysis/transmission) or the filler ones (by KBr pellet/transmission and ATR or UATR/reflection). This methodology can be applied to other types of rubber, particularly silicone formulations that might or might not contain silica filler. This aspect can be easily verified by using reflection analysis (ATR or UATR).
- The studied EPDM/NR mixture can be identified only by using the pyrolysis technique and after treatment

with ortho-dichlorobenzene. This method is suitable only for mixtures whose characteristic bands do not overlap.

- The UATR technique, without grinding of preservatives, did not allow the direct analysis of the painted dry film, for the samples analyzed. However, after the preservatives had been grinded, it was possible to observe bands around 3300 and 1330 cm^{-1} (carbendazim), 1625 cm^{-1} (carbendazim and/or OIT), 870 cm^{-1} (diuron and/or carbendazim), and 782 cm^{-1} (OIT).
- By using different FT-IR techniques, the preservatives carbendazim and OIT allow better visualization of the painted surface after grinding, because of their characteristics bands (medium and intense bands of functional groups and/or higher diffusion).

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