

FTIR, A POWERFUL TECHNIQUE IN ORGANIC COATINGS FAILURE DIAGNOSIS*

Trabalho submetido em Março de 2011
e aceite em Abril de 2011

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Abstract

FTIR spectrometry (Fourier Transform Infrared) is an instrumental technique of analysis that presents significant advantages on the dispersive traditional system, such as the increase of the relation signal-noise, the capacity of getting absorption spectra of low energy and therefore, bands of absorption of weak intensity. This technique is widely used in the study of resin characterization and evaluation of polymeric materials as well as degradation when polymers and coatings are exposed to various conditions of service, or still in the analysis and diagnosis of defects that occur during the application or production process. Techniques connected to the FTIR have appeared such as the photoacoustic (PAS-FTIR), the microscopy (MCT-FTIR) and the attenuated total reflectance (ATR), which allows to analysis of weekly transparent and dark samples without removal of coatings from the substrates. The choice of the technique to use depends on the morphology of the surfaces to analyze and the type of failure (lack of adhesion, contamination, aging degradation, etc). This work illustrates the application of FTIR and associated techniques to identify causes of diverse types of defects in applied organic coatings on polymeric materials.

Keywords: FTIR, Organic Coatings, Failure Diagnosis

FTIR, UMA TÉCNICA FUNDAMENTAL NO DIAGNÓSTICO DE FALHA DE REVESTIMENTOS ORGÂNICOS

Resumo

A espectrometria de FTIR (Fourier Transform Infrared) é uma técnica instrumental de análise que apresenta vantagens significativas sobre o sistema tradicional dispersivo, nomeadamente o aumento da relação sinal-ruído, a capacidade de registar espectros de absorção de baixa energia e portanto, bandas de absorção de fraca intensidade. Esta técnica é amplamente utilizada no estudo de caracterização e avaliação de materiais poliméricos bem como da sua degradação por exposição às mais variadas condições de serviço, ou ainda na análise e diagnóstico de defeitos que ocorram durante o processo de fabrico ou de aplicação. Mais recentemente surgiram técnicas acopladas ao FTIR como a fotoacústica (PAS-FTIR), a microscopia (MCT-FTIR) e a reflectância total atenuada (ATR), as quais permitem analisar amostras opacas e escuras sem necessidade de remoção dos revestimentos dos respectivos substratos. A selecção da técnica a usar depende da morfologia das superfícies a analisar e do tipo de defeito em causa (falta de aderência, contaminação, degradação por envelhecimento, etc).

Este trabalho demonstra a importância da utilização da espectrometria de FTIR e das diferentes técnicas acopladas no diagnóstico das causas do aparecimento de diferentes tipos de defeitos em revestimentos orgânicos aplicados em materiais poliméricos.

Palavras-Chave: FTIR, Revestimentos Orgânicos, Diagnóstico de Falha

(*) Paper presented at the EUROCORR 2009

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1. INTRODUCTION

The Fourier Transform Infra-Red Spectrometry (FTIR) is considered a valuable analytical technique in the study, characterization and evaluation of organic coatings degradation. Its development in the last few decades allowed it to become a versatile technique, presenting significant advantages over the traditional infra-red dispersive methods [1-5]. Since organic coatings and other polymeric materials suffer degradation by natural or accelerated exposure, it is possible to study the degradation of their surfaces through FTIR spectrometry. FTIR presents some advantages facing the dispersive methods such as the increase of the relation signal-noise and the possibility of getting spectra of low energy, that is, absorption bands of weak intensity [6].

This allows detecting chemical changes in the composition of coatings and the presence of contaminants [6]. Additionally it has the possibility of spectra storage in the "digital library", allowing through its "software" the search, comparison and use of the spectra in the most convenient way for each case under study [7-10]. The use of FTIR spectrometers of raised energy and sensitivity, still allowed the development of new techniques of analysis, with great potential, as it is the case of Attenuated Total Reflectance (ATR), of Diffuse Reflectance (DRIFT) and other techniques associated to the FTIR, as the Photoacoustic Spectroscopy associated with FTIR (PAS/FTIR) and the Infrared Microscopy (MCT/FTIR) [11-12].

ATR was initially developed and commercialized to analyse samples of difficult preparation or insoluble, such as rubbers and cured resins. The sample is placed in contact with a crystal of ATR, absorbent of the near infra-red radiation (IR) and of high refractive index, where part of the radiation penetrates in the sample and part is reflected [13-14]. The depth of penetration of the beam is a function of the wave length, the angle

of incidence and the refractive index of the crystal itself. Since there must exist a close contact between the surface of the sample and the crystal, this method has a significant disadvantage in the case of heterogeneous surfaces, as it happens with many coatings. Also partially transparent and highly pigmented coatings are difficult to analyze by this technique [13-14].

In the case of DRIFT, it has been widely used for the study of individual components of inks, fibers and powders [12,15-16]. Both ATR and DRIFT demand preparation of the sample, which can modify its characteristics, which does not happen with PAS/FTIR and MCT/FTIR. PAS/FTIR [11, 17] is based on the principle of absorption of radiation by the sample, which leads to an increase in the temperature of the surface and to the formation of thermal waves that cause changes in the pressure of the surrounding gas in the chamber where the sample is located, being converted later into an acoustic signal. This technique produces spectra of good quality and is widely used in the study of pigments and in the study of weekly transparent samples (black) that could only be very hardly analyzed by other methodologies of IR. The InspectIR microscope is an accessory associated to FTIR (MCT/FTIR) with respective software, which allows the mapping of the sample surface through the monitor of the video connected to the FTIR. This microscope has installed a MCT (mercury, cadmium and tellurium) detector, cooled with liquid nitrogen and equipped with a germanium crystal, allowing the analysis of very reduced areas (100 μm) and the mapping of a heterogeneous sample, which would be impossible to study by another IR technique. The MCT/FTIR is a method of fast analysis, allowing the microanalysis without sample preparation, having the only disadvantage that the detector only operates in the range 4000-650 cm^{-1} .

Problems of lack of adhesion of applied organic coatings appear with great

frequency on polymeric substrates. Thus, this work intends to show how the FTIR technique (PAS and MCT) is fundamental in diagnosing and analyzing the cause of lack of adhesion in organic coatings. Polymeric substrates are found in many of the available products in the world-wide market. Although different parts with complex forms, textures and with great diversity of colors can be produced, there is a frequent necessity of coating them, basically for aesthetic and technical reasons. The technical reasons involve, among others, the requirements of the production, specifications of engineering, parameters of resistance, taking in account the functionality, greater resistance to the abrasion, protection against the chemical and atmospheric agents and reduction of surface permeability [18].

The objectives of this work were to show how powerful FTIR and associated techniques are in failure diagnosis of organic coatings applied on polymeric materials. In this work three different cases are presented.

2. EXPERIMENTAL

2.1 Methodologies

Methodologies of sample preparation commonly used for the several techniques associated to the FTIR are described.

2.1.1 KBr Pellets

This method involves the scraping of some milligrams of the coating to be analyzed, its fine milling in agate mortar and posterior close mixture with anhydrous KBr (100-200 mg), until attainment of a fine and very well homogeneous mixture. The mixture is then placed in an adequate mold, introduced in a press and submitted to a pressure of about 10 tons. The final pellet will have to be translucent; then it is mounted in an appropriate support which is introduced in the spectrometer. The "background" spectrum is obtained

by comparison with atmospheric air.

2.1.2 NaCl or KBr Plates

In this case the sample is first dissolved in an adequate solvent and then is left to evaporate on a blade of NaCl (4000 - 650 cm^{-1}) or KBr (4000 - 400 cm^{-1}) which will be placed in the sample holder.

2.1.3 PAS/FTIR

For this technique a sample with (0.5 mm x 0.5 mm) must be cut, which is then introduced in the suitable support, in the chamber of the photoacoustic detector. The chamber is then purged with helium at about 20 psi during 5 minutes. The system gain is then adjusted to get a good signal (less than 10), and the spectrum is obtained afterwards. The "background" spectrum is obtained using a black absorbent standard (graphite), acquired together with the photoacoustic accessory.

2.1.4 MCT/FTIR

In this case the sample is cut to fit in the support (70 mm x 20 mm). The sample area to be studied is then visualized and focused in the monitor connected to the microscope. The ATR crystal is then adjusted to the surface of the sample, so that a good contact with the sample is created, and the spectrum can be obtained. The majority of the cases studied of diagnosis of organic coatings defects,

applied on polymeric substrates, involve a generic methodology, as described:

- drawing of FTIR spectra of reference samples as they are - primer, paint, varnish, hardener, solvent, lubricant, coating, etc, depending upon the case;
- drying in oven of the reference samples and drawing of respective FTIR spectra;

- drawing of FTIR spectra of the front and back of the coated samples by MCT/FTIR or PAS/FTIR;
- removal of the loose coating of the samples with lack of adhesion and its study by MCT/FTIR and KBr pellet;
- extraction of the loose coating and of the surface of the sample with an appropriate solvent, such as carbon tetrachloride (CCl_4), for detection of eventual contaminants.



Fig. 1 - Samples with adhesion problems.

In this work the FTIR spectra had been obtained with the NICOLET MAGNA System 560 spectrometer, in spectral range 4000 - 400 cm^{-1} , with software OMNIC for data processing. A photoacoustic detector MTEC 300 and a MCT (InspectIR) detector were used. The general conditions of operation are listed in Table 1.

2.2 Case Studies

Three samples, from automotive industry, with organic coatings adhesion problems are show in Figure 1.

3. CASE STUDIES RESULTS AND PARTIAL CONCLUSIONS

3.1 Study of the lack of adhesion of sample A coating by PAS/FTIR

3.1.1 Organic coating

The spectrum of delaminated coating, as it is, obtained from the surface of a

Table 1- Comparative operational conditions of the FTIR.

Operating conditions	Photoacoustic Detector - PAS	MCT Detector	KBr Pellet	NaCl or KBr Plate
Number of sample scannings	200	200	55	55
Number of "background" scannings	200	200	55	55
Resolution (cm^{-1})	16	16	16	16
Gain	auto	auto	auto	auto
Mirror velocity (cm/sec)	0.1581	4.4303	0.6329	0.6329
Aperture	138	138	100	95

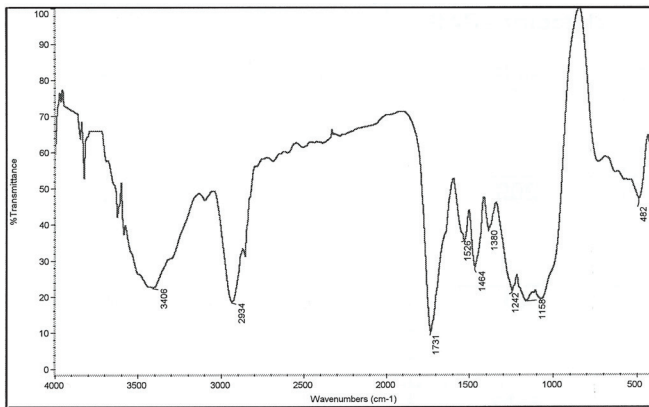


Fig. 2- FTIR spectrum of delaminated coating, as it is (sample A).

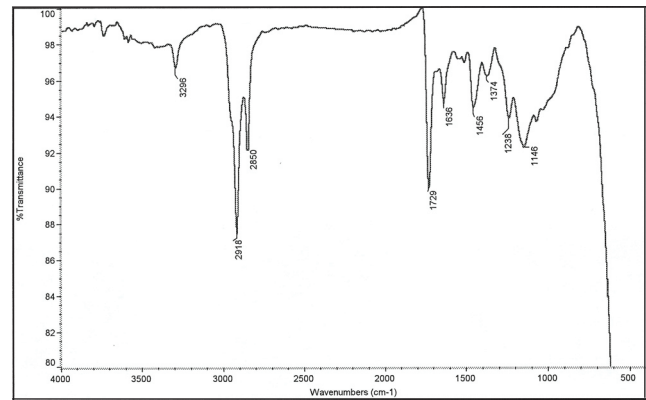


Fig. 3 - Extract in CCl₄ of delaminated coating (sample A).

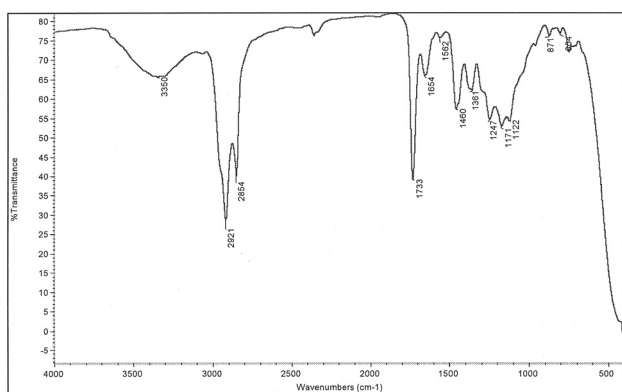


Fig. 4 - Extract in ethyl ether of the coating (sample A).

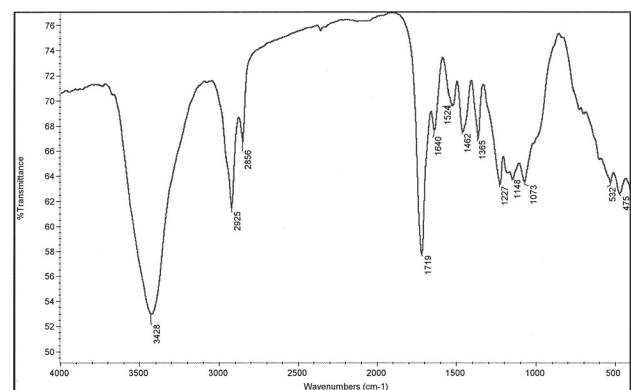


Fig. 5 - Coating after extraction with ethyl ether (sample A).

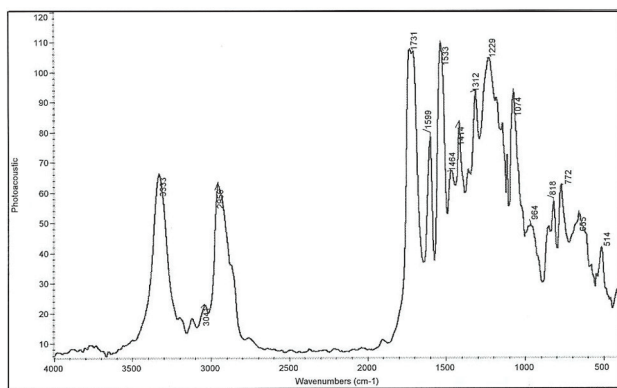


Fig. 6 - Substrate without coating (substrate) (sample A).

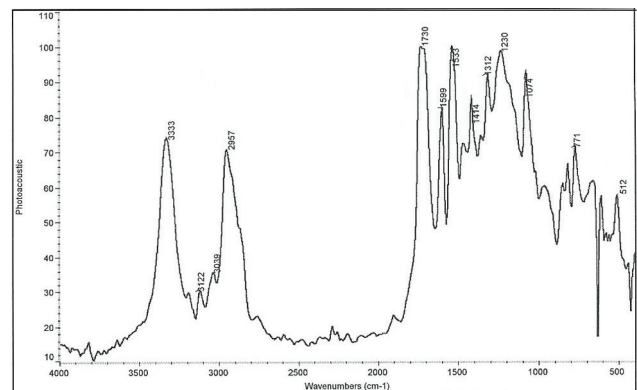


Fig. 7 - Surface after coating removal (sample A).

sample with coating adhesion problems is shown in **Figure 2**. Main absorption bands are found at $\approx 3406\text{ cm}^{-1}$; $\approx 1731\text{ cm}^{-1}$; $\approx 1526\text{ cm}^{-1}$; $\approx 1464\text{ cm}^{-1}$; $\approx 1380\text{ cm}^{-1}$ and $\approx 1242\text{ cm}^{-1}$, which can be assigned to the vibration of groups N-H, C=O (ester), C=O (amide), CH₂ and CH₃. In this case we can say that the organic coating contains ester and amide groups. The spectrum of extracted delaminated coating with CCl₄ is shown in **Figure 3**. This is similar to **Figure 2**, which means

that the coating was dissolved in the solvent used in the extraction (CCl₄). The organic coating was also extracted with ethyl ether, trying to isolate a possible contaminant. **Figures 4** and **5** show the FTIR spectra of the extract and of the coating after extraction, respectively. They are similar and present absorption bands characteristic of a polyamide. Nevertheless can be seen a decrease in the absorption bands at $\approx 3350\text{ cm}^{-1}$ and $\approx 1562\text{ cm}^{-1}$ regarding

the vibration of N-H (amide), as well as the appearing of absorption bands at $\approx 1122\text{ cm}^{-1}$; $\approx 871\text{ cm}^{-1}$ and $\approx 800\text{ cm}^{-1}$, which may be assigned to the vibration of [CO₃]²⁻ and Si-O groups. This means that the coating was partially dissolved in ether, also entraining compounds like carbonates and silicates.

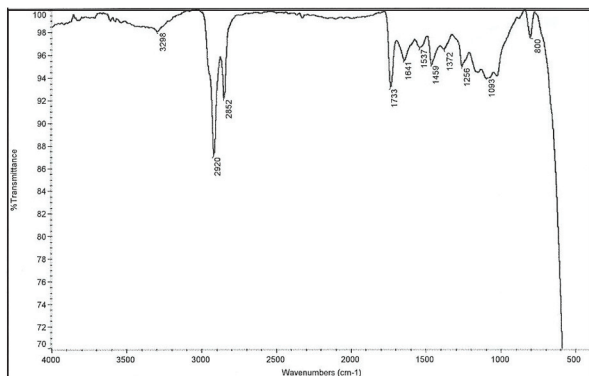


Fig. 8 - FTIR spectrum of the extract in CCl_4 after coating removal (sample A).

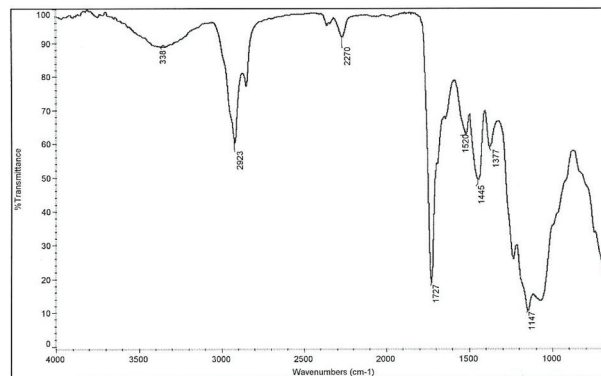


Fig. 9 - FTIR/MCT spectrum of the organic coating of sample B without defect – front side.

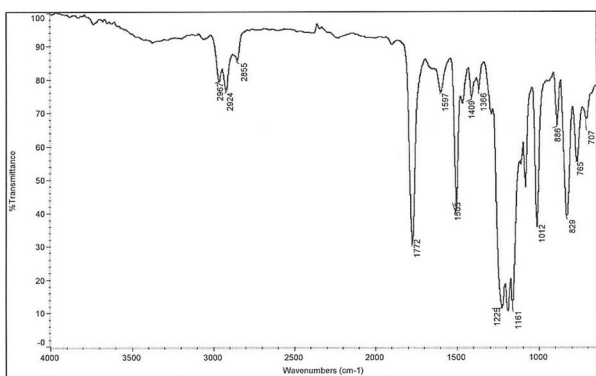


Fig. 10 - FTIR/MCT spectrum of the surface of sample B without defect – back side.

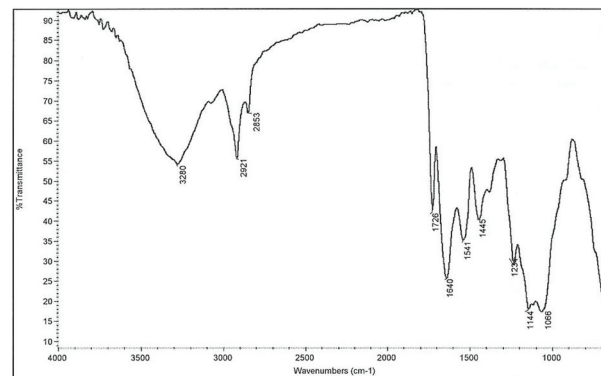


Fig. 11 - FTIR/MCT of the organic coating of sample B with defect – front side.

3.1.2 Surface without organic coating (substrate)

Spectra of PAS/FTIR of uncoated surface (substrate) (Figure 6), as well as the surface after coating removal (Figure 7) show that absorption bands present in substrate are characteristic of a polyurethane. The surface of sample was contacted with carbon tetrachloride with the aim of extracting the contaminant that caused the lack of adhesion. The spectrum of Figure 8 is similar to the previous ones, which means the presence of a polyamide. Nevertheless there are absorption bands at $\approx 1256 \text{ cm}^{-1}$; $\approx 1093 \text{ cm}^{-1}$ (double band) and $\approx 800 \text{ cm}^{-1}$, which can be assigned to the vibration of Si-O group. The presence in the extract of an organic compound with silicon, meaning a silicone may be assumed.

Conclusion:

The contaminant present on the surface of sample A that may have caused the lack of adhesion, is probably a

silicon containing organic compound: a silicone.

3.2 Analysis by PAS/FTIR and FTIR/MCT of a coating defect in sample B

In this case, sample B with good and with lack of adhesion of the organic coating zones was studied.

3.2.1 Sample B with good coating adhesion

MCT/FTIR spectra from the coated sample surface were collected (Figure 9), showing absorption bands at $\approx 3380 \text{ cm}^{-1}$; $\approx 2270 \text{ cm}^{-1}$; $\approx 1727 \text{ cm}^{-1}$; $\approx 1520 \text{ cm}^{-1}$; $\approx 1445 \text{ cm}^{-1}$; $\approx 1377 \text{ cm}^{-1}$ and $\approx 1250 \text{ cm}^{-1}$, which can be assigned to the vibration of groups OH or NH, N=C=O (isocyanate), NH, CH_2 and CH_3 , and C=O (urethane). Comparing the spectrum with the bibliography it can be concluded that it is similar to a polyurethane. The MCT/FTIR spectrum of the back side of the uncoated sample was

also collected (Figure 10), which shows as main absorption bands those verified at $\approx 1772 \text{ cm}^{-1}$; $\approx 1597 \text{ cm}^{-1}$; $\approx 1503 \text{ cm}^{-1}$; $\approx 1225 \text{ cm}^{-1}$; $\approx 829 \text{ cm}^{-1}$ and $\approx 765 \text{ cm}^{-1}$, possibly assigned to the vibration of C=O (ester) and all the other bands assigned to aromatic ring vibration. This analysis shows the possibility of a polycarbonate polystyrene as a substrate.

3.2.2 Sample B with lack of adhesion of the organic coating

MCT/FTIR spectrum of the surface of the sample with lack of adhesion is shown in Figure 11, showing absorption bands at $\approx 3380 \text{ cm}^{-1}$; $\approx 1726 \text{ cm}^{-1}$; $\approx 1640 \text{ cm}^{-1}$; $\approx 1541 \text{ cm}^{-1}$; $\approx 1445 \text{ cm}^{-1}$ and $\approx 1234 \text{ cm}^{-1}$, which can be assigned to the vibration of OH or NH, CH_2 , CH_3 , and C-O (urethane). This spectrum is similar to a polyurethane. MCT/FTIR spectrum was also collected for the back side of the sample

(uncoated). It shows the same main absorption bands found in Figure 10, at $\approx 1772\text{ cm}^{-1}$; $\approx 1640\text{ cm}^{-1}$; $\approx 1543\text{ cm}^{-1}$; $\approx 1226\text{ cm}^{-1}$; $\approx 826\text{ cm}^{-1}$ and $\approx 762\text{ cm}^{-1}$ which can be assigned to the vibration of C=O (ester) and all other bands to the vibration of the aromatic ring, pointing out to a polycarbonate polystyrene. The FTIR spectrum of the front side of the coated surface shows an absorption band at $\approx 1640\text{ cm}^{-1}$ as an inflection, while for the sample surface with lack of adhesion it is more intense. The same also happens to the absorption band at $\approx 3280\text{ cm}^{-1}$, both assigned to different vibration modes of NH group. In the sample with lack of adhesion some part of the substrate could be seen together with the coating as a white film, leading to a FTIR spectrum similar to the backside of the sample (polycarbonate substrate). The bands at 3288 , 1644 and 1543 cm^{-1} have higher intensity and can be assigned to the NH vibration, probably an amide.

Conclusion:

The contamination present on the surface of sample B, which caused lack of adhesion may be an organic compound containing nitrogen, such as an amide.

3.3 PAS/FTIR study of a defect in the coating of sample C

In this case reference samples of thinner, different paint components (A and B) as well as sample C without defect (sample C1) and with defect (sample C2) were studied.

3.3.1 Thinner

FTIR spectrum of the thinner as it is, is shown in Figure 12. Main absorption bands could be found at $\approx 1717\text{ cm}^{-1}$; $\approx 1427\text{ cm}^{-1}$; $\approx 1363\text{ cm}^{-1}$ and $\approx 1221\text{ cm}^{-1}$, and can be assigned to the vibration of functional groups C=O (ketone), CH_3 , CH_2 and C-O-C, exactly to 2-propanone.

3.3.2 Paint - Component A

FTIR spectrum of the hardener, as it is, is shown in Figure 13, where absorption bands at $\approx 2273\text{ cm}^{-1}$; $\approx 1694\text{ cm}^{-1}$; $\approx 1643\text{ cm}^{-1}$; $\approx 1516\text{ cm}^{-1}$; $\approx 864\text{ cm}^{-1}$ and $\approx 771\text{ cm}^{-1}$, may be assigned to the vibration of N=C=O (isocyanate), C=C, N-H and absorption bands of aromatic ring substitution, corresponding to an isocyanate. This kind of isocyanate seems to be based in hexamethylene diisocyanate.

3.3.3 Paint – Component B

FTIR spectrum of the paint, as it is, was registered for a NaCl plate. The spectrum is shown in Figure 14, where the most relevant band is found at $\approx 1733\text{ cm}^{-1}$ and may be assigned to the vibration of C=O of an ester.

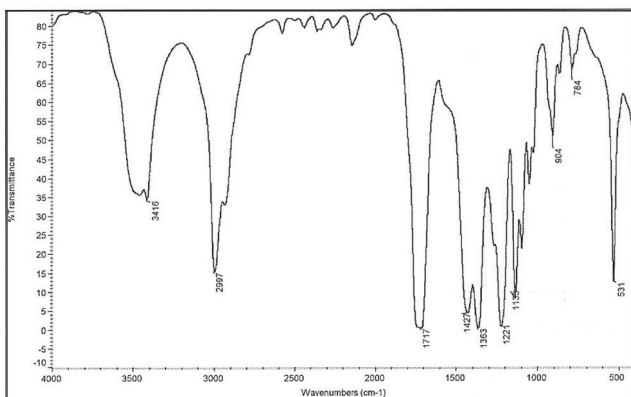


Fig. 12 - FTIR spectrum of the thinner.

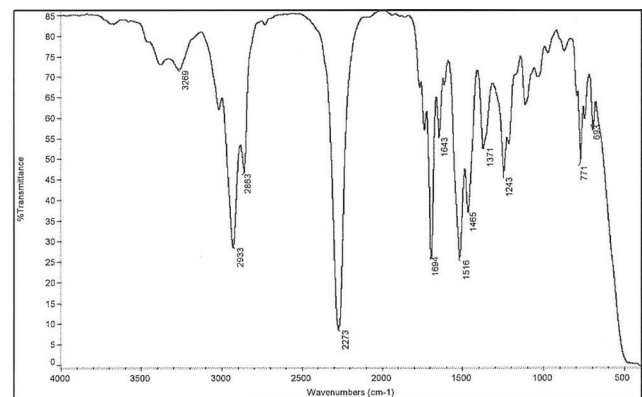


Fig. 13 - FTIR spectrum of the component A (hardener).

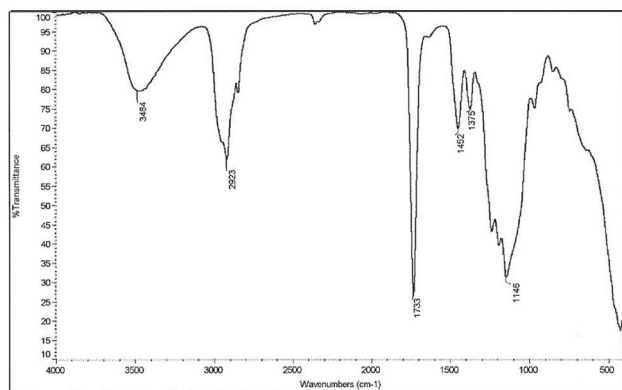


Fig. 14 - FTIR spectrum of the component B.

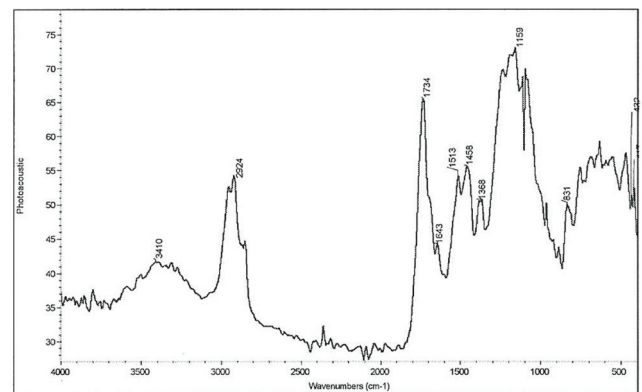


Fig. 15 - PAS/FTIR spectrum of the organic coating of sample C1 (without defect) – front side.

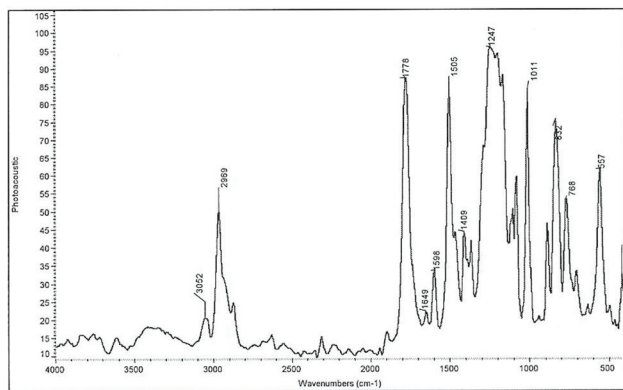


Fig. 16 - PAS/FTIR spectrum of the surface of sample C1 (without defect) – back side.

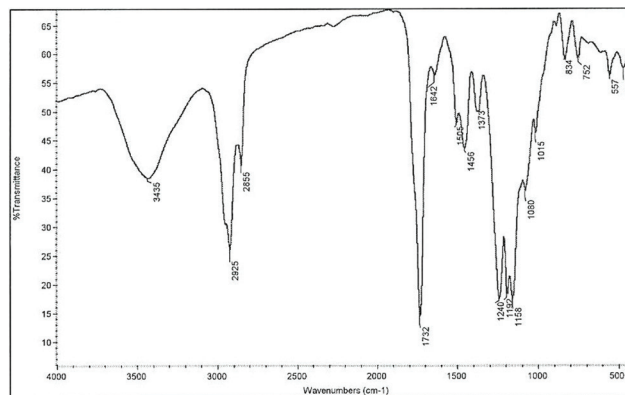


Fig. 17 - FTIR spectrum of the organic coating of sample C1 – front side.

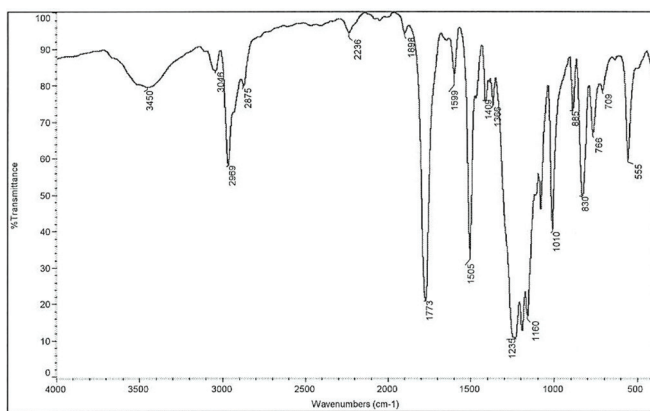


Fig. 18 - FTIR of sample C1- backside.

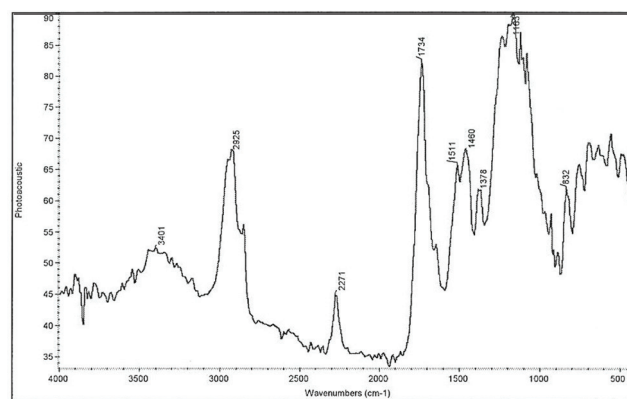


Fig. 19 - PAS/FTIR spectrum of the organic coating of sample C2 – front side.

3.3.4 Sample without coating defect (C1)

PAS/FTIR spectrum of sample C1 coated surface is shown in Figure 15. Absorption bands found at ≈ 3410 cm^{-1} ; ≈ 1734 cm^{-1} ; ≈ 1643 cm^{-1} ; ≈ 1513 cm^{-1} ; ≈ 1458 cm^{-1} ; ≈ 1368 cm^{-1} and ≈ 1250 cm^{-1} , may be assigned to the vibration of OH or NH, NH, CH₂, CH₃ and C-O (urethane) groups, indicating a polyurethane coating. PAS/FTIR spectrum of the uncoated backside of sample C1 is shown in Figure 16. Main absorption bands were found at ≈ 1778 cm^{-1} ; ≈ 1598 cm^{-1} ; ≈ 1505 cm^{-1} ; ≈ 1247 cm^{-1} ; ≈ 832 cm^{-1} and ≈ 768 cm^{-1} may be assigned to the vibration of C=O (ester) and of aromatic ring, suggesting a polycarbonate polystyrene substrate. These two PAS/FTIR spectra have an acceptable definition, but also present some noise which may hide some bands or lead to misunderstanding.

That is why KBr plates were done after coating removal by scraping. FTIR spectra of the coated surface as well as of the backside of sample C1 are shown in Figures 17 and 18, corresponding to a polyurethane and to a polycarbonate polystyrene.

3.3.5 Sample with coating defect (C2)

PAS/FTIR spectrum of the coated surface of sample C2 is shown in Figure 19, where absorption bands at ≈ 3401 cm^{-1} ; ≈ 2925 cm^{-1} ; ≈ 2271 cm^{-1} ; ≈ 1734 cm^{-1} ; ≈ 1640 cm^{-1} ; ≈ 1511 cm^{-1} ; ≈ 1460 cm^{-1} and ≈ 1234 cm^{-1} may be assigned to the vibration of OH or NH, CH₂, CH₃, N=C=O and C-O (urethane) groups. This spectrum is similar to the one of a polyurethane containing some residual isocyanate (absorption band at 2271 cm^{-1}). PAS/FTIR was also collected for the backside of sample C2 (Figure 20 -

uncoated). The spectrum is similar to that presented in Figure 16, showing as main absorption bands those found at ≈ 1778 cm^{-1} ; ≈ 1652 cm^{-1} ; ≈ 1505 cm^{-1} ; ≈ 1247 cm^{-1} ; ≈ 832 cm^{-1} and ≈ 767 cm^{-1} which may be assigned to C=O (ester) and the other bands assigned to aromatic ring vibration, indicating the same substrate, a polycarbonate polystyrene.

From the FTIR spectra for case study of sample C we can conclude that the thinner used in the production process was 2-propanone, that the hardener used was hexamethylene diisocyanate and that the applied paint (component B) was mainly formulated with an ester. The organic coating of sample C1 (without defect) and C2 (with defect) was a polyurethane. However, sample C2 also presented a residual isocyanate which was not present in sample C1.

Conclusion:

The lack of adhesion may be assigned to a different coating cure degree,

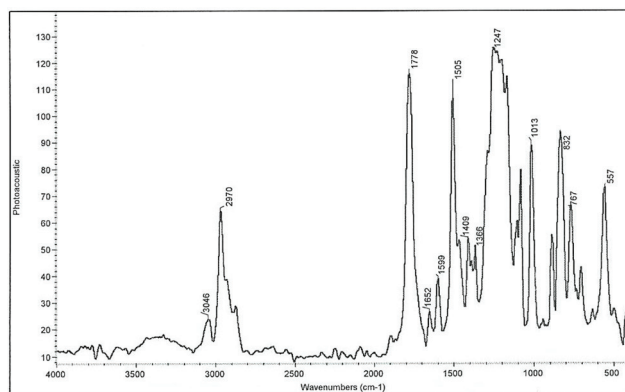


Fig. 20 - PAS/FTIR spectrum of the surface of sample C2 - backside.

which is indicated by the presence of the unreacted functional group $N=C=O$ (isocyanate).

4. CONCLUSIONS

FTIR with coupled techniques has indeed many advantages over traditional dispersive techniques, since it increases the ratio signal to noise, allowing the detection of weak intensity bands.

Trough this study the usefulness of FTIR with coupled techniques for the study of dark and weakly transparent samples was confirmed, since direct sample observation was realized, without previous preparation.

MCT/FTIR is also one of the most powerful techniques since the organic coating can be analyzed in extremely small areas, which is very important in contaminants identification, as shown in Case 2 (sample B).

From the three cases presented, which were only a small part of the several failure diagnosis cases studied concerning organic coatings applied on polymeric substrates, it may be concluded that FTIR and coupled techniques PAS/FTIR and FTIR/MCT are a powerful tool for this purpose, although it sometimes requires a detailed sample preparation, depending upon each case to be analyzed.

It is a step by step process which may differ from case to case depending upon the problem and the substrate on which the coating is applied.

However when inorganic contaminants are present it is also very often necessary

to use other complementary analytical techniques (Spectroscopy Dispersive Energy - EDS, X-Ray Fluorescence, Raman Spectroscopy, etc).

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