FTIR, A POWERFUL TECHNIQUE IN ORGANIC COATINGS FAILURE DIAGNOSIS

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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 study, resin characterization and evaluation of polymeric materials as well as of its degradation when exposed to the most varied 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 had more recently appeared as the photoacoustic (PAS-FTIR), the microscopy (MCT-FTIR) and the attenuated total reflectance (ATR), which allow to analyze 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 in cause (lack of adhesion, contamination, aging degradation, etc). In this work the application of FTIR and techniques associates to the identification of the causes that had originated diverse types of defect in applied organic coatings on polymeric materials is presented. Key words: FTIR, Organic Coatings, Failure Diagnosis

1. Introduction

The Fourier Transform Infra-Red Spectrometry (FTIR) is considered a valuable analytical technique in the study, characterization and evaluation of coatings degradation. Its development in the last few decades allowed it to become a versatile technique, presenting significant advantages on the traditional infra-red dispersive systems [1-5]. Since organic coatings and other polymeric materials suffer degradation by natural or accelerated exposure, it is possible to study the degradation of the surfaces through the 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 to eventually 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 [7-11]. The use of FTIR spectrometers of raised

energy and sensitivity, still allowed the development of new techniques of analysis, with great potentialities, as it is the case of Attenuated Total Reflectance (ATR), of Diffuse Reflectance (DRIFT) and more recently of techniques associated to the FTIR, as the Photoacustic Spectroscopy associated with FTIR (PAS/FTIR) and the Infrared Microscopy (MCT/FTIR) [12,13].

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 (IV) and of high refractive index, where part of the radiation penetrates in the sample and part is reflected [14,15]. 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 weekly transparent and highly pigmented coatings are hardly analyzed by this technique. [14,15].

In the case of DRIFT, it has been widely used for the study of individual components of inks, fibers and powders [13,16,17]. Both ATR and DRIFT demand previous preparation of the sample, which can modify its characteristics, which does not happen with PAS/FTIR and MCT/FTIR. PAS/FTIR [12,18] 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 on 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 IV. 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 technique of IV. 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 plastic 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 the majority of the available products in the world-wide market [19]. 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 [20].

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 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 (7 x 2 cm). 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 then 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, 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.

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.

Table 1 - Comparative operational conditions of the FTIR

Operating conditions	Photoacoustic Detector - PAS	MCT Detector	KBr Pellet	NaCl or KBr Plate
N. of sample scannings	200	200	55	55
N. of "background" scannings	200	200	55	55
Resolution (cm^{-1})	16	16	16	16
Gain	auto	auto	auto	auto
Mirror speed (cm. s^{-1})	0,1581	4,4303	0,6329	0,6329
Aperture	138	138	100	95

2.2 Case studies

Three samples with organic coatings adhesion problems are shown in Figure 1.

Figure 1 – *Samples with adhesion problems*

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 sample with coating adhesion problems is shown in Figure 2. Main absorption bands are found at $\approx 3406 cm^{-1}$; $\approx 1731 cm^{-1}$; $\approx 1526 cm^{-1}$; $\approx 1464 cm^{-1}$; $\approx 1380 cm^{-1}$ e $\approx 1242 cm^{-1}$, which can be assigned to the vibration of groups N-H, C=O (ester), C=O (amide), CH_2 and CH_3. In this case we can say that we are in the presence of an ester and an amide.
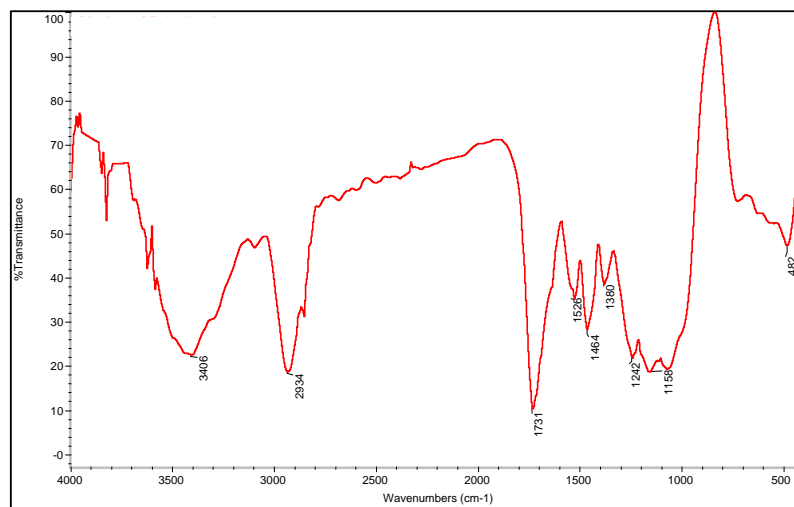
Figure 2 *– FTIR spectrum of delaminated coating, as it is*

The spectrum of extracted delaminated coating with CCl_4 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 (CCl_4).
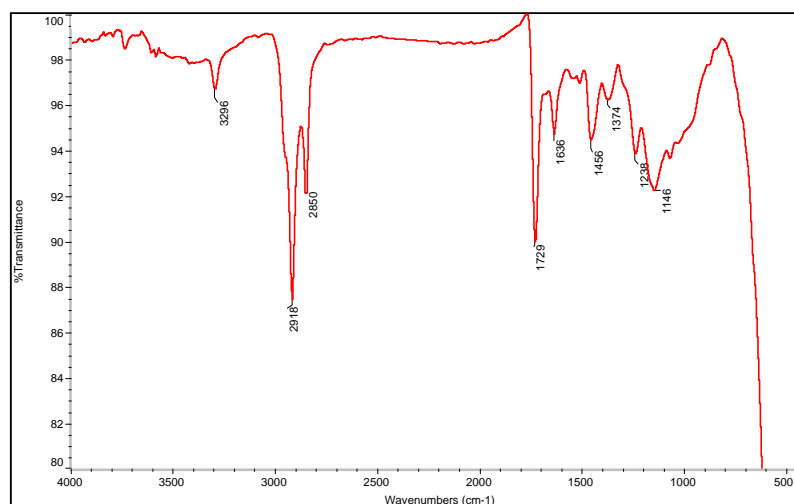
Figure 3 *– Extract in CCl_4 of delaminated coating*

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. They are similar and present absorption bands characteristic of a polyamide. Nevertheless we can see a decrease in the absorption bands at $\approx 3350 cm^{-1}$ and $\approx 1562 cm^{-1}$ regarding the vibration of N-H (amide), as well as the appearing of absorption bands at $\approx 1122 cm^{-1}$; $\approx 871 cm^{-1}$ and $\approx 800 cm^{-1}$, which may be assigned to the vibration of $(CO_3)^{2-}$ and Si-O groups. This means that the coating was partially dissolved in ether, also entraining compounds like carbonates and silicates.
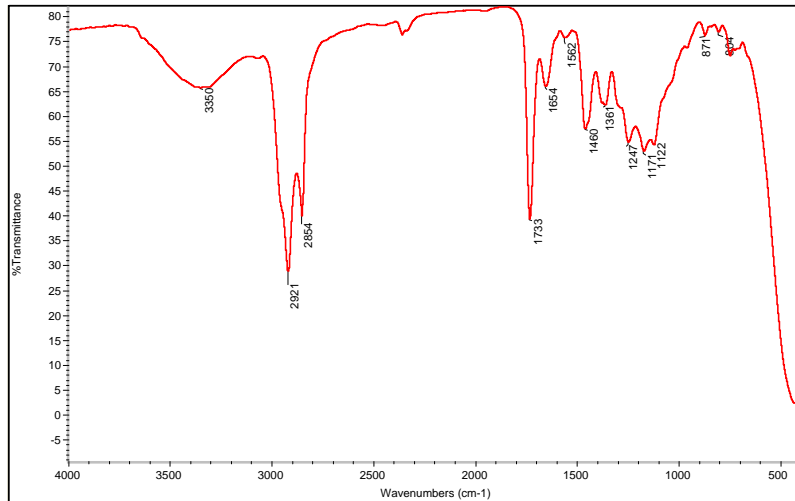
Figure 4 –*Extract in ethyl ether of the coating*
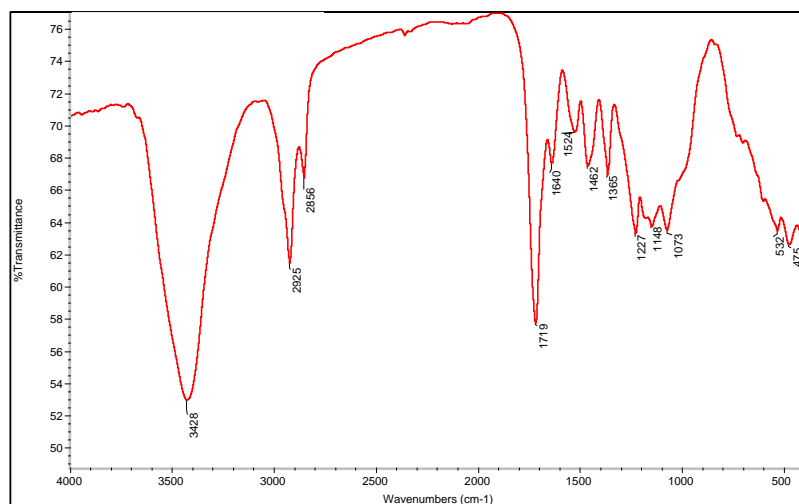
Figure 5 – *Coating after extraction with ethyl ether*

3.1.2 – Surface without organic coating (substrate)

Spectra of PAS/FTIR of front and back side of uncoated surface (substrate), as well as the surface after coating removal, are shown in Figures 6 to 8. These are similar and present absorption bands characteristic of a polyurethane.
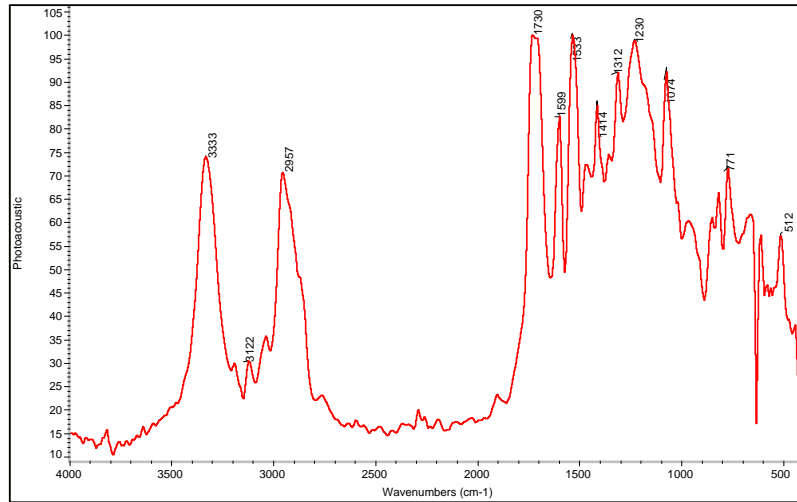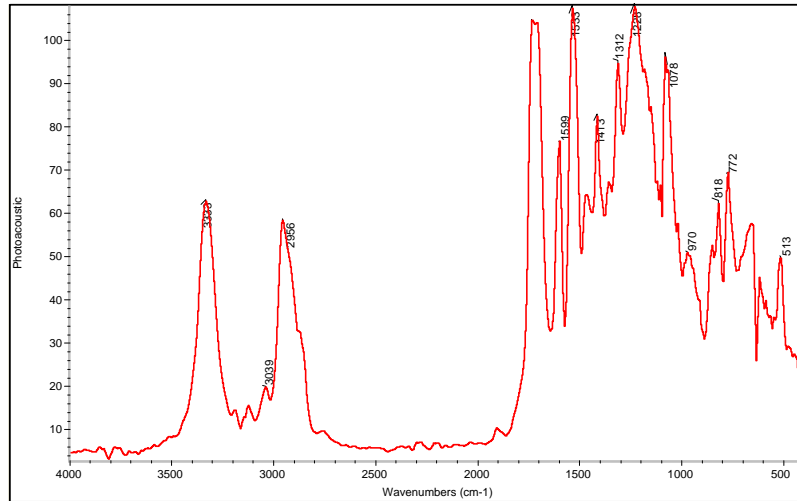

Figure 6 *– Front of uncoated surface (substrate)*
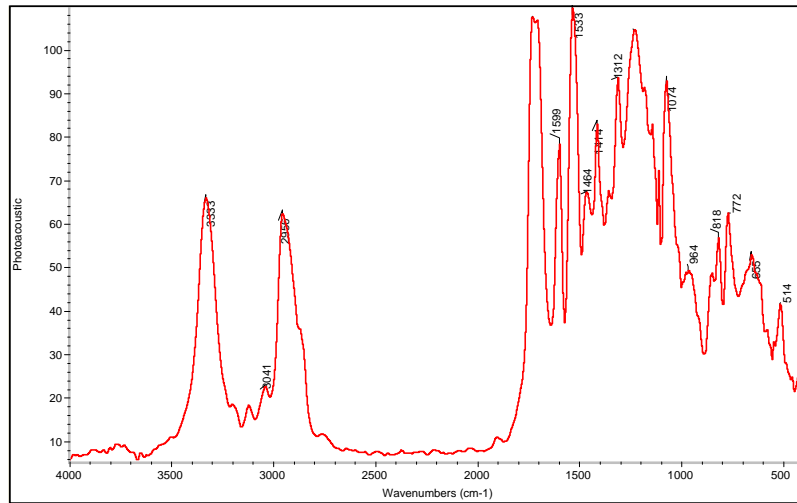

Figure 7 *– Back side of uncoated surface (substrate)*

Figure 8 – Substrate without coating

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 9 is similar to the previous ones, which means the presence of a polyamide. Nevertheless there absorption bands at $\approx 1256 cm^{-1}$; $\approx 1093 cm^{-1}$ (double band) and $\approx 800 cm^{-1}$, which can be assigned to the vibration of Si-O group. The presence in the extract of an organic compound with silicium, meaning a silicone may be assumed.
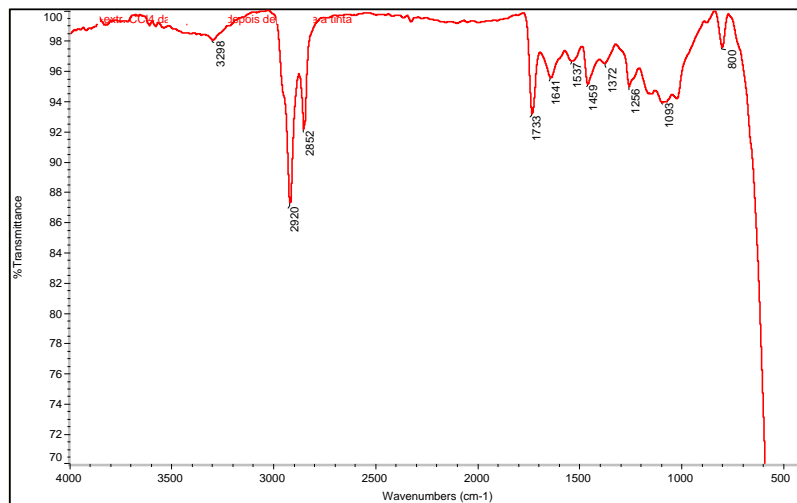
Figure 9 – FTIR spectrum of the extract in CCl4 after coating removal

Conclusion:

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

3.2.1 – Sample B with good coating adhesion

MCT/FTIR spectra from the coated sample surface were collected (Figure 10), showing absorption bands at $\approx$3380cm^{-1}; $\approx$2270cm^{-1}; $\approx$1727cm^{-1}; $\approx$1520cm^{-1}; $\approx$1445cm^{-1}; $\approx$1377cm^{-1}; $\approx$1250cm^{-1}, which can be assigned to the vibration of groups OH or NH, N=C=O (isocyanate), NH, CH$_2$ and CH$_3$, e C-O (urethane). Comparing the spectrum with the bibliography it can concluded that it is similar to a polyurethane. The MCT/FTIR spectrum of the back side of the uncoated sample was also collected (Figure 11), which shows as main absorptions bands those verified at $\approx$1772cm^{-1}; $\approx$1597cm^{-1}; $\approx$1503cm^{-1}; $\approx$1225cm^{-1}; $\approx$829cm^{-1} $\approx$765cm^{-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.
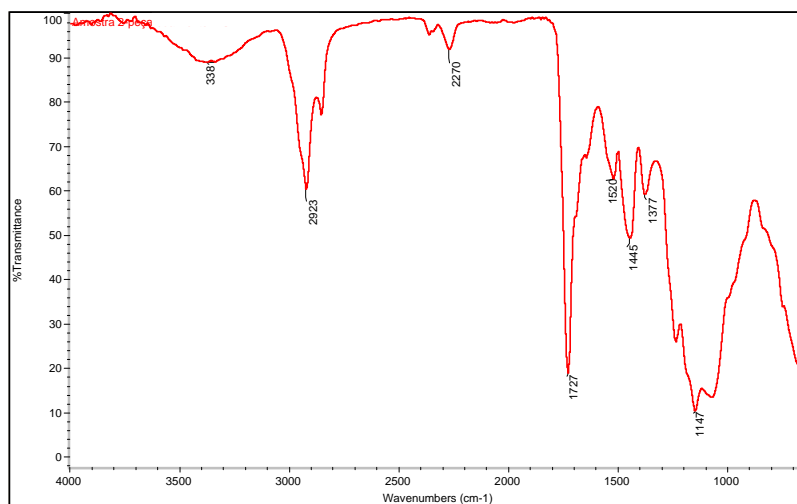

***Figure 10**- FTIR/MCT spectrum of the organic coating of sample B without defect – front side*
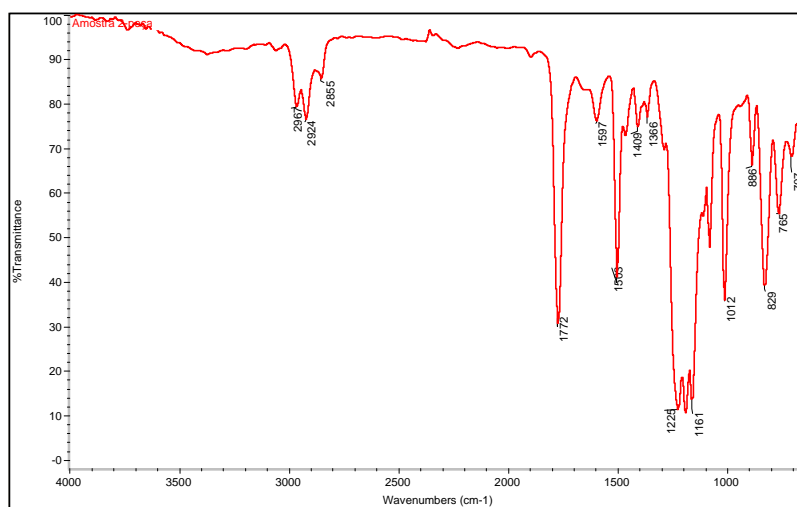

***Figure 11**- FTIR/MCT spectrum of the surface of sample B without defect – back side*

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 12, showing absorption bands at $\approx 3380 cm^{-1}$; $\approx 1726 cm^{-1}$; $\approx 1640 cm^{-1}$; $\approx 1541 cm^{-1}$; $\approx 1445 cm^{-1}$; $\approx 1234 cm^{-1}$, 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.
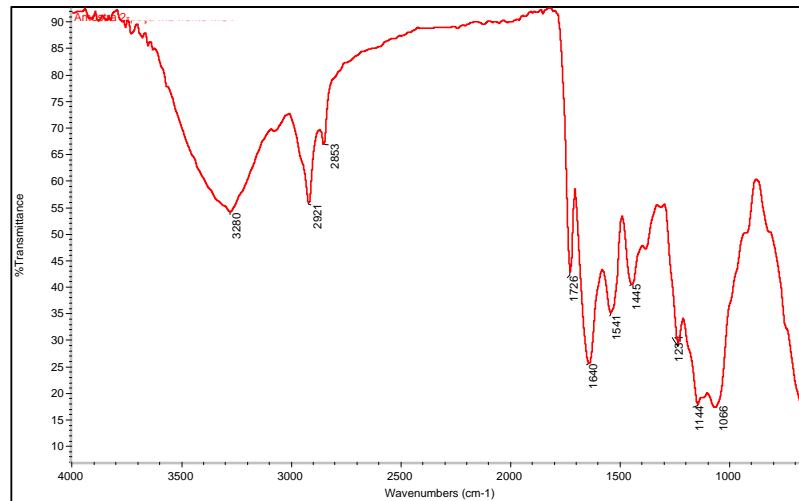

Figure 12-FTIR/MCT of the organic coating of sample B with defect – front side

MCT/FTIR spectrum was also collected for the back side of the sample (uncoated) (Figure 13). It shows the main absorption bands at $\approx 1772 cm^{-1}$; $\approx 1640 cm^{-1}$; $\approx 1543 cm^{-1}$; $\approx 1226 cm^{-1}$; $\approx 826 cm^{-1}$ $\approx 762 cm^{-1}$ 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.
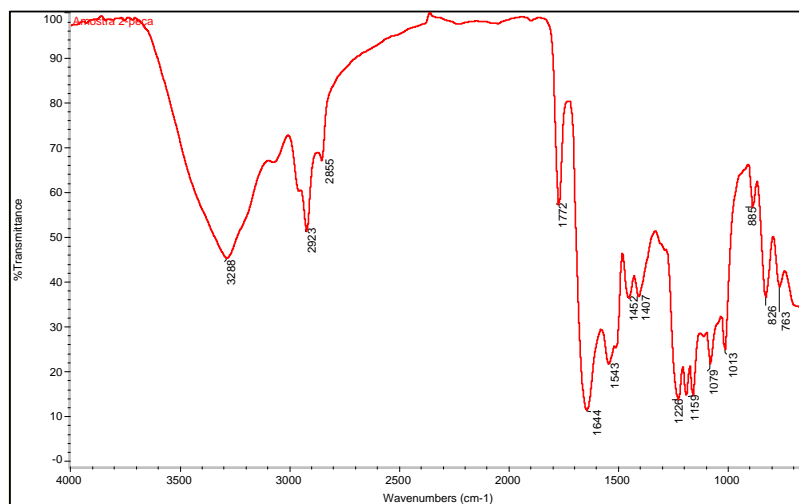

Figure 13- FTIR/MCT of the organic coating of sample B with defect – back side

The FTIR spectrum of the front side of the coated surface shows an absorption band at $\approx 1640\, cm^{-1}$ as an inflexion, while for the sample surface with lack of adhesion it is more intense. The same

also happens to the absorption band at $\approx 3280 cm^{-1}$, 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 (thinner, paint, hardener) were studied as well as sample C, with defect (sample C1) and without defect (sample C2).

3.3.1 – Thinner

FTIR spectrum of the thinner as it is, is shown in Figure 14. Main absorption bands could be found at ≈ 1717 cm^{-1}; $\approx 1427 cm^{-1}$; $\approx 1363 cm^{-1}$ e $\approx 1221 cm^{-1}$, 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.
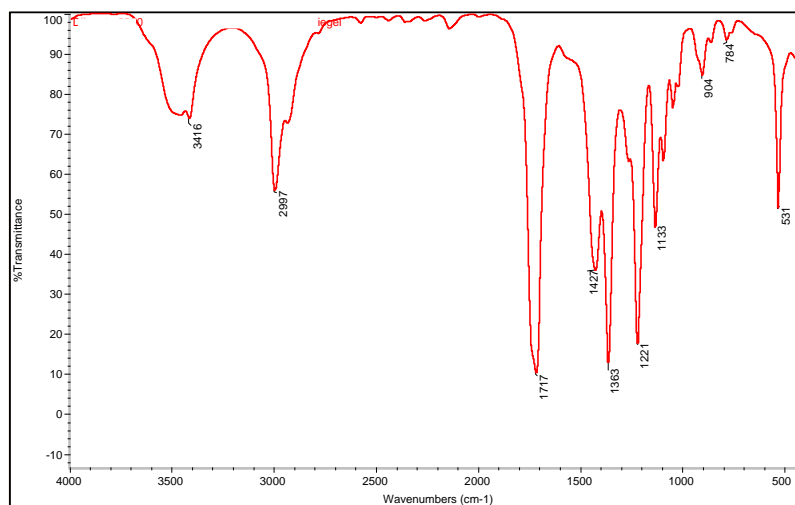

Figure 14 *– FTIR spectrum of 2-propanone.*

3.3.2 - Hardener

FTIR spectrum of the hardener, as it is, is shown in Figure 15, where absorption bands at $\approx 2273 cm^{-1}$; $\approx 1694 cm^{-1}$; $\approx 1643 cm^{-1}$; $\approx 1516 cm^{-1}$; $\approx 864 cm^{-1}$ e $\approx 771 cm^{-1}$, may be assigned to the vibration of N=C=O (isocyanate), C=C, N-H and absorption bands of aromatic ring substitution.
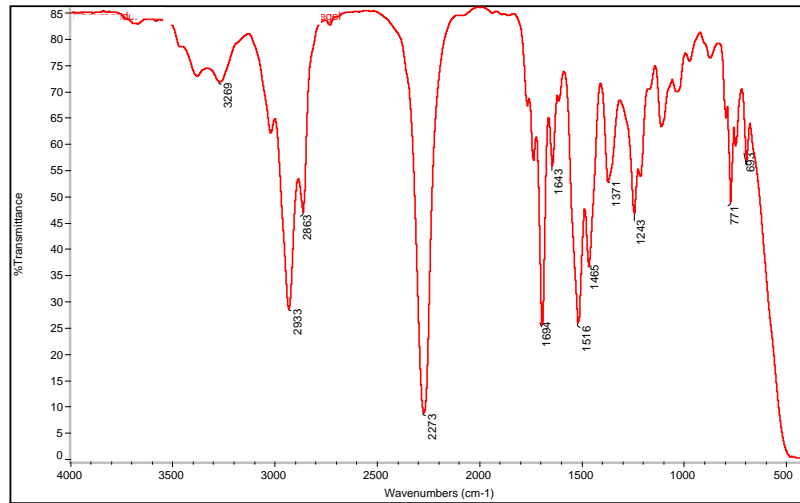
Figure 15 - FTIR spectrum of the hardener

This kind of isocyanate seems to be based in hexamethylene diisocyanate.

3.3.3 – Paint

FTIR spectrum of the paint, as it is, was registered for a NaCl plate. The spectrum is shown in Figure 16, where the most relevant band is found at ≈ 1733 cm^{-1} and may be assigned to the vibration of C=O of an ester.
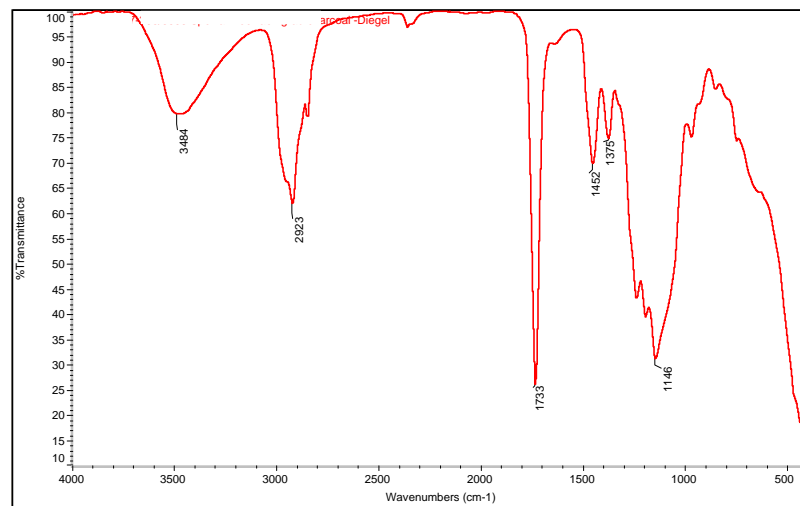

Figure 16 - FTIR spectrum of the paint

3.3.4 – Sample without coating defect (C1)

PAS/FTIR spectrum of sample C1 coated surface is shown in Figure 17.

Absorption bands found at $\approx 3410 cm^{-1}$; $\approx 1734 cm^{-1}$; $\approx 1643 cm^{-1}$ $\approx 1513 cm^{-1}$; $\approx 1458 cm^{-1}$; $\approx 1368 cm^{-1}$; $\approx 1250 cm^{-1}$, may be assigned to the vibration of OH or NH, NH, CH_2, CH_3 and C-O (urethane) groups, indicating a polyurethane coating.

PAS/FTIR spectrum of the uncoated backside of sample C1 is shown in Figure 18. Main absorption bands were found at $\approx 1778 cm^{-1}$; $\approx 1598 cm^{-1}$; $\approx 1505 cm^{-1}$; $\approx 1247 cm^{-1}$; $\approx 832 cm^{-1}$ $\approx 768 cm^{-1}$ and may be assigned to the vibration of C=O (ester) and of aromatic ring, suggesting a polycarbonate with styrene substrate.

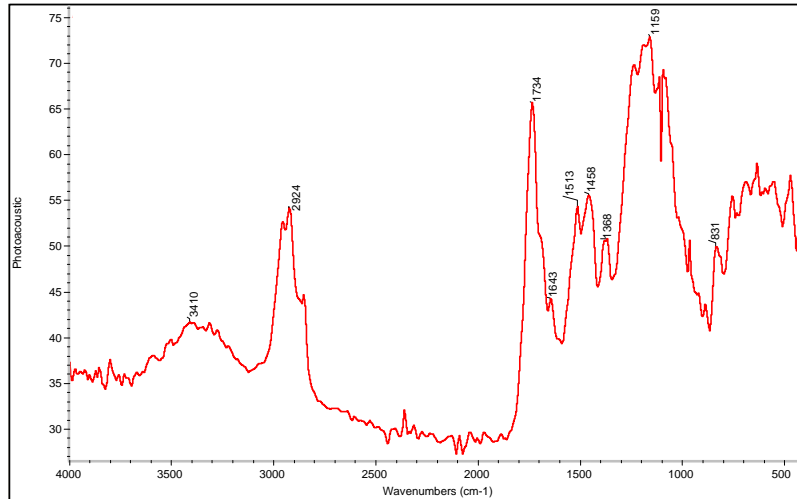***Figure 17*** *- PAS/FTIR spectrum of the organic coating of sample C1 (without defect) – front side*
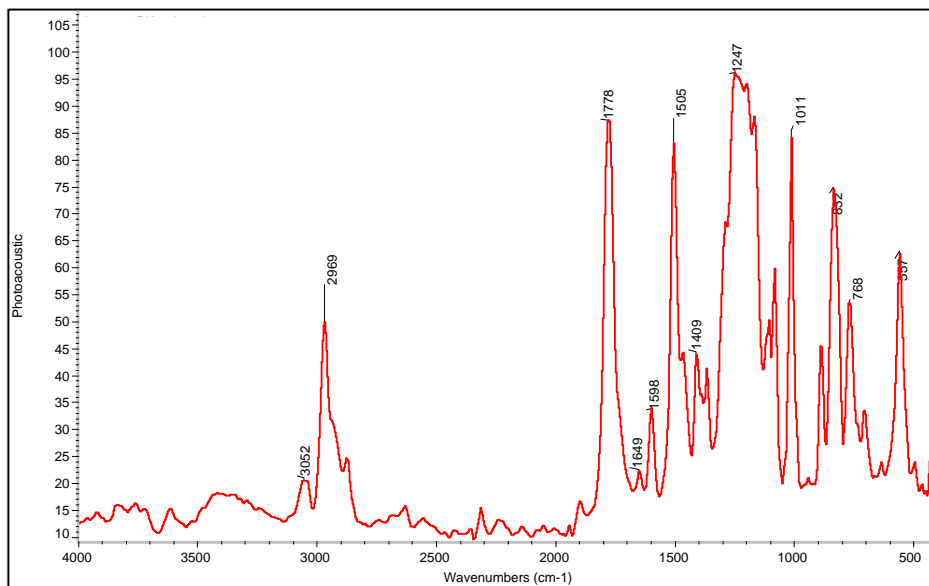

Figure 18 - *PAS/FTIR spectrum of the surface of sample C1 (without defect) – back side*

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 19 and 20, corresponding to a polyurethane and to a polycarbonate with styrene.
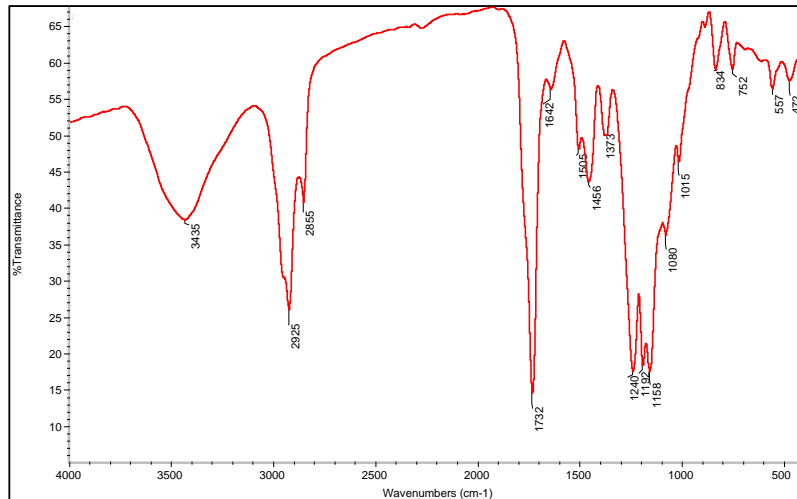

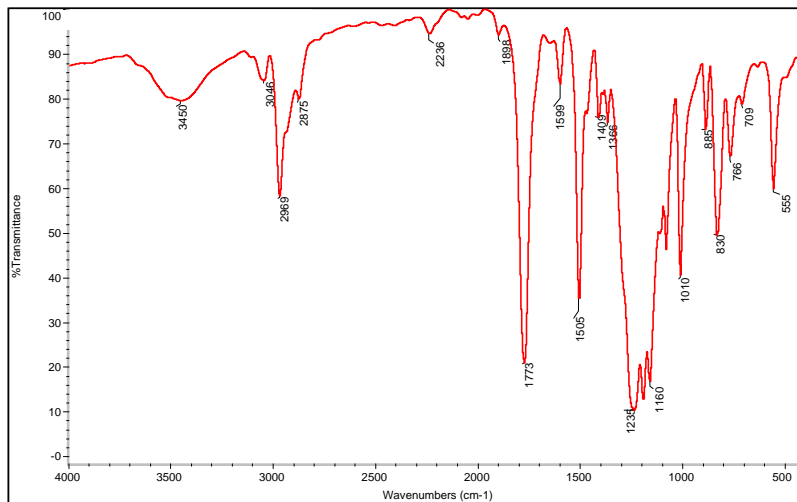*Figure 19* - *FTIR spectrum of the organic coating of sample C1 – front side*

Figure 20 - *FTIR of sample C1- backside*

3.3.5 – Sample with coating defect (C2)

PAS/FTIR spectrum of the coated surface of sample C2 is shown in Figure 21, where absorption bands at $\approx 3401 cm^{-1}$; $\approx 2925 cm-1$; $\approx 2271 cm-1$; $\approx 1734 cm^{-1}$; $\approx 1640 cm^{-1}$; $\approx 1511 cm^{-1}$; $\approx 1460 cm^{-1}$; $\approx 1234 cm^{-1}$ may be assigned to the vibration of OH or NH, CH_2, CH_3, 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 $2271 cm^{-1}$).
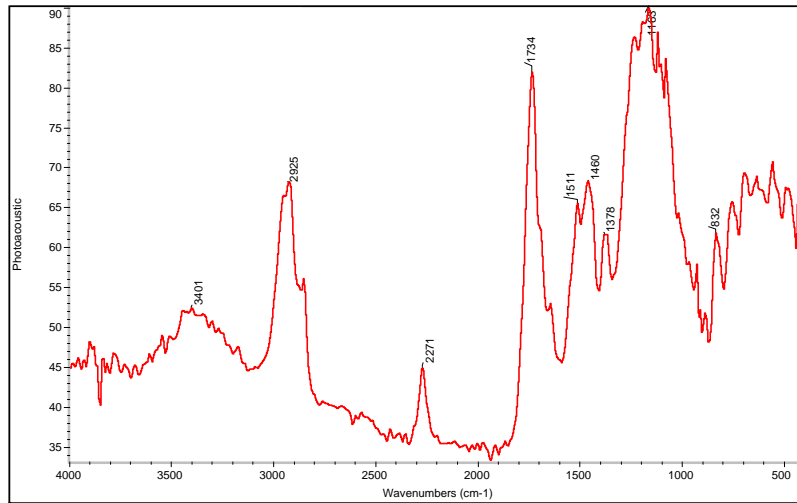
Figure 21 *- PAS/FTIR spectrum of the organic coating of sample C2 – front side*

PAS/FTIR was also collected for the backside of sample C2 (uncoated) (Figure 22), showing as main absorption bands those found at ≈1778cm^{-1}; ≈1652cm^{-1}; ≈1505cm^{-1}; ≈1247cm^{-1}; ≈832cm^{-1} ≈767cm^{-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.
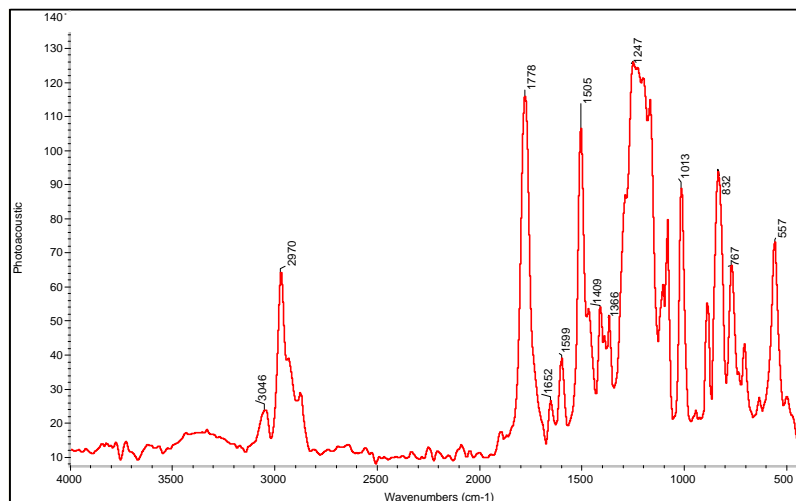

Figure 22 *- PAS/FTIR spectrum of the surface of sample C2 – backside*

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 hexamethilene diisocyanate that the applied paint was mainly formulated with an ester, that the organic coating of sample C1 (without defect) and C2 (with defect) was a polyurethane, and that the organic coating of sample C2 also presented a residual isocyanate which was not present in sample Cl.

Conclusion:

The lack of adhesion may be assigned to a different coating cure degree, which is indicated by the presence of the functional group N=C=O (isocyanate).

4. CONCLUSIONS

From the three cases presented, which were only a small part of the several failure diagnosis cases studied in Laboratory of Materials and Coatings (LMR) 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, as well as a specific "creativity" 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.

When inorganic contaminants are present it is also very often necessary to use other analytical techniques.

REFERENCES

[1] D. Santos, C. Brites, M.R. Costa, M. T.Santos, *Progress in Organic Coatings*, **54** (2005), 344-352.

[2] S. Chaudhari, A.B. Gaikwad, P.P. Patil , *Current Applied Physics*, **9** (2009), 206-218.

[3] N. Guermazi, A. Boubakri, K. Elleuch, H. F. Ayedi, *Materials and Design* , doi 10.1016/j.matdes 2008-11-06 (2008).

[4] M. PolisKie, J. O. Clevenger, *Metal Finishing,* (2008) 44-47.

[5] E. Almeida, M. Balmayore, T. Santos, *Progress in Organic Coatings*, **44** (2002) 233-242.

[6] R. O. Carter, M. C. Paputa et al*, Polymer Degradation and Stability*, **23** (1989), 121-134.

[7] Marek, W. Urban, *Progress in Organic Coatings*, **16** (1989), 321-353.

[8] P. R. Griffiths, *Chemical Infrared Transform Spectroscopy*, Wiley New York (1975).

[9] J. L. Koenig, *Appl. Spectroscopy*, **29** (1975), 293-297.

[10] S. Chandhan, A. B. Garkwad., P. P. Patil, *Current Applied Physics*, **9** (2009), 206-218.

[11] Marek, W. Urban, *Journal of Coatings Technology*, 59 (1987), 745-749.

[12] KirK H. Michaelian, *Photoacustic Infrared Spectroscopy,* Wiley Interscience (2003)

[13] B. Stuart, W. O. George and P. S. McIntyre, *Modern Infrared Spectroscopy*, John Wiley&Sons (1998).

[14] Urban, M. W., Koenig, J. L., *Applied. Spectroscopy*, **41** (1987), 590-598.

[15] Belton, D. J., Stupp, S. I., *Adhesion Aspects of Polymeric Coatings*, Plenum N. Y., (1975), 285.

[16] M. Gilbert, I. Sutherland, A. Guest, *Journal of Materials Science*, **35** (2000), 391-397.

[17] D. H. Lee and R. A. Condrate, *Journal of Materials Science*, **34** (1999), 139-146.

[18] R. Jakobsen, *Fourier Transform Infrared Spectroscopy, Application to* Chemical *Systems*, Vol. 2 Academic Press N. Y. (1979).

[19] C. A. Hemais, *Polímeros*, **13** (2003), 1-7.

[20] E. Porta, *Cursillo de Pintado de Plásticos*, AKZO NOBEL COATINGS – ICE Plastics, Barcelona, Spain (2006).