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Methodologies for Characterization of Aerospace Polymers/Energetic Materials – a Short Review

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ABSTRACT: Fourier transform infrared spectroscopy techniques, associated or not to others, are a well-studied subject used for characterizing polymers/energetic materials that have been employed mainly in aerospace industries. However, the infrared analyses are usually qualitative and performed using the mid-infrared. This paper discusses the Fourier transform infrared spectroscopy qualitative and quantitative methodologies, coupled or not with thin layer chromatography and thermogravimetric analysis, for characterization of aerospace polymer systems, in some cases, using mid-infrared, near-infrared and far-infrared regions, by traditional accessories and the latest generation spectra mode, universal attenuated total reflection. This short review was made based on methodologies developed during the last two decades and published by many scientific and industrial research groups, emphasizing studies usually carried out in the last five years. A critical assessment and future trends were included.

KEYWORDS: Aerospace polymer, Energetic material, FT-IR, Methodologies.

INTRODUCTION

STUDIES ABOUT BINDERS OF PROPELLANTS

As well-known, hydroxyl-terminated polybutadiene (HTPB) reacts with isocyanate (curing agent) to obtain polyurethane (PU) formation and it is the usual binder used in solid propellant grain of the rocket motors. Thus, the determination of its hydroxyl (-OH) and isocyanate (-NCO) groups by instrumental techniques is an important parameter for predicting properties of these composites.

Hydroxyl and isocyanate numbers could be faster determined by Fourier transform infrared spectroscopy (FT-IR) methodologies than wet chemical method, and the functionality distribution of HTPB binder, by specific methodology, is a good example and we can include these determinations among the several studies, developed in our laboratories (Takahashi *et al.* 1996; Lourenço *et al.* 2006).

Takahashi *et al.* (1996) applied FT-IR analysis for determining contents of hydroxyl groups (IOH) in HTPB resins and free NCO groups in diisocyanates and NCO-terminated prepolymers. FT-IR methodology provided accurate results equivalent (IOH) or higher (% NCO) than classic wet methods and within the FT-IR instrument accuracy limit, ≤ 2%. The FT-IR methodology has the additional advantages of being fast, inexpensive and requiring small amount of sample and solvent, e.g. CS_2 (IOH) and CCl_4 (% NCO). These methods have some advantages that may be useful in industries and research centers, especially to those who work with polyurethanes, for characterization of

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raw materials (resins and isocyanates) and product control (NCO-terminated prepolymers).

This methodology for determining hydroxyl groups is important, but it is necessary to know how these groups were distributed in the molecular chain. Lourenço *et al.* (2006) developed a size exclusion chromatography (SEC) methodology, with double detection, to determine the functionality distribution of HTPB polymer. This method showed to be sensitive to small differences in the functionality distribution of the HTPB, affecting the tensile tests performed with HTPB polyurethane.

Recent study about HTPB was developed by Clemente *et al.* (2014). Polyurethane polymer matrix was synthesized using polyols as a raw material to obtain a binder such as (HTPB) prepolymer in energetic material formulation. They concluded that the soybean-based polyol was the best starting raw material for producing binder. Characterization of the binder was carried out by employing FT-IR analysis to the mid-infrared (MIR) region and thermal techniques, such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Glass transition (Tg) (−39 °C) of the polyol derived from soybean oil was determined by employing DSC technique. It was considered a good value because the Tg of the HTPB-based polymer matrix is around −50 °C. By TG, it was possible to evaluate the thermal degradation process of polymer obtained and to determine the activation energy (Ea) (122.4 kJ·mol^{-1}), whose value is very close to the HTPB-based polymer matrix. Thus, the application of synthesized material as solid fuel has shown promising results for tests in rocket engines. They showed good results by using soybean-based polyol as a raw material to obtain a binder, such as HTPB prepolymer in energetic material formulation, but the IR region used for the qualitative characterization was just the usual MIR.

The energetic binders are usually low-molecular-weight hydroxyl-terminated polyethers, with nitro or azido groups, capable of holding together fuel and oxidizer compounds from the propellant. These chemical groups give a significant contribution to the propellant impulse characteristics. The energetic binders can produce propellants systems in which metal fuels, such as aluminum, can be reduced. Glicidyl azide polymer (GAP) (Kawamoto *et al.* 2008; Sciamareli *et al.* 2009a, 2009b), GAP/BAMO (Kawamoto *et al.* 2010), poly[3,3-bis(azidomethyl)oxetane] (poly-BAMO) and 3-azidomethyl-3-methyl oxetane polymer (poly-AMMO) (Oliveira *et al.* 2006, 2007; Kawamoto *et al.* 2009) have been studied by AQI group from Instituto de Aeronáutica e Espaço in the last decade.

In relation to FT-IR characterization methodologies of energetic materials used in propellants, it is possible to include the characterization of poly-AMMO and poly-BAMO and their precursors as energetic binders in the near-infrared (NIR), MIR and far-infrared (FIR) regions by Oliveira *et al* (2006). Their study was focused on the characterization of polymers containing energetic groups that have been synthesized at ICT (Fraunhofer Institute for Chemical Technology) group, an important Germany Research Center of propellants. This characterization identified analytical bands and allowed quantitative and/or kinetic studies of these compounds, using the whole spectral ranges of NIR/MIR/FIR. Basically, it was possible to visualize differences between chemical structures of these compounds and also to identify spectrometric changes (formation or disappearance of functional groups) that can occur during the polymerization process. It is also possible to use the absorptions around 4200, 2100 and 550 cm^{-1} as analytical bands to study these compounds containing azide groups for quantitative determinations. Bands found in the region of 1250 and 660 cm^{-1} can be used in similar studies of Br-substituted binders. Bands near 980 cm^{-1} can be used to study the ring opening polymerization reaction of compounds containing azide and/or bromine.

Oliveira *et al.* (2007) analyzed azide polymers samples by FT-MIR in order to develop a quantitative methodology to determine the C, H and N content in energetic polymers used in propellants. The elemental analysis data were used as reference. The FT-MIR results showed a good agreement with CHN analysis, and a good linear relationship was obtained, suggesting that the developed methodology can be useful for quality control of these energetic polymers.

In another study about energetic material (Ribeiro *et al.* 2012), GAP was synthesized and characterized by FT-IR, ultraviolet spectroscopy (UV), nuclear magnetic resonance spectroscopy (NMR), DSC, elemental analysis (CHN), TG and SEC. Through these conventional techniques, it was possible to identify the material content and some of its properties related to its use as an energy plasticizer in propellants. This new method with dimetylformamide (DMF) solvent was effective in obtaining high molecular weight, high yield and better conversion of azide.

Oliveira *et al.* (2014) evaluated the interaction between two energetic polymer/oxidizer systems, GAP and ADN (ammonium dinitramide, a chlorine-free oxidizer) as well as GAP and AP (ammonium perchlorate) by FT-IR spectroscopy, in the NIR and MIR regions. Major spectrometric changes were observed for the GAP/ADN system, with a broadening of the bands in the region between 3100 – 3500 cm^{-1}, pointing to interactions between OH groups from GAP and NH_4^+ groups from ADN or AP. A decrease in band intensity was observed for the N_3 group in GAP as well as an increase of nitronium (NO_2^+) of ADN, suggesting interaction between these groups in the GAP/ADN system.

POLYMERS USED IN COATING PROCESS OF ENERGETIC MATERIALS

FT-IR surface techniques have been used for characterization and/or quantification of different polymers applied in coating process of energetic material (Mattos *et al.* 2004a, 2004b, 2008; 2009).

Mattos *et al.* (2008) made a surface characterization of RDX/fluoroelastomer (Viton®) system by FT-IR techniques such as transmission, photoacoustic (PAS) and attenuated total reflectance (ATR). The transmission spectrum of the cast film showed some evidence of the presence of fluoroelastomer, which covers the energetic material. ATR showed excellent results to analyze HMX/Viton® system for characterization of Viton® bands.

Mattos *et al.* (2009) developed a new FT-IR methodology to characterize quantitatively the polymer content in PBX (HMX/Viton®) using the TG as reference technique. ATR was used as surface technique and showed excellent results, being faster than the usual methodologies, as high performance liquid chromatography (HPLC).

According to Tourné (2013), in the field of explosives and other energetic materials, detection and characterization brought new challenges. Detection schemes at the molecular level provide a wide variety of analytical technique, such as Raman, Infrared (IR) and Mass Spectroscopy, among others. However, studies cited in the IR part of her paper are only about the characterization of explosives without reference to polymer/explosive (PBX); probably, the main objective was only to identify some micromolecules. Thus, qualitative characterization and quantification of polymer that can be found on the surface of this system can be contributive for the area of energetic materials.

THERMAL INSULATION STUDIES

RUBBERS

Main methodologies developed by AQI group on rubbers, such as natural rubber (NR), ethylene propylene diene monomer (EPDM) and butadiene and acrylonitrile copolymer (NBR) used in the aerospace industry, are discussed below and related to other publications (Lanxess Rubber 2012; ASTM D3900 – 05a 2010; Chitta 2014). The topics are organized by methodologies, including also the IR or FT-IR techniques couplings with thin layer chromatography (TLC/IR) (Dutra 1996; Damazio 2015; Damazio *et al.* 2014, 2015) and thermogravimetric analysis (TG/FT-IR) (Sanches 2015; Sanches *et al.* 2014, 2015).

TLC and IR Methods for the Characterization of Rubbers and Their Additives

Analysis of vulcanized elastomer composition is often an important quality control requirement and suitable for determining rubber formulation. Dutra (1996) developed a methodology for separating and identifying additives in rubber, by TLC/IR coupling techniques. This study was carried out by two methods: one that uses potassium bromide (KBr) pyramids and another, more simple, without the use of pyramids, to reduce costs.

According to the first method, the material obtained by solvent extraction is applied in an appropriate silica plate, in which it is developed in a closed vessel chromatography, using a mobile phase. The plate is dried and reveals deposits with suitable developer. Deposits are scraped and placed in a tube containing KBr pyramids. Small amount of solvent used in the extraction is added to bring the sample to the top of the pyramid. After solvent evaporation, this top is removed, crushed and compressed in the form of KBr disc for transmission infrared analysis. Basically, in the second method, the deposits are scraped and treated with the solvent used in the extraction, filtered to remove silica, dried, mixed with KBr (200 mg) in order to obtain pellets and analyzed by transmission.

It was concluded that the TLC/IR coupling, for both methods, is particularly useful for polymer research centers to expand knowledge on identification and characterization of the main constituents of rubbers, such as antioxidants and plasticizers in previously known formulations. The choice of a suitable analysis condition allows the evaluation of other components.

The development of quantitative methods which detect low content of components of elastomeric system, especially in compounds, is still a challenge. Damazio *et al.* (2014) developed a methodology by FT-IR (UATR and transmission techniques) for determining the ethylene (ET) and propylene (P) content on rubber samples (neat, raw and vulcanized elastomer) EPDM (ethylene propylene diene monomer), used in aerospace industry. Both techniques showed good accuracy, being

UATR analysis the most appropriate for neat elastomer. Transmission/pyrolysis was suitable for analyzing all types of EPDM (neat, raw and vulcanized elastomer), suggesting to be useful for similar formulations.

Damazio *et al.* (2015) developed a method using FT-IR transmission for determining the content of 5-ethylidene-2-norbornene (ENB) on rubber samples (neat elastomer) burned in controlled pyrolysis and Bunsen burner. The determination was done by observing the variation of relative band and relative concentration, and they were also suitable for estimating ET and P contents of the same rubber.

TLC/IR using UATR accessory was applied for characterization of additives, in order to evaluate the applicability of these techniques together. Two formulations were used in this elastomer – a type of eluent system and the Gibbs reagent, the developer. Basically, all organic components were detected by this methodology that showed to be promising for detecting additives of similar chemical structures, though small quantities of some components presented in the formulation (Damazio *et al.* 2016).

Lanxess Rubber (2012) developed on an industrial laboratory a methodology for determining the ET, ENB and 2-vinyl norbornene (VNB) content in EPDM, but only applied to EPDM rubber which does not have a plasticizer. For extended rubber, oil extraction must be made in advance, because plasticizer interferes with proper execution of the analysis. It may take more time for the process to be finished.

Another method (ASTM D3900 – 05a 2010) for the determination in question uses EPDM samples with ET content (35 – 85%) established by nuclear magnetic resonance of carbon 13 (^{13}C NMR) and analyzed by FT-IR transmission. Samples were prepared as films without plasticizer. Four methods have been established as well as the analytical bands (cm^{-1}) of P and ET used, being on the relative band (P/ET): 1156/722; 1379/722; 1379/1460; 1156/4255 (by using band in NIR region for ET, which, although, did not found the assignment in the text, being a combination of bands at the same region). Some interference in determining proper baseline was cited due the presence of additive bands around 1156 cm^{-1} of P, recommending the use of other bands. Lanxess Rubber (2012) obtained spectra by transmission mode, but details of sample preparation, number of replications and error methodology are not mentioned.

The methodology was fairly detailed on ASTM standard (ASTM D3900 – 05a 2010), but some points should be highlighted: (a) pressed samples are not suitable for vulcanized materials; (b) the presence of additives in one of the methods interferes in the choice of baseline, implying the use of other bands; (c) the use of a non-selective band of ethylene (1460 cm^{-1}), which is attributed to the CH_2 and CH_3 angular deformation, indicating that the best analytical bands would be found at 1379 cm^{-1} to P and 722 cm^{-1} to ET.

Recent study (Chitta 2014) applied HPLC to separate EPDM terpolymers based on diene content. It was found that the nature of diene contributes with the retention. According to the author, the difference between the elution volume obtained experimentally from an EPDM sample and the expected elution volume of an EP sample, with identical ethylene content, contributes to calculate the diene content of EPDM. HPLC analysis of polymers is a prerequisite to determine solubility of macromolecules in the corresponding sample solvent or mobile phase, at a specific temperature. Complete dissolution of polymer molecules is important for liquid adsorption chromatographic separation and also to avoid any blockage in the chromatographic system during analysis. Damazio (2015) developed a quantitative analysis. As HPLC analysis conditions are more complex than other techniques, TLC/IR can be used for separation and identification of additives.

TG and IR Methods for Characterization of Rubbers and Their Additives

The main methodologies that have been developed for additives analysis generally involve solvent extraction step, increasing analysis time. Sanches (2015) investigated unvulcanized and vulcanized EPDM and their additives by FT-IR analysis of gaseous pyrolysates (PIR-G/FT-IR) (Sanches *et al.* 2014) and by thermogravimetric analysis coupled with FT-IR (TG/FT-IR) (Sanches *et al.* 2015), both without solvent extraction step. A comparison between these two methodologies was also carried out. The results showed that functional groups of additives can be detected from unvulcanized and vulcanized rubbers, without prior extraction. The sulfur additives, monossulfide of tetrametil tiuram (TMTM) and 2-mercaptobenzothiazole (MBT), at levels as low as 0.7 phr (0.63 wt %), were detected by both methods. However, other additives such as paraffin oil, stearic acid and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) can not be identified by these methodologies. Individually, all analyzed additives presented distinct FT-IR spectra and were also identified from each other by coupled PIR-G/FT-IR and TG/FT-IR methodologies.

Sanches *et al.* (2006) used PIR-G/FT-IR technique for investigating gaseous products of other rubbers. The developed methodology was suitable to identify different elastomers and elastomer blends, including rubbers that present similar IR spectra of pyrolyzed liquid products, such as halogenated forms of copolymer of isobutylene and isoprene rubber (CIIR and BIIR), natural and copolymer of butadiene and styrene rubber (NR/SBR) as well as EPDM/SBR, SBR and butadiene rubber (SBR/BR) and SBR.

Arockiasamy *et al.* (2012) studied the decomposition behaviour of SBR using a system equipped with TG, DSC, FT-IR and mass spectroscopy (MS). Thermal decomposition and oxidation of SBR rubber was examined with focus on the composition of evolved gases during the process. FT-IR detected the presence of the following functional groups: OH, C–H and C=C, C=O and O–C–O. The interaction of these techniques proved to be useful for this kind of characterization.

Sanches *et al.* (2015) developed a methodology of TG/IR in order to evaluate additives in EPDM rubber composition. Unvulcanized and vulcanized EPDM rubbers and their additives were investigated by TG/FT-IR without solvent extraction and in a wide temperature range. TG/FT-IR detected absorptions due to the additives tetramethylthiuram monosulfide and 2-mercaptobenzothiazole present in the EPDM formulation at concentrations of 0.7 phr (0.63 wt %). Paraffin oil, stearic acid and 2,2,4-trimethyl-1,2-dihydroquinoline functional groups were not observed in either the unvulcanized or vulcanized EPDM. Nevertheless, in addition to the ability of this method to detect sulfur-containing groups, the lack of a pre-extraction reduces the time and effort required for additive analysis in rubbers. Therefore, the TG/FT-IR technique can be employed for analyzing additives separately, neat rubber (raw), vulcanized and unvulcanized compounds. Additives degradation can also be investigated by TG/FT-IR, because of the temperature selectivity.

FT-IR Surface Analysis of EPDM Rubber

Elastomers of the ethylene-propylene, such as EPDM, are apolar and present low adhesion properties, in most cases, requiring surface treatment. Plasma surface treatments have been an alternative to improve these characteristics, besides being harmless to the environment.

Most of mentioned studies and reviewed literature have shown the contribution of FT-IR to characterize chemical species formed on surface as a consequence of the treatment. Some studies in which plasmas were used to treat EPDM rubbers also showed a good response and sensitivity by using some FT-IR techniques to analyze their surfaces (Moraes *et al.* 2007; Grythe and Hansen 2006; Awaja *et al.* 2009). Spectra of EPDM and polyolefin treated by plasmas were obtained with ATR, but UATR, the new generation of the FT-IR technique, has not been used to study polymer surfaces.

Santos (2013) modified the surface of vulcanized EPDM, Nordel IP 3430 and Nordel IP 4520 with plasma excited by microwaves in Ar, N_2, Ar/O_2, N_2/O_2, N_2/H_2 and N_2/H_2/Ar, aiming the improvement of their adhesive properties. The characterization was made by FT-IR techniques of reflection: UATR, MIC with ATR objective and PAS (Santos *et al.* 2012b, 2013, 2014). They were used to evaluate the degrees of different sampling depth for the characterization of rubbers after plasma treatments, mainly by the different permeability of gases (oxygen and nitrogen) chosen to form gaseous mixtures. UATR technique was the most suitable for this purpose, because it showed less interference with the components of the rubber formulation, detecting spectrometric changes arising from the formation of polar groups promoted by the plasma treatment. In order to validate the results obtained by FT-IR, X-ray photoelectron spectroscopy (XPS) analysis was performed before and after treatment, and it was observed an increase in the percentage of atomic oxygenated and nitrogenated groups on the surface after treatments by Ar/O_2 plasma and N_2/H_2, confirming the results found by FT-IR. It was observed a reduction in the values of the contact angle, high values of work of adhesion and peel strength test of adhesive gasket (EPDM/Adhesive PU/PVC). These results were attributed to the improvement in adhesive properties of treated surface. After Ar/O_2, N_2/H_2 and N_2/H_2/Ar plasma treatments, Nordel IP 4520 rubber showed fairly aging stability, evaluated by measuring contact angle. Nordel IP 3430 achieved its best result just with Ar/O_2 plasma. Samples submitted to mechanical tests were characterized by FT-IR/UATR, and bond failures were confirmed between the interface of the adhesive film of PU and EPDM (Nordel IP 3430) rubber, noticing the contribution of this technique for studying interfaces.

A recent study (Pistor and Zattera 2014) about reclaiming of elastomer residues has used instrumental techniques for characterization of devulcanization caused by microwaves exposure. The efficiency of devulcanization of EPDM was determined by subjecting the elastomer samples to 2, 3 and 4 min of microwaves exposure. Scanning electron microscopy (SEM) and TG using different heating rates were used to determine the kinetic degradation parameters according to the Flynn-Wall-Ozawa method. It was observed that, up to 4 min of devulcanization exposure period, the degradation temperature of EPDM was not exceeded. Microwaves exposure delivered a maximum devulcanization temperature range that is consistent with the degradation temperatures observed by TG. The morphology of the samples was altered by the microwave treatment. The devulcanization process favored particle size reduction, while additionally increasing the particles surface roughness after the devulcanization process. Activation energy values were also reduced as a result of the change in morphology, probably due to the diminished concentration in polysulfide links characteristic of the vulcanized EPDM-r 3-D network.

FT-IR ANALYSIS OF COMPOSITE SYSTEMS

Epoxy systems (ES) are very important due their versatility and potential of use, including the aerospace area. Depending on the physical and chemical properties of the curing agents (CA) and the process conditions, it is possible to vary significantly the properties of the final material, such as mechanical strength, thermal and chemical resistance etc. Therefore, the mechanism of cure must be known in order to establish the relationship between structure and properties of the material, optimizing how it will be used, i.e. adhesive, coating or matrix composites. Thus, it is evident the importance of characterization and identification of curing agents in ES.

Romão (2003) studied ES based on diglycidyl ether of bisphenol A (DGEBA) cured with nine CA. The characterization of these ES and CA was done by DSC, FT-IR, TG and coupling TG/FT-IR. The curing conditions of ES were determined by DSC. Chemical changes that occurred during the curing reaction of certain systems were evaluated by MIR and NIR spectroscopy. The ES decomposition temperature determined by TG was used for identifying the respective CA by controlled pyrolysis FT-IR (CONTROLPIR/FT-IR).

A recent study (Ahamad and Alshehri 2014), including epoxy resin and coupled methodologies for its characterization, was found. A polymeric blend has been prepared using urea formaldehyde (UF) and epoxy resin (DGEBA) in 1:1 mass ratio. TG coupled with FT-IR and spectrometric mass (MS) technique were used to study the thermal degradation of UF/epoxy resin blend (UFE). The TG results showed the pyrolysis process divided into three stages: drying process, fast thermal decomposition and cracking of the sample. There were no solid products except ash content for UFE during ignition at high temperature. Volatile products, such as CO_2, CO, H_2O, HCN, HNCO, and NH_3, were identified during thermal degradation of UFE. These two techniques could be complementary since they were refined to identify more precisely evolved gases.

FUTURE TRENDS

There are new studies being carried out in different areas, such as polymers systems for hybrid propulsion (Santos *et al.* 2012a), FT-IR characterization of polymers used in microencapsulation of oxidizer for propellants (Oliveira 2014) and substitution of asbestos in polymers thermal insulation compositions.

In recent publications found in literature about these subjects, we can cite the "Review on the fundamentals of polymer combustion and flammability characteristics for hybrid propulsion" (Chen and Gao 2014), which emphasizes properties of potential polymeric fuels and their modification.

Novozhilov et al. (2011), in a review, cites that hybrid propulsion is an attractive alternative to conventional liquid and solid rocket motors, which has been an active area of research and technological developments. Fundamental flammability characteristics of polymeric fuels have been discussed. Success of polymer fuel applications to hybrid propulsion depends on further improvement of their combustion characteristics, by the enhancement of regression rates. Estimates suggest that the regression rate needs to be increased dramatically, but chemical fuel modification is a promising route to overcome this bottleneck.

Santhosh (2010) discussed about the use of ethyl cellulose (EC) and poly(methyl methacrylate) (PMMA) as coating materials of spherical grains of ADN. A comparison of the moisture absorption profiles of ADN coated with EC and PMMA was made. Preliminary coating studies on spherical ADN grains were carried out using EC and PMMA at relative humidity of 62 and 74%. ADN coated with PMMA showed better properties than EC. The moisture pickup was reduced over 50% for the ADN grains coated with either EC or PMMA.

Virta (2005) noticed a considerable decline consumption of asbestos in the United States, part of Europe and some other countries. In fact, many asbestos substitutes have been successful used for a long time, being an integral part of the product. Asbestos still have been used in some places; however, it is observed a considerable expansion in sales of substitutes or alternative materials.

In this context, Maxim *et al.* (2014) show in a review the perlite toxicology and epidemiology, being used as asbestos substitute. They concluded that the available data are not reliable to use for risk calculations of perlite-exposed populations and warn that perlite is regulated as a nuisance dust in some countries.

According to future trends, characterization of these polymer/energetic materials, based on FT-IR and other complementary techniques, could be suitable mainly for aerospace technology.

CONCLUSIONS

This review focused on the recent developments of aerospace polymers/energetic materials. The characterization of aerospace polymers/energetic materials can be considered a dynamic process presenting new challenges for the future. Many developments have been made in recent years towards this goal. Characterization schemes help to provide researchers with a wide variety of analytical techniques. It was realized that there is a small number of FT-IR studies on the NIR region, coupling techniques application, measurement and surface analysis by UATR of aerospace polymers. Thus, studies that have been developed in this area can contribute for the increase in technical and scientific research of these materials.

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