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FTIR – An Essential Characterization Technique for Polymeric Materials

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1. Introduction

Infrared spectroscopy is an essential and crucial characterization technique to elucidate the structure of matter at the molecular scale. The chemical composition and the bonding arrangement of constituents in a homopolymer, copolymer, polymer composite and polymeric materials in general can be obtained using Infrared (IR) spectroscopy (Bhargava et al. 2003)

The FTIR spectrometers obtain the IR spectrum by Fourier transformation of the signal from an interferometer with a moving mirror to produce an optical transform of the infrared signal. Numerical Fourier analysis gives the relation of intensity and frequency, that is, the IR spectrum. The FTIR technique can be used to analyze gases, liquids, and solids with minimal preparation. (Lee, 1977).

The spectrometer may operate in transmission or reflection, but also in attenuated total reflection (ATR) mode, which have been widely used during the last two decades. The transmission mode is very suitable for quantitative analysis, since the main parameters to apply on the Beer-Lambert law are known or easily estimated. The reflection mode is used when polymer is not well dissolved at room temperature, and a film or pellets of the sample is characterized. Such is the case of polyolefins and some engineering polymers like PET.

The ATR objective has a polished face of diamond, germanium or zinc selenide (ZnSe) that is pressed into contact with the sample (Sawyer et al. 2008). Infrared reflection is attenuated by absorption within a surface layer a few micrometers deep. In this case, a good contact is required, but that is easy for most polymers, and the advantage is that no sample preparation is required. Therefore, powders, films, gels and even polymer solutions can be characterized.

The absorption versus frequency characteristics of light transmitted through a specimen irradiated with a beam of infrared radiation provides a fingerprint of molecular structure. Infrared radiation is absorbed when a dipole vibrates naturally at the same frequency in the absorber. The pattern of vibrations is unique for a given molecule, and the intensity of absorption is related to the quantity of absorber. In the IR region, each group has several

and different patterns of vibration such as: stretching, bending, rocking, etc. The absorbance of these bands is proportional to their content based on the Lambert–Beer law. Because of the complexities of the structures (for example, polybutadiene unit has 1,4-cis, 1,4-trans and 1,2-vinyl microstructure while polyisoprene unit has other additional 3,4-microstructure), the general methods for quantitative analysis require external standards, which are usually characterized by primary technique like Nuclear Magnetic Resonance (Zhang et al, 2007). Nevertheless, it is possible to characterize polymers, quantitatively, using FTIR as it will be discussed later.

Thus, infrared spectroscopy permits the determination of components or groups of atoms that absorb in the infrared at specific frequencies, permitting identification of the molecular structure (Bower, 1989; Koenig, 2001). These techniques are not limited to chemical analysis. In addition, the tacticity, crystallinity, and molecular strain can also be measured. Copolymer compositions can be determined as block copolymers absorb additively, and alternating copolymers deviate from this additivity due to interaction of neighboring groups.

The aim of this chapter is to present some examples in the context of different areas, in order to remark the importance of FTIR to determine different aspects as identification of functional groups, to elucidate mechanisms of reaction or even to determine the time of reaction.

The track of a reaction in real time when xerogels are synthesized, interaction of different materials like chitin with polyurethane during synthesis of biocomposite, identification of functional groups attached to nanotubes during their modification and establishment of microstructure of polybutadiene during its hydrogenation are the main examples of the use of FTIR, even being semi-quantitative, quantitative or qualitative analysis, that will be presented and analyzed.

The synthesis of xerogels involves basically two steps, hydrolysis and condensation. The follow of such steps is important to establish the time needed to change process conditions and optimize the xerogel. Even when FTIR analysis is a qualitative technique, this analysis could be used as a semi-quantitative indirect measure of the variation of functional groups, during hydrolysis or condensation reactions.

Biocomposites are very fascinating materials since they offer characteristics of two or more different materials, in order to have very specific features that would be practically impossible to obtain by every single material of biocomposite. Chitin is an abundant biopolymer obtained from shrimp, insects and some vegetal species. This material is capable to remove some contaminants like fluoride from water. Nevertheless, in order to improve the mechanical characteristics of chitin, in order to be applied in water treatment in real conditions, it must be supported. Polyurethane is a very versatile polymer due to its chemical structure. During its synthesis, interactions between functional groups take place in order to create the urethane group. The synthesis of biocomposite must bear in mind that interaction between compounds is essential to create a mechanical and chemical resistant material. FTIR with ATR analysis was carried out to characterize a biocomposite based on chitin and polyurethane, demonstrating that interaction between them occurs.

The characterization of carbon nanotubes usually is carried out using Raman spectroscopy. Nonetheless, the use of FTIR allows the determination of functional groups when carbon

nanotubes are chemically treated in order to improve its interaction with other entities like polymeric matrix, for example. In this sense, oxidized nitrogen-doped nanotubes were analyzed by FTIR, corroborating that functional groups are present in these carbon nanotubes.

2. Xerogels

The xerogels are materials that have precise microstructure and they are synthesized by sol-gel synthesis. Two steps are implied in the sol-gel process, hydrolysis and condensation, which are very sensitive to reaction conditions, being faster or slower and giving xerogels with different characteristics, in terms of structure, surface area, and porosity (Fidalgo and Ilharco, 2005).

In this sense, the trace of each reaction with time, hydrolysis and condensation, is important in order to establish the end and beginning of each of these reactions. FTIR is a very useful characterization technique to follow reactions during sol-gel synthesis, since there are specific functional groups that participate in the sol-gel process.

In the case of hydrolysis, silanol is produced from reaction between silane and water molecules. The silanol exhibits a strong absorbance around 945 cm^{-1} , which can be followed during the reaction.

The condensation reaction, where the silanol groups react between them, creating siloxane groups, gives an intense absorbance band at 1080 cm^{-1} . Therefore, it is also possible to see variation of such band with time (Andrade et al., 2010).

2.1 Kinetics by FTIR

The main functional group that is produced during hydrolysis of silanes is silanol, which has a characteristic absorbance band at 945 cm^{-1} . The hydrolysis reaction, usually, is carried out in presence of some alcohol, depending of the silane. For example, if the hydrolysis is carried out with tetra methoxy silane, then the chosen alcohol is methanol, or with tetra ethoxy silane, the preferred alcohol is ethanol. This is because the by-product of hydrolysis reaction is an alcohol. Therefore, the intense signals in the infrared bands located at 945 and 880 cm^{-1} , corresponding to silanol and ethanol (for example) can be followed during hydrolysis reaction.

In the Figure 1 it is shown the spectra for hydrolysis of tetra ethoxy silane (TEOS) in presence of ethanol at different reaction time. The absorbance band at 945 cm^{-1} can be assigned to the vibration of the Si-O from the silanol residual groups $[\text{Si}-(\text{OH})_4]$, whereas the band at 880 cm^{-1} can be assigned to OH groups from ethanol. The time at which no more increment of the absorbance band of silanol and OH groups occurs was established as the time at which the hydrolysis reaction was completed.

From Figure 1, it can be seen that the absorbance bands corresponding to silanol and OH, from ethanol, increased up to 30 min. After this time, there was no increase of these bands (spectra not shown), which can indicate that the hydrolysis reaction has been completed.

Determination of the time needed to carry out the hydrolysis reaction is critical since the knowledge of the complete conversion to silanol groups is required to promote a more efficient condensation reaction.

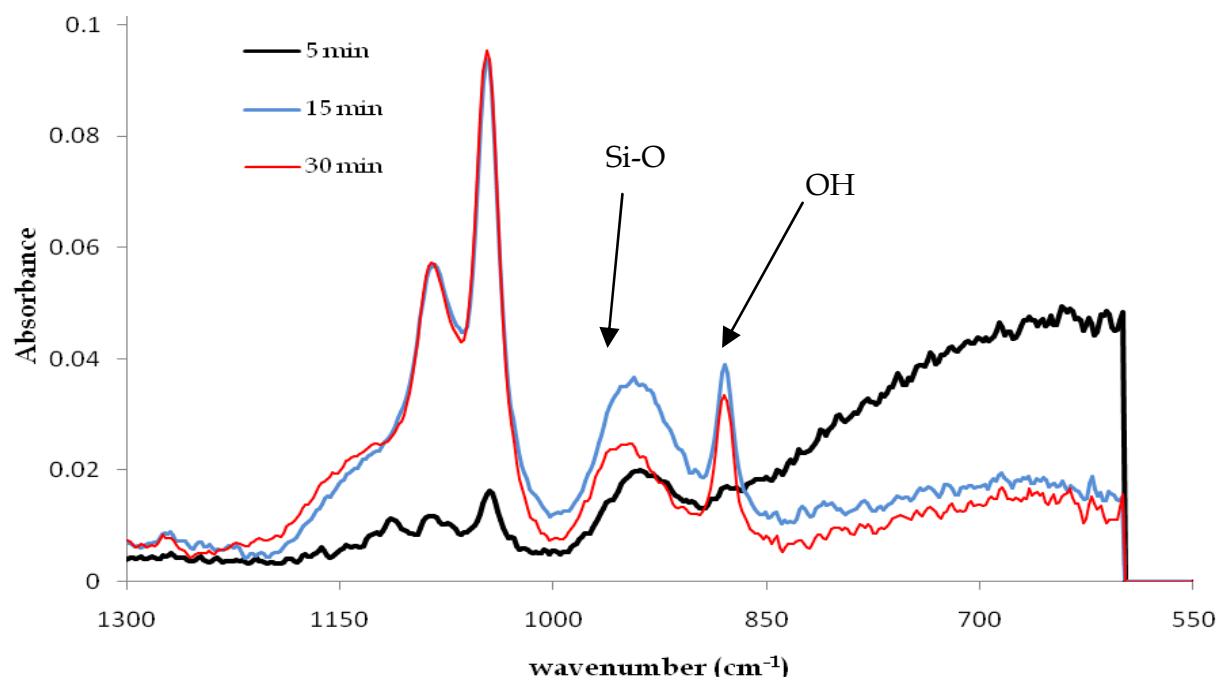


Fig. 1. Spectra of hydrolysis of TEOS at different times.

In the case of the condensation reaction, the silanols are reacting, between them, to produce siloxane groups. The siloxane group has a characteristic absorbance band, corresponding to the vibration mode (Si-O-Si) at 1080 cm^{-1} , that can be followed with time. In fact, from Figure 1, it is noted that after 15 minutes of reaction, there is an important increment of the band at 1080 cm^{-1} compared to the spectrum at 5 minutes of reaction. It is important to have in mind that hydrolysis and condensation can take place at same time, but condensation is catalyzed with alkaline chemicals, as amines. The fact that the band at 1080 cm^{-1} had not an increment, from 15 to 30 minutes, could be attributed to the absence of alkaline catalyst in the media reaction. It was shown (Andrade et al., 2010) that the absorbance was increased when an alkaline catalyst was added to the media reaction, and the band corresponding to silanol (945 cm^{-1}) was reduced with time.

3. Biocomposites

Biocomposites i.e. composite materials comprising one or more phase(s) derived from a biological origin (Fowler et al., 2006), are very interesting materials since they offer characteristics of two or more different materials, in order to have very specific features that would be practically impossible to obtain by every single material of biocomposite. Many types of biocomposites have been proposed, depending of the application objective of each material. Water treatment researchers have recently proposed the use of biocomposites as adsorbent materials, in order to remove many different contaminants from water. Synthesis of biocomposites to use them as adsorbents has been necessary, for example, because biosorbents (adsorbents from a biological origin) usually have poor physical/chemical resistance. The roll of the matrix in biocomposite is to reinforce the biosorbent, by establishing physical and/or chemical links between both phases.

One of the most studied biosorbent is chitin, which is an abundant biopolymer found in crustaceans, insects and fungus. This biopolymer is commercially purified by alkaline deproteinization, acid demineralization and decoloration by organic solvents of crustaceans wastes (Pastor, 2004). An additional stronger alkaline treatment of chitin produces deacetylated chitin. If the acetylation degree (DA) decreases at 39% or less, the biopolymer is named chitosan. Hence, the DA of chitin is variable and depends on the process conditions (alkali concentration, contact time, temperature, etc.), which produces DA values from 100 to 0%. Because of this, chitin is known as the biopolymer which has a DA from 100 to 40%; likewise, when the chitinous biopolymer has DA lower than 40%, the biopolymer is named chitosan. Chitosan is, therefore, a biopolymer with structure very similar to that of chitin (see Figure 2); however, chitosan solubility is much greater, especially in acid mediums.

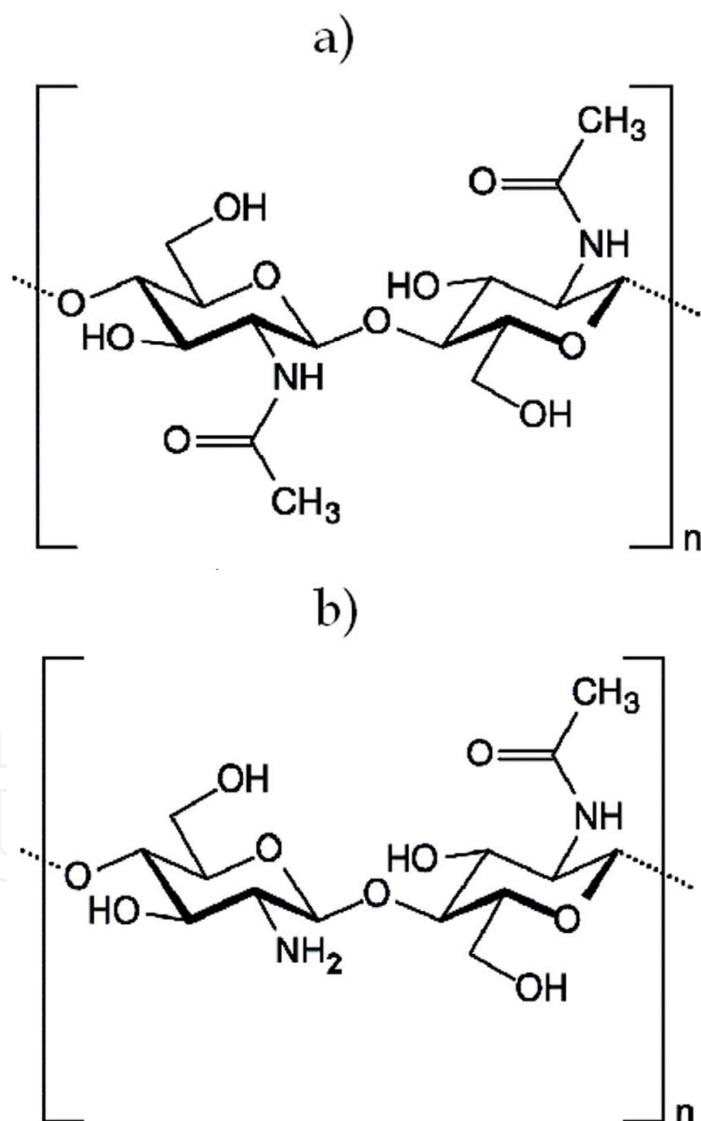


Fig. 2. Chemical structures of a) chitin and b) chitosan (Elnashar, 2010).

Chitin is capable to remove many contaminants from water. A wide variety of studies have demonstrated the ability of chitin to uptake substances as metals, anions and organics.

Nevertheless, in order to improve the mechanical characteristics of chitin to be applied for water treatment in real conditions, it must be supported. The use of polymers as supporting matrix of biosorbents has given encouraging results. In this sense, polyurethane has been one of the most used polymers.

Polyurethane includes a group of polymers derived from the isocyanates, organic compounds which have the isocyanate group ($-N=C=O$) in their structures and, owing to this, are very reactive. Polyurethane shows advantages as easy handling and the possibility to obtain malleable and resistant biocomposites. The Figure 3 shows a general polyurethane prepolymer structure and how isocyanate group reaction gives rise to different type of chemical linkages.

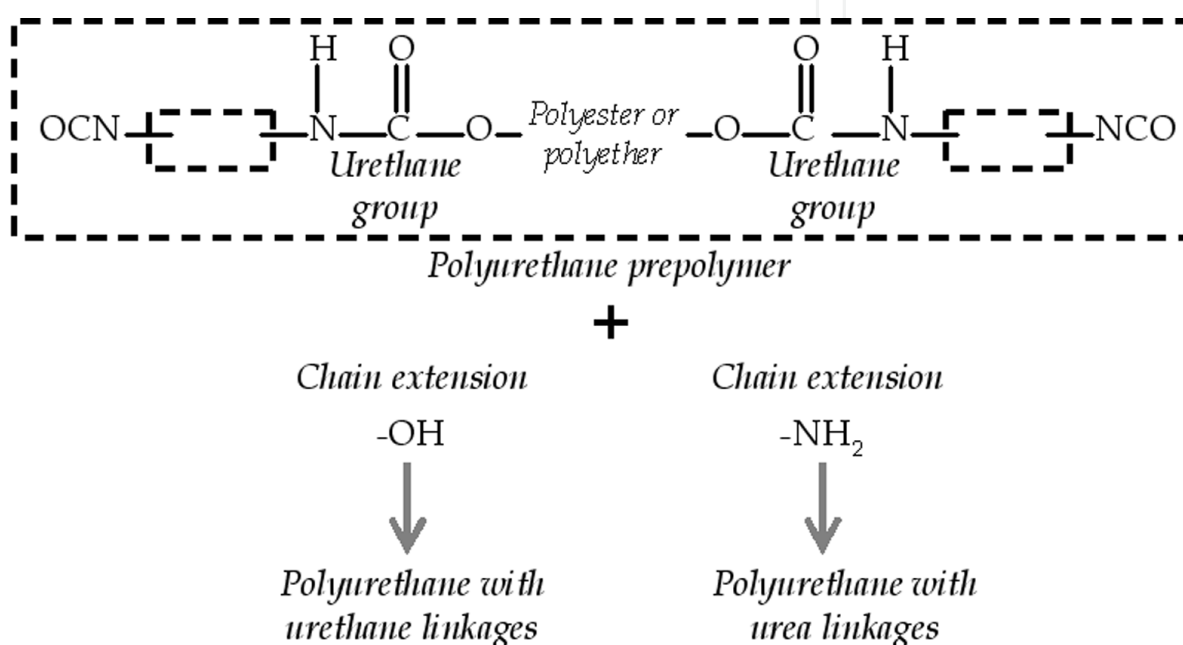


Fig. 3. General chemical structure of polyurethane prepolymer (modified from Hepburn, 1982).

Chemical reaction between the isocyanate and a primary amine group produces the urea group, whereas the reaction between isocyanate and hydroxyl group forms the urethane group. Both urea and urethane are very stable chemical groups, which make the polyurethane a polymer very useful in applications that must resist extreme conditions of temperature, friction and UV radiation (Hepburn, 1982). Due to the high reactivity of the isocyanate with the primary amine and hydroxyl groups, it is valid to assume that the polyurethane establish strong unions with biosorbents to form biocomposites. Hence, such unions make polyurethane a good support matrix for biosorbents. In fact, more and more studies have been recently published about the use of polyurethane as support of biosorbents as seaweed (Alhakawati & Banks, 2004; Zhang & Banks, 2006), moss, sunflower waste and maize plant (Zhang & Banks, 2006), bacteria (Vullo et al., 2008; Mao et al., 2010), fungi (Sudha & Abraham, 2003; Li et al., 2008) and chitin (Davila-Rodriguez et al., 2009). Most of these studies have focused on the biocomposite biosorption capacity; however, the interaction polyurethane-biosorbent has been practically not studied. Infrared spectroscopy is a good methodology to characterize such interaction.

3.1 Methods

One research has recently reported characterization of the polyurethane-chitin interaction in a novel fluoride biosorbent biocomposite, using attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR) (Davila-Rodriguez et al., 2009). Such a biocomposite was produced by mixing chitin flakes with polyurethane (60:40 w/w) during the polymerization reaction, which was carried out under intense stirring. The biocomposite consisted, therefore, of chitin flakes covered by a thin film of polyurethane of approximately 1 μm thickness, according to different observations performed by scanning electron microscopy. The novel composite material showed greater chemical resistance compared to pure chitin, measured as a decrease of around ten times in the loss of mass when the material was submerged in an acid aqueous medium at pH 5 (from 19.6 to 1.5%). These results demonstrated the strong interaction between chitin and polyurethane on their contact surface. Nevertheless, FTIR-ATR methodology was used in order to get a better understanding of the biopolymer-matrix links formed during the biocomposite synthesis. For the FTIR-ATR analysis, a sample of the chitin-polyurethane biocomposite was used as produced. The FTIR-ATR instrument used was a Nicolet 6700 (Thermo Scientific) operating in the wavenumber range of 650 to 4000 cm^{-1} , with ZnSe crystal, 32 scans and 4 cm^{-1} resolution.

3.2 Results and discussion

Analysis of FTIR-ATR spectra showed that the biocomposite spectrum was very similar to that of polyurethane. In addition, it is important to point out that main bands of chitin spectrum were at the same wavenumber intervals that those of polyurethane (see Figure 4).

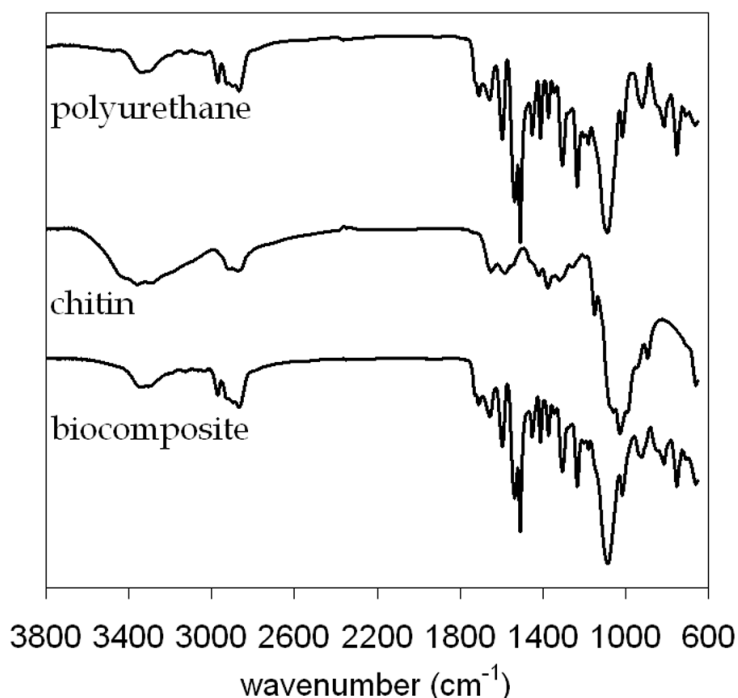


Fig. 4. FTIR-ATR spectra of chitin, polyurethane and chitin-polyurethane biocomposite (modified from Davila-Rodriguez et al., 2009).

Such an aspect contributed to produce the similarity between biocomposite and polyurethane spectra. This fact was predictable because chitin and polyurethane have similar chemical groups on their structures, including amine, amide and carbonyl. Nevertheless, some of the bands observed in the biocomposite spectrum were different in intensity compared to those of polyurethane and chitin. Bands located at 660, 1590 and 3300 cm^{-1} , corresponding to amine/amide groups, and the band located at 3350 cm^{-1} , corresponding to hydroxyl group, experimented appreciable changes in intensity. This phenomenon could be due to the chitin-polyurethane chemical interaction. As previously mentioned, primary amine and hydroxyl groups (both present in chitin structure) are able to react chemically with the polymer functional groups i.e. isocyanate, to form urea and urethane groups, respectively.

On the other hand, it is important to say that chitin-polyurethane interaction has an important physical component, since attraction forces as Van der Waals interactions and hydrogen bonds are present at the interface chitin-polyurethane. This aspect could have caused that chitin-polyurethane chemical interaction was not strong enough to be more clearly observed by means of the FTIR-ATR analysis. In addition, chitin was added to the biocomposite in solid form, which limits the achievability of amine and hydroxyl groups of chitin surface due to a steric impediment. Other important aspect to point out is that polyurethane film thickness over the interface chitin-polyurethane could be irregular, which could difficult to reach the chitin-polyurethane interface by infrared light.

FTIR-ATR characterization of interface chitin-polyurethane could be improved by controlling the uniformity of polyurethane film thickness. This would be achieved by polymerizing the polyurethane in the necessary quantity to cover a high-sized chitin flake (e.g. 1 cm diameter), trying to produce a very thin film. As reported in literature, infrared light penetration depth can range from some hundred nanometers to several micrometers (Kane et al., 2009). Therefore, 1 μm thickness for polyurethane film is sufficient to infrared light reaches the chitin-polyurethane interface; this is part of future work in this research.

4. Carbon nanotubes: Synthesis, properties and modification

Carbon nanotubes (CNT) are key elements in nanotechnology. The structure of carbon nanotubes is depicted as a rolled segment of a graphene sheet, formed by linking each carbon atom to three equivalent neighbors by covalent bonds resulting in a hexagonal network. Carbon nanotubes can be structured by only one graphene sheet (single-wall carbon nanotubes, SWCNT) or by several coaxial graphene sheets (multiwall carbon nanotubes, MWCNT) (Dresselhaus et al., 2001). Synthesis of carbon nanotubes can be carried out by catalytic chemical vapor deposition (CVD) from carbon-containing gaseous compounds which decompose catalytically on transition-metal particles at temperatures lower than 1000 $^{\circ}\text{C}$. CVD processes are becoming the major way for synthesizing carbon nanotubes in a controlled way (Loiseau et al., 2006). It is possible to modify and control the physicochemical properties of carbon nanotubes by doping processes, introducing either non-carbon atoms or molecules at small concentrations in the plane of the graphene lattice.

Doping carbon nanotubes with nitrogen atoms at lower concentrations than 6.5 wt% induce crystalline disorder in the graphene sheets, as well as an excess of electron donors on the nitrogen-rich areas may result in a more reactive structure compared to pure carbon nanotubes. For nitrogen-doped carbon nanotubes (N-MWCNT) two types of C-N bonds

could occur: the first is a three-coordinated N atom within the sp^2 - hybridized network, with the presence of additional electrons. The second type is the pyridine type (two-coordinated N) which can be incorporated in the nanotube lattice; an additional carbon atom is removed from the framework. N-MWCNTs have stacked-cone morphology (bamboo-type) and the degree of tubular perfection decreases as a result of the N incorporation into the hexagonal carbon lattice (Terrones et al., 2002). Moreover, properties of CNTs can also be modified by oxidation with thermal treatment or with acidic solutions (HNO_3 , $KMnO_4^+$, H_2SO_4 , $K_2Cr_2O_7$, H_2O_2). Under acidic oxidation bonds of carbon nanotubes could follow several reactions, for example the formation of quinones which further evolve to different oxygen acidic groups, such as phenolic, lactonic and carboxylic groups. The attached oxygenated groups change the surface chemistry of carbon nanotubes, in particular their wetting behavior and also can be used to attach different chemical groups or to improve their chemical interaction with other substances (Hirsch, 2002; Niyogi et al., 2002). Studies reported previously about oxidation of CNTs in liquid phase suggest that defects at the tips and sidewalls are the most reactive sites to attach oxygen functional groups to the nanotubes structure. These bonded atoms pull the reactive C atom out of the base plane, reducing the curvature strain of nanotubes and creating holes and pores. Long periods of oxidation lead to the shortening and destruction of the nanotubes (Ago et al., 1999; Ovejero et al., 2006; Zhang et al., 2003).

Raman spectroscopy is widely used to evidence the enhancement in defects density along the walls of the carbon nanotubes when oxidation is applied. The main bands of carbon materials are the graphite band (G-band) and the disorder-induced phonon mode (D-band). The relative intensity between the D-band and G-band (ID/IG ratio) indicate a continuously covalent bonding of oxygenated groups along the walls of nanotubes, disrupting the aromatic system of π -electrons (Liu et al., 2004). Complementary information can be obtained with FTIR spectroscopy; it allows determination of functional groups attached to surface of CNTs. This tool was used in some studies carried out by our research group with N-MWCNT, MWCNT and SWCNT, which were oxidized with nitric acid solution (70%) at $80 \pm 3^\circ C$ for 5 h, as detailed by Perez-Aguilar et al., (2010). Oxidized carbon nanotubes were identified as ox-N-MWCNT, ox-MWCNT and ox-SWCNT, and their morphology was observed by electronic microscopy (Figure 5). As the oxidation of carbon nanotubes was carried out in liquid phase, oxygen containing functional groups were attached along their entire length. Reactions between carbon materials and nitric acid involve strong electrophilic species in solution, which form nitrogen oxides that eventually are reduced to N_2 through oxidation of carbon. Introduction of a small content of nitrogen has been reported, mainly due to the introduction of nitro ($-NO_2$) groups (Chen and Wu, 2004; Zawadski, 1980).

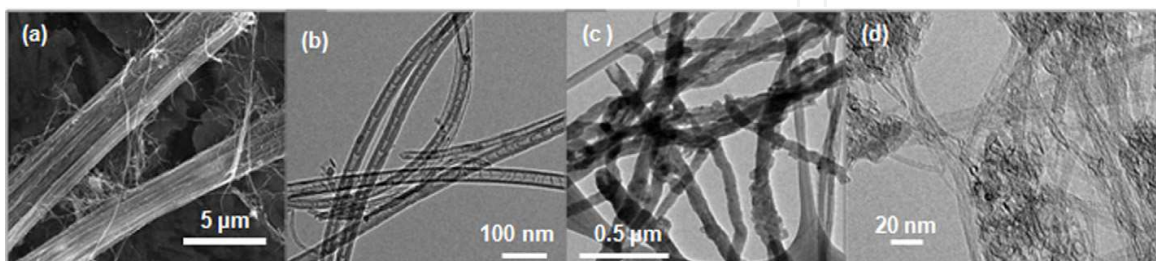


Fig. 5. Micrographs of carbon nanotubes observed by (a) SEM and (b) HRTEM for oxidized N-MWCNTs; HRTEM for (c) oxidized MWCNTs and (d) oxidized SWCNTs. Oxidation with nitric acid at $80 \pm 3^\circ C$ by 5 h

After the oxidation Van der Waals forces that kept CNTs aggregated were overcome by repulsion forces, as result of reducing the π -conjugation of nanotubes and enhancing the surface dipoles by oxygen-containing functional groups. This effect was monitored by determining the elemental composition of pristine nanotubes and partially oxidized CNTs.

An important increment in oxygen content was registered as the carbon content was reduced, caused by the destruction of graphene lattice by electrophilic reaction. The hydrogen content also increased in oxidized nanotubes, maybe as a result of the introduction of carboxylic groups. However, for N-MWCNTs the nitrogen content remained almost constant, probably these atoms might change from pyridinic-type or quaternary-type to an aliphatic form. Equilibrium could be established between the consumption of nitrogen atoms of the lattice and the attachment of nitrogen atoms in some sites of the lattice as nitro groups, as occurs when oxidizing some organic molecules or activated carbons with nitric acid (Zawadski, 1980; Chen and Wu, 2004).

4.1 FTIR characterization of oxidized carbon nanotubes

Functional groups attached to oxidized carbon nanotubes were identified by Fourier-transformed infrared spectroscopy by attenuated total reflectance, ATR-FTIR in a Nicolet 6700 FT-IR spectrophotometer at 1068 scans, in the frequency interval of 4000 cm^{-1} to 650 cm^{-1} with resolution of 8 cm^{-1} .

The main functional group attached to oxidized carbon nanotubes was carboxylic. Comparison between spectra of pristine nanotubes and oxidized N-MWCNTs showed that the bands at 1444 cm^{-1} , 1373 cm^{-1} and 1251 cm^{-1} , attributed to vibration of MWCNTs and C-N bonding in N-MWCNTs, were overcome by several vibrations in carbonyl and carboxylic functionalities in the range of 1720 to 1250 cm^{-1} (Choi et al., 2004; Misra et al., 2007). A strong band appeared from 3600 cm^{-1} to 3300 cm^{-1} by the stretching of the bonding -OH of carboxylic group in oxidized nanotubes (Zawadski, 1980; Chen and Wu, 2004).

The nitro group ($-\text{NO}_2$) is isoelectronic with the carboxylate ion group and their spectra are very similar, but a weak feature related to nitro group was observed at 1535 cm^{-1} for oxidized nanotubes (Zawadski, 1980). By other side, spectra obtained for three types of oxidized CNTs (Figure 6) showed broad features from 3400 cm^{-1} to 3000 cm^{-1} by the stretching of the bonding -OH in carboxylic and hydroxyl groups. Signals near 1710 cm^{-1} and 1685 cm^{-1} were of carbonyl vibrations in carboxyl bonding, a weak band about 1640 cm^{-1} of quinones, and the broad band from 1200 to 1000 cm^{-1} was attributed to single-bonded oxygen atoms such as phenols and lactones.

Two weak signals related to the nitro group were observed at 1538 and 1340 cm^{-1} for ox-N-MWCNTs. Similar spectra have been reported for oxidized multiwall carbon nanotubes; characteristic peaks were assigned to carboxylic, carbonyl, and hydroxyl groups (Wang et al., 2007). These results have probe that spectra carefully acquired by FTIR-ATR are a useful tool for identification of chemical groups attached to surface of carbon nanotubes chemically modified.

5. Microstructure of styrene-butadiene copolymers and its hydrogenation

Elastomers like polybutadiene or thermoplastic elastomers like styrene-butadiene-styrene copolymers are widely used in diverse industries. However, the presence of double bonds

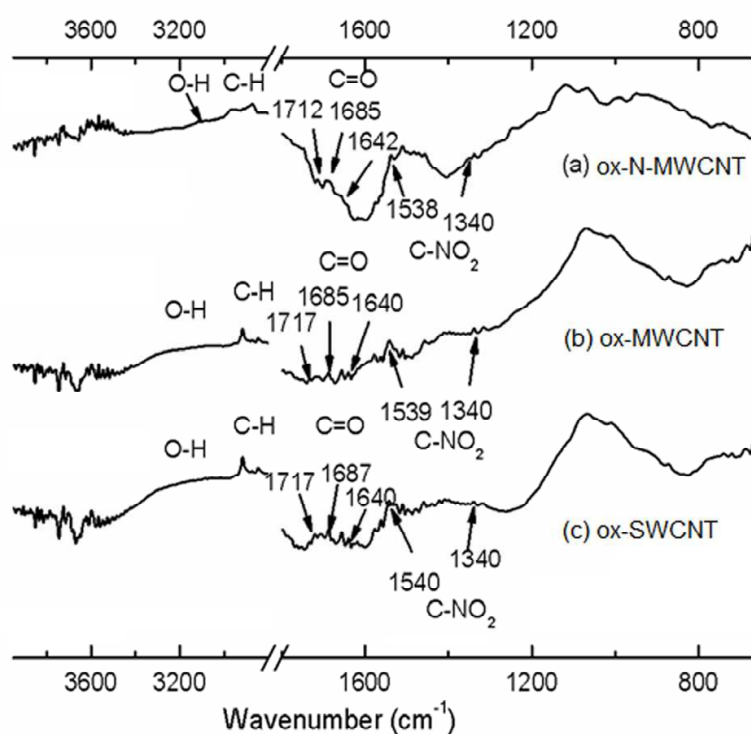


Fig. 6. FTIR spectra of (a) oxidized nitrogen-doped carbon nanotubes, ox-N-MWCNT; (b) oxidized multiwall carbon nanotubes, ox-MWCNT; (c) oxidized single-wall carbon nanotubes, ox-SWCNT, obtained by attenuated total reflectance (ATR)

into their structures promotes degradation by heat or light, making them materials with low outdoor resistance. The hydrogenation of these materials is an effective method to improve their performance for outdoor or high temperatures applications (De Sarkar et al., 1997). In this context, the determination of microstructure (relative quantities of isomers), before and after the hydrogenation, is important since chemical and mechanical resistances are related to it.

In the case of butadiene-containing polymers, the microstructure of the polybutadiene segment (i.e. the relative amount of 1,2 vinyl, 1,4-trans and 1,4-cis bonds) plays an important role in determining their thermal and mechanical properties, as well as their interaction with other materials in the production of composites, such as high-impact polystyrene, modified asphalt, pressure sensitive adhesives, etc. It is also known that anionic polymerization gives copolymers with well-controlled monomer distribution and microstructure, a narrow molecular weight distribution, and the possibility to have end group functionality (Escobar et al., 2000). Hydrogenation of styrene-diene copolymers has received special interest (Bhattacharjee et al., 1993) since the double bond present in the diene segment of the elastomer is susceptible to thermal and oxidative degradation. Hydrogenation of styrene-diene block copolymers allows the production of thermo-oxidative resistant thermoplastics, and selective saturation of diene units (over the rigid units of styrene) permits to control mechanical and thermal properties. Thus, FTIR is essential to determine quantitatively the microstructure, using a liquid cell. Microstructure can be evaluated with time of hydrogenation by FTIR, allowing the establishment of the mechanism of hydrogenation for styrene-butadiene copolymers.

Most of styrene-butadiene copolymers hydrogenation studies have focused on global saturation of polybutadiene double bonds (i.e. 1,4-trans, 1,4-cis and 1,2-vinyl) and on obtaining high saturation percentages (>90%), however, only a few of them have made a distinction on the saturation of the different types of double bonds present in polybutadiene (Escobar et al., 2000).

The evaluation of microstructure and composition (relative quantity of polystyrene in the copolymer) in styrene-butadiene copolymers by FTIR has been conventionally carried out considering just two of three isomers, and the third isomer percentage has been obtained by difference. The previous characterization by RMN is essential in order to contrast the results. However, if it is considered that evaluation of microstructure and composition, of such butadiene-based copolymers, by FTIR takes in account the Beer-Lambert law, expressed as:

$$A = K C L \quad (1)$$

where:

A represents the absorbance at certain wave number,
K is the extinction coefficient at certain wave number,
C is the solution concentration,
L is the path length for the laser light

Therefore, it is possible to express the Beer-Lambert law (Huang, 1995) for each component as follows:

$$A_i = K_{ij} C_j L \quad (2)$$

where:

A_i represents the absorbance at wave number i ,
 K_{ij} represents the extinction coefficient for j unit at wave number i ,
 C_j is the solution concentration of j unit,
L is the path length for the laser light

In the case of liquid cell the path length, L, is the spacer thickness between the KBr windows.

5.1 Experimental

The samples of commercial products were weighted (0.25 g) and dissolved in carbon bisulfide (10 ml). A liquid cell with KBr window was used with a spacer thickness of 0.2 mm. The FTIR equipment was a Magna 560 from Nicolet, with 32 scans, in the mid-red: 4000 a 400 cm^{-1} . These samples also were characterized by ^1H NMR.

5.2 Results and discussion

The results for microstructure and composition determination of polybutadiene portion in styrene-butadiene copolymers are presented in the following section. Such characterization was carried out using the indicated spectrometer and contrasted with the results obtained by ^1H NMR.

The structures corresponding to the polybutadiene isomers, which can be evaluated as it is detailed in the next section, are shown in Figure 7.

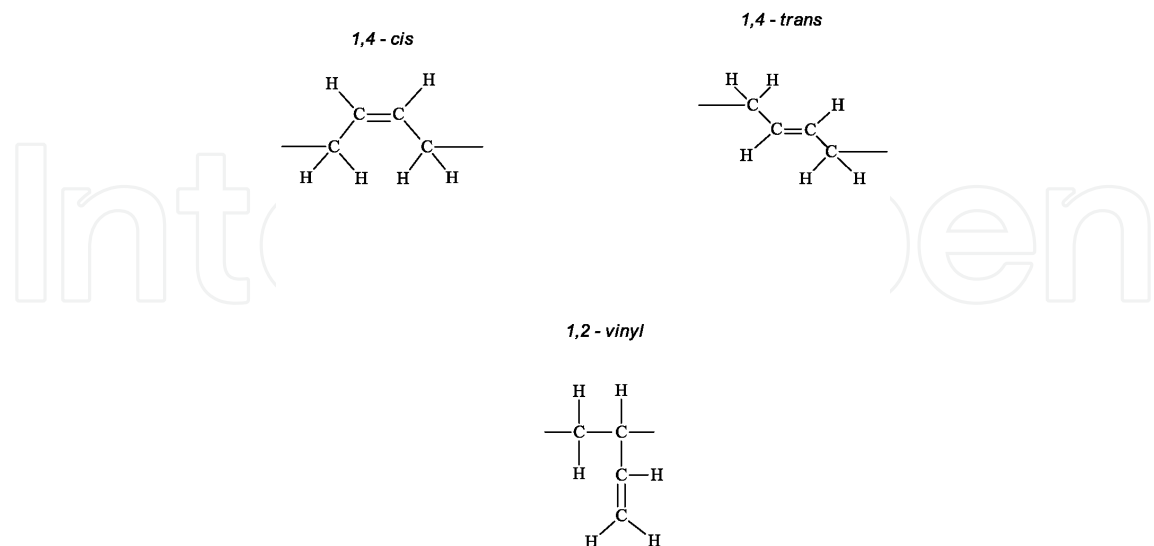


Fig. 7. Isomer structure for the polybutadiene

It is important to mention that the studied styrene-butadiene copolymers and the polybutadiene homopolymer were synthesized by anionic polymerization. Therefore, just three isomers are possible to obtain, the 1,4-cis; 1,4-trans and the 1,2-vinyl.

These isomers are present at different relative quantities, depending on the polymerization conditions. One key factor to modify the microstructure is the presence of chemical named microstructure modifier, which has an interaction with the counterion of the initiator, modifying the bond length and promotes the ion pair formation.

5.2.1 Microstructure and composition

Considering the Beer-Lambert law, and knowing the extinction coefficients for each isomer at specifics wave numbers: 698, 728, 910 and 966 cm⁻¹, for the case of styrene-butadiene copolymers, it is possible to evaluate microstructure. The Beer-Lambert law can be expressed as:

$$A_i = \sum K_{ij} C_j L$$

(3)

Thus, the equation system can be expressed as a matrix, which can be solved since L and K_{ij} are constants. The reported (Huang, 1995) values for the extinction coefficient are shown in Table 1.

| Entity | Extinction coefficient (K) | | | |
|-----------|----------------------------|------------------|------------------|------------------|
| | A ₆₉₈ | A ₇₂₈ | A ₉₁₀ | A ₉₆₆ |
| 1,4-cis | 0.385 | 0.551 | 0.037 | 0.058 |
| 1,4-trans | 0.005 | 0.007 | 0.055 | 2.542 |
| 1,2-vinyl | 0.153 | 0.05 | 3.193 | 0.098 |
| styrene | 2.703 | 0.038 | 0.064 | 0.05 |

Table 1. Extinction coefficients for styrene and isomers of styrene-butadiene copolymers

The path length was constant (0.02 cm). Therefore, the matrix is:

$$\begin{aligned} A_{698} &= 7.7 \times 10^{-3} \quad C_{\text{cis}} + 3.06 \times 10^{-3} \quad C_{\text{vinyl}} + 1 \times 10^{-4} \quad C_{\text{trans}} + 5.406 \times 10^{-2} \quad C_{\text{St}} \\ A_{728} &= 1.102 \times 10^{-2} \quad C_{\text{cis}} + 1 \times 10^{-3} \quad C_{\text{vinyl}} + 1.4 \times 10^{-4} \quad C_{\text{trans}} + 7.6 \times 10^{-4} \quad C_{\text{St}} \\ A_{910} &= 7.4 \times 10^{-4} \quad C_{\text{cis}} + 6.386 \times 10^{-2} \quad C_{\text{vinyl}} + 1.1 \times 10^{-4} \quad C_{\text{trans}} + 1.28 \times 10^{-3} \quad C_{\text{St}} \\ A_{966} &= 1.16 \times 10^{-3} \quad C_{\text{cis}} + 1.96 \times 10^{-3} \quad C_{\text{vinyl}} + 5.084 \times 10^{-2} \quad C_{\text{trans}} + 1 \times 10^{-3} \quad C_{\text{St}} \end{aligned}$$

Once it was established the equations, they were solved. Thus, several commercial samples were evaluated according with matrix. The obtained values are shown in Table 2.

As it can be seen from Table 2, there is a good agreement in the microstructure calculated by FTIR and ¹H NMR. Bearing in mind that microstructure and composition calculated by ¹H NMR are the real values, the higher deviation, for cis and trans values, was achieved when the styrene content was above 39 % w/w. The last is probably due for overtones for vinyl and trans isomers, which appear with such styrene content.

| Sample | % St (¹ H NMR) | % Vinyl (¹ H NMR) | % Cis (¹ H NMR) | % Trans (¹ H NMR) | % St | % Vinyl | % Cis | % Trans |
|--------|-------------------------------|----------------------------------|--------------------------------|----------------------------------|-------|---------|-------|---------|
| S-200 | 0 | 9.12 | 40.21 | 50.67 | 0 | 9.51 | 42.39 | 48.1 |
| S-1110 | 16.15 | 9.12 | 38.95 | 51.93 | 15.43 | 9.43 | 40.11 | 50.44 |
| S-1205 | 24.39 | 9.39 | 40.63 | 49.98 | 24.05 | 9.74 | 38.5 | 51.76 |
| S-1322 | 30.43 | 8.59 | 40.18 | 51.22 | 29.72 | 8.87 | 42.68 | 48.44 |
| S-1430 | 39.94 | 8.82 | 39.07 | 52.12 | 39.14 | 8.74 | 43.21 | 48.05 |
| S-314 | 69.69 | 16.89 | 27.12 | 55.98 | 67.35 | 14.79 | 33.78 | 51.43 |
| S-411 | 30.37 | 14.56 | 35.54 | 49.89 | 29.7 | 15.07 | 35.71 | 49.23 |
| S-416 | 29.96 | 12.69 | 36.51 | 50.79 | 29.37 | 13.71 | 36.89 | 49.39 |
| S-4318 | 33.17 | 13.44 | 36.12 | 50.44 | 32.04 | 14.05 | 37.29 | 49.39 |

Table 2. Microstructure and composition of several commercial samples.

Nevertheless, there was a good correlation between the obtained results by both methods, corroborating that FTIR can be used with confidence, in order to evaluate composition and microstructure of styrene-butadiene copolymers. Nevertheless, it is important to mention that the use of the liquid cell is not infallible, since the path length can be modified when the cell is cleaned.

5.2.2 Hydrogenation

Once the method for microstructure by FTIR was established, the hydrogenation of butadiene-based copolymers can be traced. Disappearance of each isomer of butadiene can be recorded with time. Thus, it is possible to see if hydrogenation is selective toward certain isomer or not, and also it is possible to see if polystyrene portion is saturated or affected by hydrogenation.

The hydrogenation of elastomeric portion (polybutadiene) in the styrene-butadiene copolymers can be visualized as it is shown the Figure 8.

The spectra of styrene-butadiene copolymer and the hydrogenated counterpart are shown in the Figure 9.

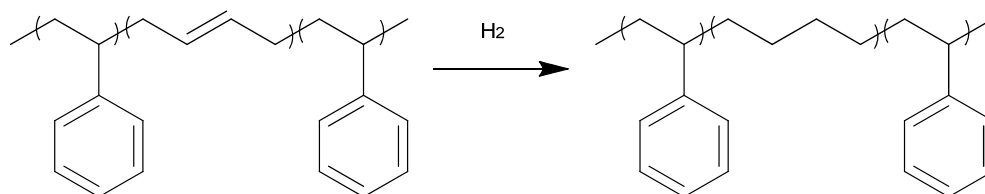


Fig. 8. Hydrogenation of styrene-butadiene copolymer

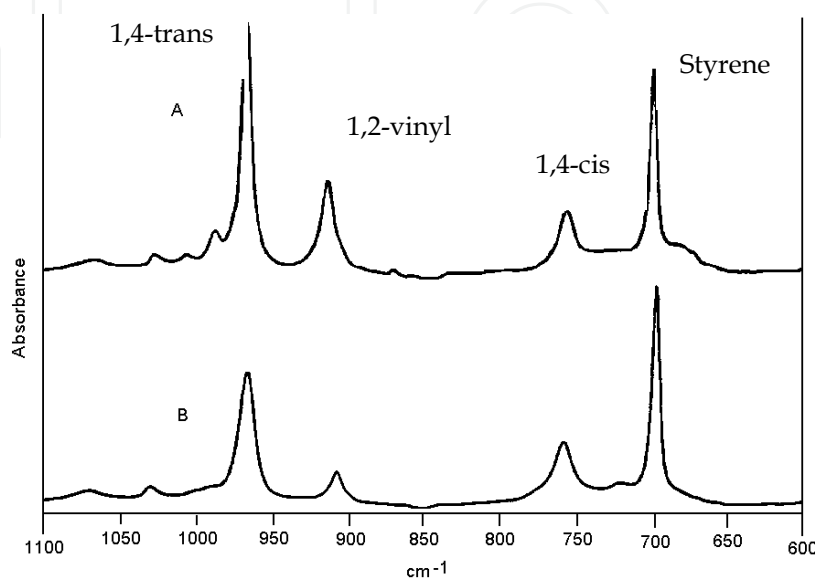


Fig. 9. Spectra of styrene-butadiene copolymer (A) and its hydrogenated product (B)

The spectra shown in Figure 9 indicate that there was a noticeable reduction of the absorbance of 1,2-vinyl, then 1,4-trans followed by 1,4-cis and the absorbance corresponding to styrene remains constant. In previous work (Escobar et al, 2000) it was shown that kinetics of hydrogenation is higher for 1,2-vinyl bonds than for 1,4-trans and 1,4-cis bonds.

The 1,2-vinyl bonds are pendant from the backbone and, therefore, they are more accessible to hydrogen. The FTIR is a useful characterization technique in this case, since it was possible to establish the hydrogenation selectivity toward the 1,2-vinyl bonds and showed that polystyrene remained unsaturated during hydrogenation.

6. Conclusions

FTIR is a powerful and useful characterization method for polymers, and materials in general. This is an economic, short time characterization that allows to establish the chemical composition, microstructure, chemical interactions and even to follow variation of specific functional groups with time, during reactions.

All this features, makes the FTIR an essential characterization technique for polymers. From homopolymers, copolymers to nanocomposites and biocomposites, can be characterized, qualitative and quantitatively, giving the possibility to understand specific interactions and to establish mechanism of reaction, between materials. Thus, the FTIR has contributed to the development of new materials in the polymer science.

In the examples presented herein, the FTIR has permitted to follow specific functional groups with time, to establish the end and/or beginning of a particular reaction.

In addition, FTIR was useful to elucidate about interactions between polymeric matrix (polyurethane) and biopolymer (chitin). However, it is necessary to obtain thinner samples in order to see specific interaction in the interface of materials.

Regarding the nanotubes, it was possible to establish carbon functional group present in the surface of them once these were chemically modified. This is important since this allows figuring out what kind of interactions with other materials could be taken place, and understanding the mechanism of such interactions.

In the case of the establishment of microstructure of styrene-butadiene copolymers, it was demonstrated the capacity of FTIR to be used with confidence as an alternative technique to primary technique like $^1\text{H-NMR}$. The FTIR gives very close values of the relative quantities of the different isomers to those obtained by NMR, besides the composition. Once the methodology was established, it was possible to follow the hydrogenation reaction, in order to see its selectivity toward the isomers.

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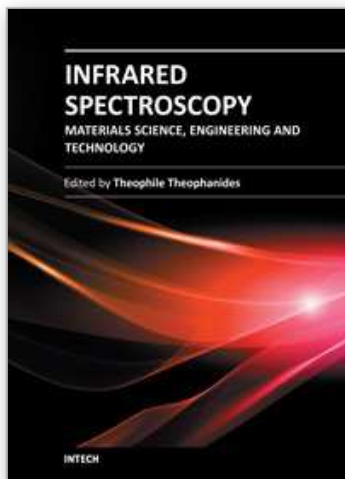
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