

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

3,500

Open access books available

108,000

International authors and editors

1.7 M

Downloads

Our authors are among the

151

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Evaluation of Graft Copolymerization of Acrylic Monomers Onto Natural Polymers by Means Infrared Spectroscopy

José Luis Rivera-Armenta<sup>1</sup>, Cynthia Graciela Flores-Hernández<sup>1</sup>,  
Ruth Zurisadai Del Angel-Aldana<sup>1</sup>, Ana María Mendoza-Martínez<sup>1</sup>,  
Carlos Velasco-Santos<sup>2</sup> and Ana Laura Martínez-Hernández<sup>2</sup>

<sup>1</sup>*Instituto Tecnológico de Ciudad Madero,  
División de Estudios de Posgrado e Investigación*

<sup>2</sup>*Instituto Tecnológico de Querétaro,  
Departamento de Metal-Mecánica  
México*

## 1. Introduction

Infrared spectroscopy (IR spectroscopy) is a technique based on the vibrations of atoms of a molecule. An IR spectrum is commonly obtained by passing IR radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule (Bickford, 2008).

For a molecule to show IR absorptions, it must possess specific feature: electric dipole moment of molecule must change during the movement that means changes in molecular dipoles which are associated with vibrations and rotations. The atoms in molecules can move relative to one another. This is a description of stretching and bending movements that are collectively referred to as vibrations. Vibrations can involve either change in bond length (stretching) or bond angle (bending). Some bonds can stretch in-phase (symmetrical stretching) or out-of-plane (asymmetric stretching) (Bickford, 2008).

The IR is divided into three regions; the near-, mid- and far- IR. The mid-IR is the most common region to identification and study of organic compounds based on fundamental vibrations and associated rotational-vibrational structure.

IR spectroscopy is a popular method for characterizing polymers. This spectroscopy may be used to identify the composition of polymers, to monitor polymerization processes, to characterize polymer structure, to examine polymer surface, and to investigate polymer degradation processes. There are several reports of use of IR spectroscopy to evaluate grafting of acrylic monomers onto natural materials as carboxymethyl cellulose (CMC) and chicken feathers (CF) (Martínez et al, 2003, 2005, Vasile et al, 2004, Zohuriann-Mehr et al, 2005, Joshi and Sinha, 2006).

Now a days have been an increasing interest in obtation and use of polymeric materials using naturals sources from a diversity of systems, getting attention such biopolymers in research areas as medicine, electronics, textil, corrosion and nanotechnology among others. This rising interest is due variety of properties that offers on depending of chemical structure and source (Martínez et al, 2008).

Use of natural fibers is an research area that allows obtain materials for cotidiane applications, using more resistance materials and with outstanding properties and specially materials that are environmental friendly. Keratin is a natural protein which can be found in wool, hair, claws, horns or nails, and is the main component in birds' feathers, represents from 5% to 7% of the body weight of chickens. Keratin is durable and resistant to organic solvents and chemically unreactive, which give benefits when is exposure to environmental conditions, thinking in industrial applications.

Chicken feathers (CF) are more abundant material of keratin in nature. Birds' feathers characterize by a complex branched structure formed by keratinic filaments that grow in a unique mechanism in cylindric feather follicles. This branched structure is a distinctive characteristic in feathers morphology and its origin is biologic evolution (Xu et al., 2001, 2003).

CF are considered residues of a byproduct of poultry, corresponding to more than 5 million tons around the world (Barone et al 2005). Aminoacids content of CF on depend of breed, feeding and environment of study animals. The aminoacids present in CF are mainly aspartic acid, glutamic acid, arginine, proline, glycine, phenylalanine, alanine, cystine, isoleucine, among others (Schmidt 1998) (see table 1).

Functional group	Aminoacid	Content (as % mole)
Negatively charged	Aspartic acid	5
	Glutamic acid	7
Positively charged	Arginine	5
Conformationally special	Proline	12
	Glycine	11
Hydrophobic	Phenylalanine	4
	Alanine	4
	Cystine	7
	Valine	9
	Isoleucine	5
	Leucine	6
	Tyrosine	1
Hydrophilic	Threonine	4
	Serine	16

Table 1. Aminoacid content in keratin fiber from chicken feather (Martínez et al 2005).

Carboxymethyl cellulose (CMC) is a very important cellulose derivative and it is known by its superabsorbent properties. It is anionic polymer water soluble. It is produced by reaction of alkali cellulose and monochloroacetic sodium salt under strict reaction conditions (Klemm et al, 1998). Byproducts as sodium chloride and sodium glycolate are obtained in reaction whose are removed obtaining CMC sodium salt highly purified. Higher swelling capacity of CMC can be reached and controlled by addition of crosslinking agent, thermal treatment or ionic state conversion. The conversion of some hydroxyl groups from cellulose in hydrophobic substituents diminishes hydrogen bonding decreasing crystallinity and increasing water solubility. Multiple applications of Na-CMC in several areas of food industry made it and almost indispensable material. Other applications are: laundry detergent for instance, mainly as a viscosity modifier or thickener, as a soil suspension to deposit onto cotton and other cellulosic fabrics (Klemm et al, 1998). Other use of CMC is as a lubricant in non-volatile eye drops. These properties on depend of preparation method, degree of polymerization and degree of substitution (DS), that means how much of hydroxylic groups are displaced for carboxymethyl groups in anhydroglucose (AGU) structure. The more useful DS value is from 0.7 to 1.5. Due these CMC is an interesting material and properties can be modify by means graft reactions.

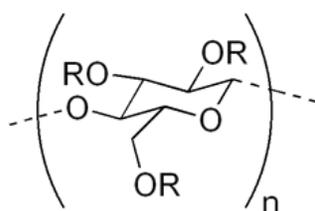


Fig. 1. Carboxymethyl cellulose structure.

Modification of natural protein through grafting have become in a widely used path and some works have carry out studies with acrylic monomers as ethylacrylate, acrylic acid, methacrylic acid and methyl methacrylate (Mostafa, 1995; Athawale and Rathi, 1997; Jia and Yong, 2006; Zampano, et al 2009), which carried out graft of natural fibers and proteins. However, just few of works report grafting of hydroxyethyl methacrylate onto naturals fibers (Joshi and Sinha, 2006) (Martínez et al., 2003, 2005).

Graft copolymerization of acrylic monomers onto natural polymers is one of the most useful paths to modify physicochemical properties on order to add new properties to final copolymer with minimal. Acrylic monomers are the most grafted monomers in this kind of research works; being acrylonitrile, acrylic acid, methyl methacrylate more studied species. Redox initiation is an efficient method frequently used to obtain graft copolymers. Polymers with OH groups can react with ceric ion or an oxidant agent to form polymer radical capable to initiate copolymerization. In a redox initiation frequently there is a minimum degree of homopolymerization, due only polymer radicals can be formed. However, limitation of this method is only useful with polymers with functional groups; there are reports of polymers with amides, urethane and nitrile groups by means redox initiation.

Several natural polymers as chitin, cellulose, functionalized cellulose and natural fibers are some of most studied natural polymers in graft copolymerization using redox system as initiator, being cerium ion one with more reports.

Infrared spectroscopy is a useful tool to identify functional groups through vibrational frequencies in polymers to evaluate changes in structure. This research was focused in graft copolymerization of Hydroxyethyl methacrylate (HEMA) onto chicken feathers fibers (CFF) and carboxymethyl cellulose (CMC), evaluating effect of reaction conditions (time reaction, monomer concentration, initiator concentrations) on grafting yield and probe presence of HEMA in copolymers by means Infrared Spectroscopy (IR).

## 2. Methodology

### 2.1 Raw materials

Chicken Feathers (CF) were obtained from a local slaughterhouse. A clean up procedure was carried out before use them for reaction, CF were washed several times with ethanol and dried at room temperature to have them clean white, sanitized and odor-free. Manual procedure by cutting to separate fibers from barbs and barbules was carried out. Chicken feather fiber (CFF) was used in graft copolymerization reaction.

CMC supplied by Sigma-Aldrich with 0.7 degree of substitution was used to graft reactions, without further purification process, same as all other reactivities: Hydroxyethyl methacrylate (HEMA) (98%) and malic acid, potassium permanganate ( $\text{KMnO}_4$ ), hydrochloric acid (HCl), methanol, ethanol, sulfuric acid ( $\text{H}_2\text{SO}_4$ ), Cerium ammonium nitrate were from Sigma-Aldrich. Distilled water was used as reaction medium and finally to wash the homopolymer residues.

### 2.2 CFF graft copolymers

To carry out the grafting reaction procedure proposed by Martínez-Hernández et al. (2003) was used. In this process the following reagents were used: 0.5 g CFF, distilled water, malic acid (0.005M), sulfuric acid (0.01M),  $\text{KMnO}_4$  (0.003M) and HEMA monomer in 3 different levels (0.025, 0.05 and 0.075 M).

The substances were mixed at a temperature of 60 °C, under constant magnetic stirring. The reactions were carried out at three different times: 2, 3 and 4 h. Once the reaction time passed, proceeded to filter and wash the reaction product with hot water and methanol in order to remove residual monomer and homopolymer. Grafting yield was evaluated after a hydrolysis to reaction product, to determinate HEMA amount grafted in CFF. Hydrolysis procedure was: 1g of CFF grafted was swamped in a 6M HCl solution at 130°C for 24 hours in a soxhlet extractor. Once the time was over, hydrolysis residue was dried and weight was determinate, this weight correspond to grafted HEMA, due CFF decompose in hydrolysis process.

Grafted polymer percentage was determinate according with next formulae (Martínez-Hernández et al, 2003; Gupta and Sahoo, 2001):

$$\% \text{Grafted PHEMA} = (X_4 / X_1) * 100 \quad (1)$$

Where:

$X_1$  = CFF without modification

$X_2$  = container

$X_3$  = container + hydrolyzed sample

$X_4$  = residual polymer after hydrolysis ( $X_3 - X_2$ )

## 2.3 CMC graft copolymers

### 2.3.1 Initiator preparation

It was necessary preparation of Ce (IV) initiator solution. The required amount of cerium ammonium nitrate salt (0.1, 0.25 and 0.5 M), was dissolved in 100 mL of 1M HNO<sub>3</sub> solution. This solution was stored under refrigeration in an amber bottle.

### 2.3.2 Grafting reaction

For graft reaction 5 g of CMC were placed in the reactor with distilled water and HEMA was added in selected amount (3 levels: 0.2, 0.3 or 0.4 M), under constant stirring at 70 ° C, the initiator was added and reaction was carried out for 3 hours. Once the reaction ends, it was necessary to neutralize the mixture with a NaOH 10% w/w solution, copolymer was precipitated with acetone, and then the material was milled and washed with 90% methanol solution, then dried. After, the material was subjected to a Soxhlet extraction with methanol, in order to extracting the material that has not been in the copolymer. Grafting yield was determined by weight differences according with next formulae:

$$\text{Grafting yield} = ((W_1 - W_0)/W_0) * 100 \quad (2)$$

Where:

$W_0$  = CMC weight

$W_1$  = graft copolymer weight

## 2.4 IR Spectroscopy characterization of graft copolymers

IR analysis was carried out to evaluate structural changes of CMC and CFF and its grafted copolymers, by means main functional groups signals. IR spectra were recorded with a Perkin-Elmer Spectrum One Fourier Transform IR spectrophotometer, using an Attenuated Total Reflectance (ATR) accessory, with ZnSe plate, using 12 scans and resolution of 4 cm<sup>-1</sup>, ranging from 4000 to 600 cm<sup>-1</sup>.

## 3. Results and discussion

Results will be presented in sections following next order. First, the effect of HEMA concentration and time reaction over grafting yield onto CFF and HEMA and CAN concentration over grafting yield onto CMC. Next, IR spectra are presented for ungrafted and grafted CFF, as well as a comparison of IR spectra for different grafting yield of CFF. Also for CMC grafted and ungrafted are presented the IR spectra and comparison to different grafting yield of HEMA onto CMC.

### 3.1 CFF-g-HEMA copolymer

Effect of reaction conditions over graft yield were studied. Table 2 shows effect of time reaction and HEMA concentration on grafting yield of CFF, initiators concentration was constant. It can observe that an HEMA concentration increase causes an increase of grafting yield value at 3 reaction times studied. That increase is due the amount of free radicals formed in reaction system, and CFF main component is keratin which posses several pendant functional groups, for like  $-NH_2$ ,  $-COOH$ ,  $-SH$  and  $-OH$ , which can form active sites where HEMA can be grafted. This behavior was also reported by Martínez et al (2003) that observed a maximum graft yield value. A higher HEMA concentration value was studied (1 M), but a fiber saturation was observed and also homopolymerization predominated over graft reaction which is not convenient for this study. Scanning Electron Microscopy shows the HEMA cover the CFF structure growing poly HEMA chains (figure 2) on fiber surface of CFF, but CFF reached a saturation of active sites and then homopolymerization happens.

Time/hr	HEMA conc./ M	Grafting yield
2	0.075	85%
2	0.05	70%
2	0.025	26%
3	0.075	92%
3	0.05	83%
3	0.025	57%
4	0.075	76%
4	0.05	38%
4	0.025	35%

Table 2. Effect of time reaction and HEMA concentration on grafting yield over CFF

The increase on graft yield can be also attributed that keratin forms a charge transfer complex with HEMA molecules, so it is possible increase monomer activity at higher concentrations of HEMA which leads homopolymerization.

Other reports (Joshi and Sinha, 2006) indicate an increase of monomer concentration increases graft yield, until a maximum and then decreases the obtained percentage. The difference is attributed to graft yield diminish due the saturation of available active sites in CFF. Also on depend of initiator system.

In the other hand, it can observe that when reaction time increase the graft yield has a maximum value at 3 h and then decrease at 4 h. this behavior is attributed that at higher reaction time the keratin pendant groups open and diffusion of HEMA molecules into the structure occurs, allowing the grafting on keratin structure not only on surface of CFF. However, when reaction time is high, a denaturalization of keratin can occurs, due the acidic medium where reaction is carried out, leading to HEMA homopolymerization. Other reason of this decrease in grafting yield is a reduction in number of free radicals available for grafting as the reaction proceeds, creating a saturation of active sites.

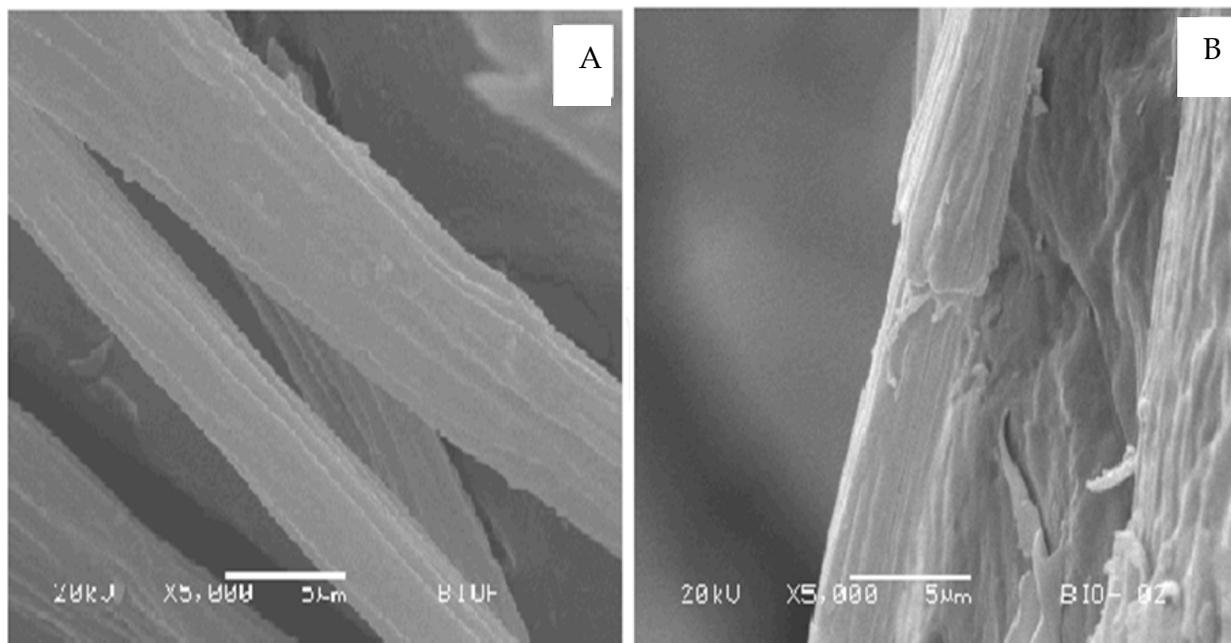


Fig. 2. SEM micrograph of CFF unmodified and CFF-g-HEMA

### 3.2 CMC-g-HEMA copolymer

The graft copolymerization of HEMA onto CMC had differences compared with HEMA-g-CFF: Redox initiator system used was CAN and was conducted at 3 different concentrations; HEMA concentrations values were higher 0.05, 0.1 and 0.15M and reaction time was constant in 3 hours. Table 3 resumes the effect of HEMA and CAN concentrations over grafting yields values of CMC.

CAN [M]	HEMA [M]	Grafting yield
0.1	0.05	69 %
0.1	0.1	207 %
0.1	0.15	249 %
0.25	0.05	88 %
0.25	0.1	214 %
0.25	0.15	275 %
0.5	0.05	82 %
0.5	0.1	179 %
0.5	0.15	397 %

Table 3. Effect of CAN and HEMA concentration on grafting yield over CMC

Graft copolymerization of HEMA onto CMC present a similar behavior as grating of HEMA onto CFF, grafting yield increased continuously with increase in concentration of HEMA when CAN concentration was constant, and reaches a maximum value with 0.15M at 3 CAN concentrations. This behavior could be explained by the fact of that an increase of HEMA

concentration lead to the accumulation of monomer molecules in close proximity to CMC backbone. There are reports of modified polysaccharides grafted with HEMA that found with CAN concentration of 0.2 M around 200% attributed the primary radicals attack the monomer instead of reacting with backbone polymer (Joshi and Sinha 2006). In this research higher CAN concentration studied was 0.5 M and higher grafting yield was reached with this concentration (397%). Also lower CAN concentrations (0.05 M) were tried in this research work, but not good results in grafting yield was obtained

In the other hand, about effect of CAN concentration over grafting yield, results show the initial increase in grafting yield with increase in initiator concentration levels off and decrease with further increase in CAN concentration. It would seem that termination of graft copolymerization would proceed by the reaction of the growing graft polymer chain with ceric ions, the reaction point is OH groups of anhydroglucose, which form a complex with ceric ion. This complex may dissociate, and giving rise to free radical sites onto the polysaccharides backbone and these radicals initiate the graft copolymerization (Zohuriaan-Mehr et al 2005).

Figure 3 shows SEM micrographs of CMC unmodified and CMC-g-HEMA. It is clearly seen that CMC morphology was totally modified by grafting of HEMA. CMC shows a porous surface which is covered by grafting of HEMA resulting in a homogeneous surface, which suggests that HEMA chains formed are long.

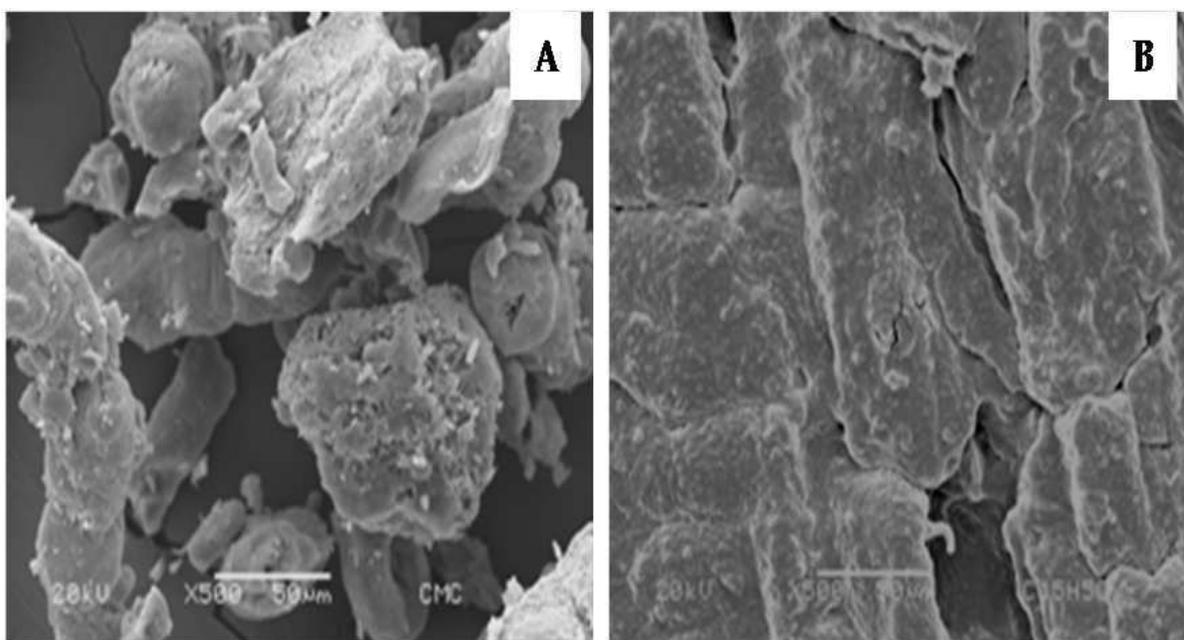


Fig. 3. SEM micrograph of CMC unmodified (A) and CMC-g-HEMA (B).

### 3.3 IR of CFF-g-HEMA copolymer

IR spectroscopy is a useful technique to evaluate if a graft reaction is carried out and also to evaluate grafting yields on graft copolymers. Several research works used IR with this purpose for keratin (Martínez et al 2003; Martínez et al 2008; Kavitha et al 2005), starch (Meshram et al 2009), modified starch (Cao et al 2002), chitosan (Mun et al 2008), carboxymethyl chitosan (Joshi and Sinha, 2006), cellulose (Zampano et al 2009),

carboxymethyl cellulose ( Okieimen and Ogbeifun, 1996; Vasile et al , 2004), ethyl cellulose (Kang et al 2006), which make it a powerfull tool in graft reactions.

Figure 4 shows IR spectrum of CFF, which main component is keratin, a mixture of aminoacids as serine, proline, glycine, valine, cysteine, and others. The main vibrations attributed to CFF structure were identified according to wavenumber. The region around  $3300\text{ cm}^{-1}$  corresponds to range of amide bands, figure shows a peak in  $3297\text{ cm}^{-1}$  associated with ordered regions of NH group of amide A  $\alpha$ -helix conformation, peak in  $2945\text{ cm}^{-1}$  is assigned to the assimetric vibration of CH group od metyl, the strong band at  $1715\text{ cm}^{-1}$  is matched with vibration of amide I of  $\beta$ -sheet conformation, band at  $1650\text{ cm}^{-1}$  assigned to C=O group of amide I  $\alpha$ -helix conformation, peaks at  $1520$ ,  $1449$  and  $1243\text{ cm}^{-1}$  attributed to in plane bending of NH group corresponding to  $\beta$ -sheet conformation, bending of  $\text{CH}_3$  group and CN group of amide III respectively; vibrations on  $1136$ ,  $1074$  and  $1023\text{ cm}^{-1}$  corresponds to assigned to vibrations of C-C group; and finally a peak around  $700\text{ cm}^{-1}$  attributed to vibration of C-S group.

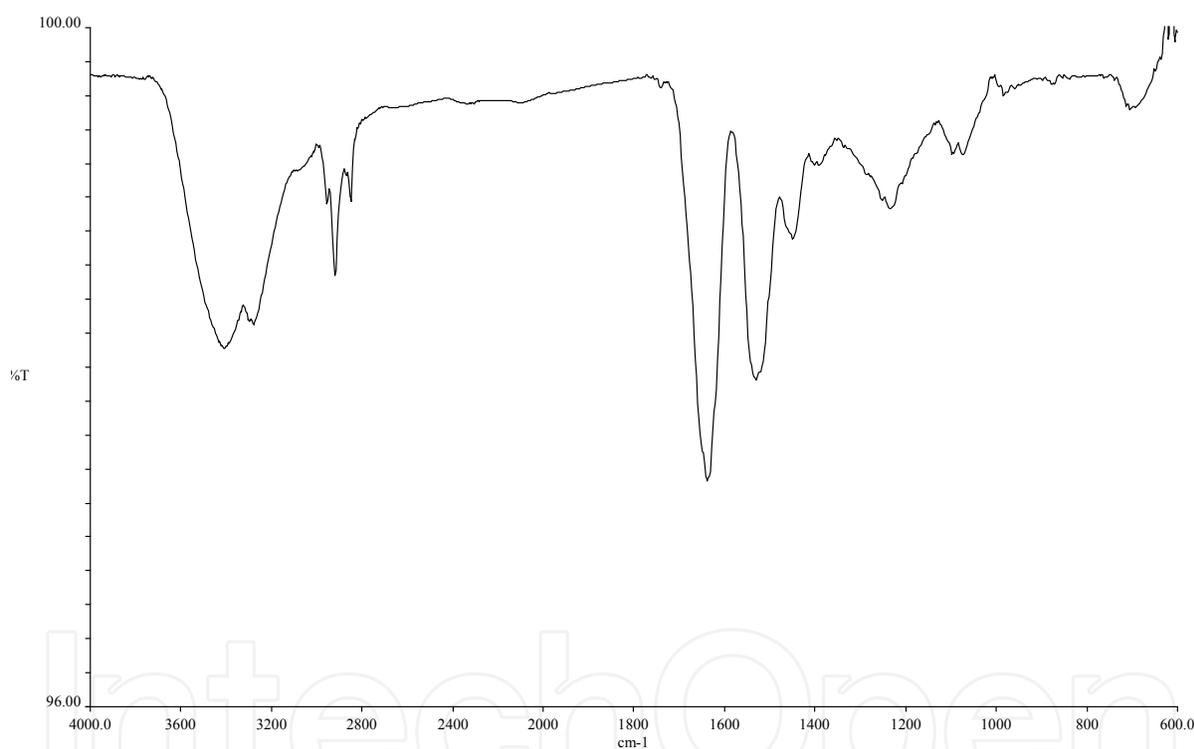


Fig. 4. IR spectrum of CFF ungrafted.

In figure 5 presents IR spectrum of PHEMA which presents signals at  $3394\text{ cm}^{-1}$  attributed to vibracion of OH group,  $2956\text{ cm}^{-1}$  from antisymmetric vibration of  $\text{CH}_2$  and  $\text{CH}_3$ ,  $2925\text{ cm}^{-1}$  symetric vibration of  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $2855\text{ cm}^{-1}$  symetric vibration of  $\text{CH}_2$ ,  $1720$  of stretching C=O, a small shoulder around  $1652$  from stretching C=C,  $1369\text{ cm}^{-1}$  deformation of  $\text{CH}_2$ ,  $\text{CH}_3$ , a shoulder at  $1260\text{ cm}^{-1}$  from C=O stretching,  $1164$  vibration of C-O-C,  $1048$  stretching of CO(H), and  $771\text{ cm}^{-1}$   $\text{CH}_2$  coupled with skeletal stretching. This is according for reports of IR spectrum of PHEMA (Prachayawarakorn and Boonsawat, 2007).

Figure 6 shows IR spectra of CFF and CFF grafted. It can observe that main differences are IR spectrum of CFF grafted show peaks at  $1720$ ,  $1160$  and a shoulder around  $1260\text{ cm}^{-1}$ ,

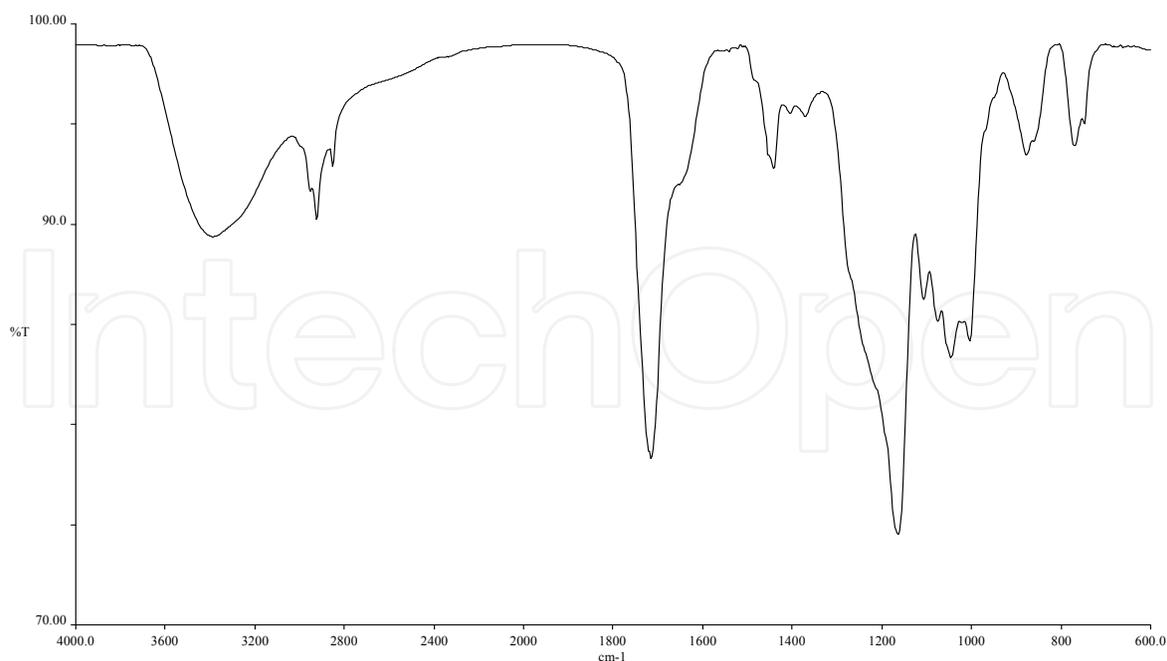


Fig. 5. IR spectrum of PHEMA

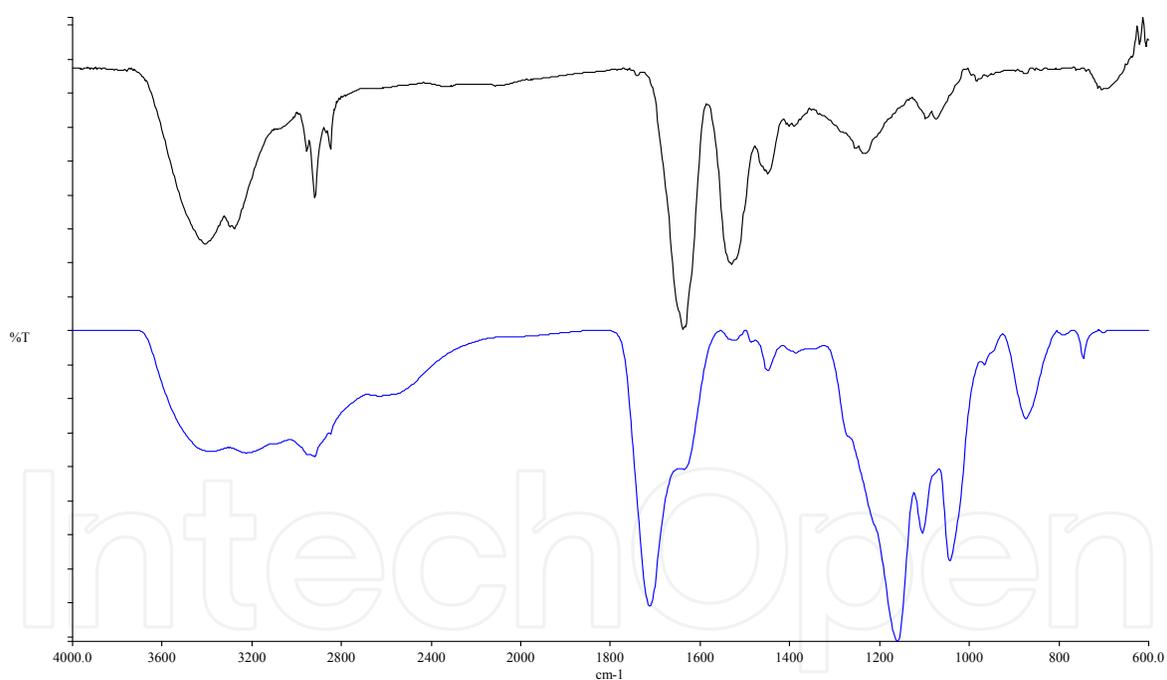


Fig. 6. IR spectra of ungrafted CFF (black) and CFF grafted (blue).

attributed to groups C=O and OH respectively, from HEMA structure, and which does not appear in CFF spectrum, which can indicate the graft reaction is carried out. CFF possesses functional groups as  $-NH_2$ ,  $-SH$  and  $-OH$  where graft reaction can carry out, signals from NH ( $3290$ ,  $3080$  and  $1525$   $cm^{-1}$ ) changed which make it suppose that graft reaction is taking place between NH groups and free radical of HEMA.

A comparison of main assignments from functional groups of ungrafted CFF and PHEMA are summarized in table 4.

PHEMA		CFF (Martínez 2005)	
Approximate assignments, cm <sup>-1</sup>	Functional groups	Approximate assignments, cm <sup>-1</sup>	Functional groups
3390	v (OH)	3290	v (NH) Amide A, $\alpha$ -helix
2950	v <sub>a</sub> (CH <sub>3</sub> , CH <sub>2</sub> )	3080	v <sub>a</sub> (NH) Amide B
2920	v <sub>s</sub> (CH <sub>3</sub> , CH <sub>2</sub> )	2930	v <sub>a</sub> (CH <sub>3</sub> )
2850	v(CH <sub>2</sub> )	1700	v(C=O) Amide I $\beta$ -sheet
1720	v(C=O) ester group	1650	v(C=O) Amide I $\alpha$ -helix
1650	(C=C) stretching	1525	$\delta$ (N-H) Amide II $\beta$ -sheet
1370	$\delta$ (CH <sub>3</sub> , CH <sub>2</sub> )	1450	$\delta_{\alpha}$ (C-H <sub>3</sub> )
1260	C=O stretching	1230	v(CN) Amide III
1160	v (C-O-C)	1170	v(C-C)
1050	(CO-H) stretching	1075	v(C-C)
770	(CH <sub>2</sub> ) stretching	685	v(C-S)

Table 4. IR assignments of main functional groups of ungrafted CFF and PHEMA.

In figure 7 present IR spectra of CFF grafted with 26 and 92% grafting yield, to evaluate effect of grafting on main assignments. It is evident when graft yield increase assignments attributed to PHEMA are more evident in spectrum (3390 and 1720, 2850 and 1150 cm<sup>-1</sup>), and signals attributed to NH and OH groups disappear because there are sites where graft reaction is carrying out. There are several reports about use of IR spectroscopy for evaluate graft reactions on keratin from chicken feathers ( Martínez et al 2003, Martínez et al 2008 and Kavitha et al 2005). They use IR spectra for identify main functional groups of keratin and of acrylic monomers in ungrafted and grafted copolymers, in addition to evaluate changes in peaks according with grafting yield.

### 3.4 IR of CMC-g-HEMA copolymer

IR spectra of the CMC is presented in figure 8. We can notice the characteristic broad band attributed to OH stretching vibration at 3360 cm<sup>-1</sup> due the CMC has a degree of substitution of 0.7, in average 2.3 OH groups of anhydroglucose ring are present in structure, peak at 2920 cm<sup>-1</sup> due stretching of C-H, peak at 1620 cm<sup>-1</sup> a strong absorption band that confirm the presence of carboxy group (COO<sup>-</sup>), 1420 and 1320 cm<sup>-1</sup> are assigned to -CH<sub>2</sub> scissoring and hydroxyl group bending vibration respectively, signal at 1060 cm<sup>-1</sup> is due to >CH-O-CH<sub>2</sub> stretching vibration and vibrations of the ether groups at 1060, 1110 cm<sup>-1</sup>. It is worth to remark that CMC used in this work was as sodium salt. The assignments are according with reports of IR spectroscopy studies of CMC (Bono et al 2009, Heydarzadeh et al 2009, Vasile et al 2004).

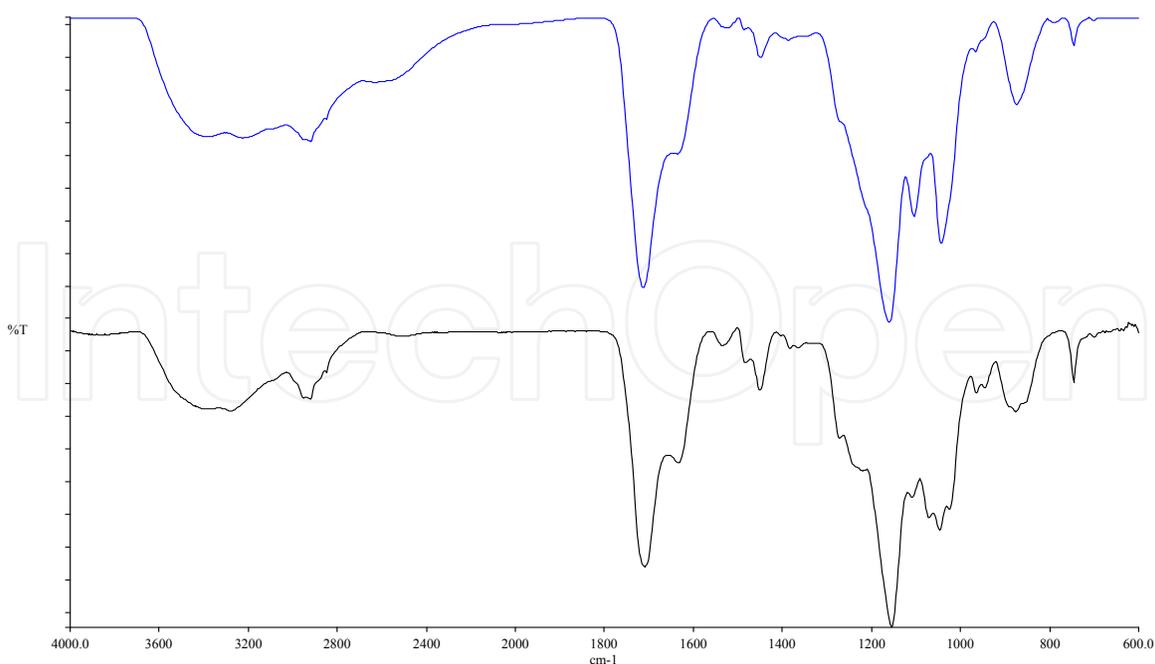


Fig. 7. IR spectra of CFF-g-HEMA with 26 (blue) and 92% (black) graft yield

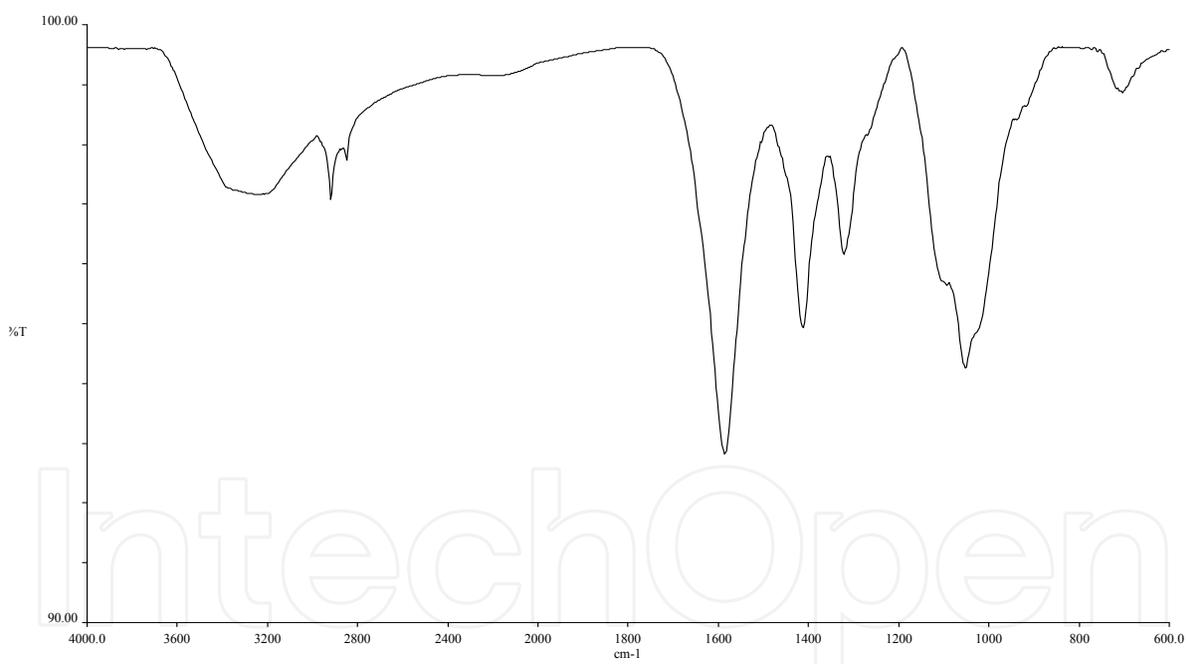


Fig. 8. IR spectrum of CMC

Figure 9 presents a comparative of IR spectra of CMC ungrafted and grafted with HEMA. Before, the main assignments for PHEMA were discussed. The CMC grafted present appearance of peak at  $2930\text{ cm}^{-1}$  due antisymmetric stretching  $\text{CH}_3$ ,  $1715\text{ cm}^{-1}$  from stretching vibration of  $\text{C}=\text{O}$  and peaks at  $1410$ ,  $1250$ ,  $1150$  and  $902\text{ cm}^{-1}$  assigned to bending vibration of  $\text{CH}_3$ ,  $\text{CH}_2$ , stretching of  $\text{C}=\text{O}$ , stretching of  $\text{CO-H}$  and  $=\text{CH}_2$  groups respectively, all those signals are from PHEMA structure, and also peaks attributed to CMC structure as  $3340$ ,  $1650$  and broad peak at  $1050\text{ cm}^{-1}$ , which are from  $\text{OH}$ ,  $\text{COO}^-$  and  $\text{C-O-C}$  from CMC, which is indicative the graft reaction was carried out.

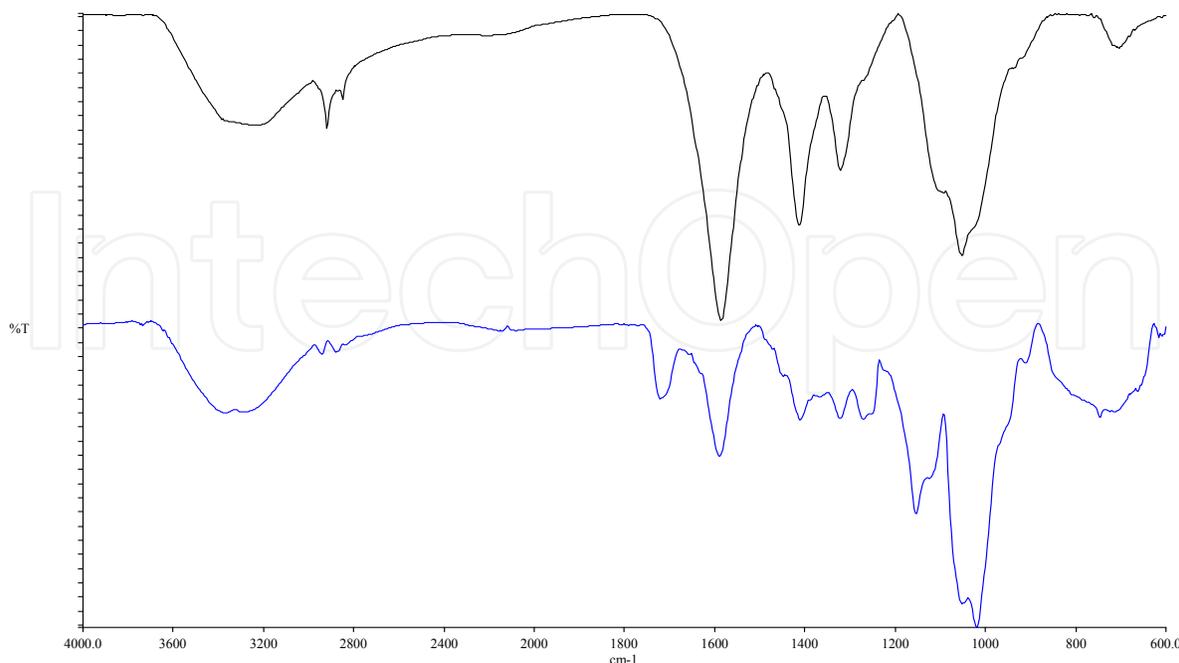


Fig. 9. IR spectra of CMC ungrafted (black) and with 69% grafting yield (blue)

Effect of grafting yield on IR assignments was evaluated in figure 10. It can observe that main peaks attributed to PHEMA (2940, 1720, 1270 and 1060  $\text{cm}^{-1}$ ) increase according with graft yield, which makes sense due the PHEMA is an higher proportion compared with CMC.

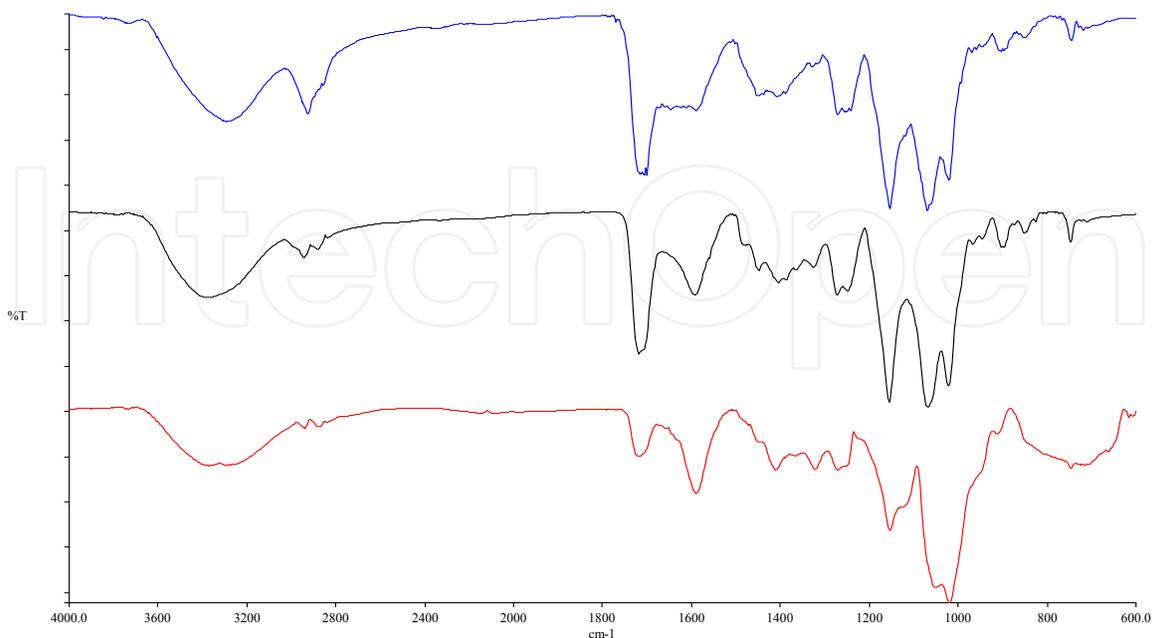


Fig. 10. IR spectra of CMC grafted with 69% (red), 249 % (black) and 397% (blue) grafting yield.

#### 4. Concluding remarks

From results presented in this research work it can be concluded that it is possible to graft HEMA onto CFF and CMC using different initiator systems, and that the grafting yield obtained depends on the kind of initiator system, being higher with the CAN initiator system than with the KMnO<sub>4</sub> malic acid. SEM micrographs give evidence that the grafting reaction takes place on the CFF and CMC surface until a saturation of active sites, and then homopolymerization happens.

One of the most common applications of IR spectroscopy is to the identification of organic compounds. In polymers, it may be used to identify the composition, to monitor the polymerization process, to characterize polymer structure. In the present research, IR spectroscopy showed to be a useful tool to evaluate if the graft reaction takes place. It was possible to identify the main functional groups of CFF and CMC ungrafted, and PHEMA. The IR spectra of grafted copolymers presented assignments due to ungrafted materials and PHEMA, giving evidence that the graft reaction carried out. Furthermore, it was possible to evaluate the changes in peaks of the grafted materials according to the grafting yield, increasing signals attributed to PHEMA.

#### 5. Acknowledgment

The financial support from Dirección General de Educación Superior Tecnológica (DGEST) from the Public Education Secretary (SEP) through projects 3616.10-P and 2203-09-P for the development of this research work is gratefully acknowledged. The authors would like to thank to Pollos Villafranca for providing chicken feathers, and the micrography department of CFATA of Universidad Nacional Autónoma de México campus Juriquilla, especially to Alicia Del Real López for technical assistance.

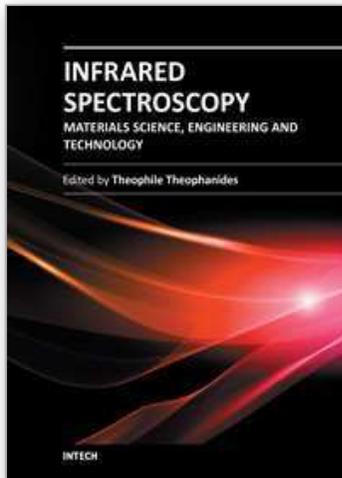
#### 6. References

- Athawale, V.D., Rathi, S.C., (1997), Effect of chain length of the alkyl group of alkyl methacrylates on graft polymerization onto starch using ceric ammonium nitrate as initiator. *European Polymer Journal*, vol. 33, No. 7, (July 1997), pp 1067-1071, ISSN 0014-3057.
- Barone, J.R., Schmidt, W.F., Liebner, C.F., (2005). Thermally processed keratin films. *Journal of Applied Polymer Science*, Vol. 97, No. 4, (August 2005), pp 1644-1651, ISSN 1097-4628.
- Bickford, M., (2008). *Characterization and Analysis of Polymers*. John Wiley and Sons. ISBN 978-0-470-23300-9, Hoboken, New Jersey, United States.
- Bono, A., Ying, P.H., Yan, F.Y., Muei, C.L., Sarbatly, R., Krishnaiah, (2009), Synthesis and Characterization of Carboxymethyl Cellulose from Palm Kernel Cake. *Advances in Natural and Applied Sciences*, Vol. 3, No. 2, (January 2009), pp 5-11, ISSN 1995-0772.
- Cao, Y., Qing, X., Sun, J., Zhou, F., Lin, S., (2002), Graft copolymerization of acrylamide onto carboxymethyl starch. *European Polymer Journal*, vol. 38, No. 9, (September 2002), pp 1921-1924, ISSN 0014-3057.
- Elizalde Peña, E., Flores Ramírez, N., Luna Barcenas, G., Vásquez García, S. R., Arámbula Villa, G., García Gaitan, B., Rutiaga-Quiñones, J.G., González-Hernández, J. (2007). Synthesis and characterization of chitosan-g-glycidyl methacrylate with methyl

- methacrylate. *European Polymer Journal*, Vol. 43, No. 9, (September 2007) pp 3963-3969, ISSN 0014-3057.
- Gupta, K.C., Sahoo, S., (2001) Graft copolymerization of 4-vinylpyridine onto cellulose using Co (III) acetylacetonate complex in aqueous medium. *Cellulose*, Vol. 8, No. 3, (September 2001), pp 233-242, ISSN 0969-0239.
- Heydarzadeh, H.D., Najafpour, G.D., Nazari-Moghaddam, A.A., (2009), Catalyst-free conversion of alkali cellulose to fine carboxymethyl cellulose at mild conditions. *World Applied Science Journal*, Vol. 6, No. 4, (2009 ), pp 564-569, ISSN 1818-4952.
- Jia, Z., Yong, Y., (2006); Surface Modification of Poly Acrylic Fibers (PAC) via Grafting of Soybean Protein Isolates (SPI). *Iranian Polymer Journal*, Vol. 15, No. 10, (October 2006), pp 789-798, ISSN 1026-1265.
- Joshi, J.M., Sinha, V.K., (2006), Graft copolymerization of 2-hydroxyethylmethacrylate onto carboxymethyl chitosan using CAN as an initiator. *Polymer*, Vol. 47, No. 6, (March 2006), pp 2198-2204, ISSN 0032-3861.
- Kang, H., Liu, W., He, B., Shen, D., Ma, L., Huang, Y., (2006), Synthesis of amphiphilic ethyl cellulose grafting poly (acrylic acid) copolymers and their self-assembly morphologies in water. *Polymer*, Vol. 47, No. 23, (October 2006), pp 7927-7934, ISSN 0032-3861.
- Klemm, D., Philipp, B., Heinze, T., Heinze, U., Wagenknecht, W., (1998). *Comprehensive cellulose chemistry volume 2*, Wiley-VCH, ISBN 3-527-29489-9, Weinheim, Federal Republic of Germany.
- Kavitha, A., Boopalan, K., Radhakrishnan, G., Sankaran, S., Das, B., Sastry, T., (2005), Preparation of Feather Keratin Hydrolyzate-Gelatin Composites and Their Graft Copolymers. *Journal of Macromolecular Science Part A: Pure and Applied Chemistry*, Vol. 42, No. 12, (December 2005), pp 1703-1713, ISSN 1060-1325.
- Martínez-Hernández, A.L., Santiago-Valtierra A. L., Alvarez-Ponce M. J., (2008), Chemical modification of keratin biofibres by graft polymerisation of methyl methacrylate using redox initiation. *Materials Research Innovations*, Vol. 12, No. 4, (December 2008), pp 184-191, ISSN 1432-8917.
- Martínez-Hernández, A.L., Velasco-Santos, C., de Icaza, M., Castaño, V.M., (2005), Microstructural characterization of keratin fibers from chicken feathers. *International Journal Environmental and Pollution*, Vol. 23, No. 2, (MES 2005), pp 162-178 ISSN 0957-4352.
- Martínez-Hernández, A.L., Velasco-Santos, C., de Icaza, M., Castaño, V.M., (2003), Grafting of Methyl methacrylate onto natural keratin. *e-polymers*, No. 016, (April 2003), pp 1-11, ISSN 1618-7229.
- Meshram, M.W., Patil, V.V., Mhaske, S.T., Thorat, B.N., (2009) Graft copolymers of starch and its application in textiles. *Carbohydrate Polymers*, 75, 1, (January 2009), pp 71-78, ISSN 0008-6215.
- Mostafa, M., Graft polymerization of methacrylic acid on starch and hydrolyzed starches. *Polymer Degradation and Stability*, (1995), Vol. 50, No. 2, (March 1995), pp 189-194, ISSN 0141-3910.
- Mun, G.A., Zauresh, S., Nurkeeva, S.A., Dergunov, I.K., Nam, T.P., Maimakov, E.M., Shaikhutdinov, Lee, S.Ch., Park, K., (2008), Studies on graft copolymerization of 2-hydroxyethyl acrylate onto chitosan. *Reactive and Functional Polymers*, Vol. 68, No. 1, (January 2008), pp 389-395, ISSN 1381-5148.

- Okieimen, F.E., Ogbeifun, D.E., (1996), Graft copolymerization of modified cellulose: grafting of methyl acrylate, ethyl acrylate and ethyl methacrylate on carboxymethyl cellulose. *European Polymer Journal*, Vol. 32, No. 3, (March 1996), pp 311-315, ISSN 0014-3057.
- Prachayawarakorn, J., Boonsawat, K., (2007), Physical, chemical and dyeing properties of bomboymori silks grafted by 2-hydroxyethyl methacrylate. *Journal of Applied Polymer Science*, Vol. 106, No. 3., (November 2007), pp 1526-1534, ISSN 1097-4628.
- Radhakumary, C., Nair, P. D., Mathew, S., Nair, C.P., (2006), HEMA-Grafted Chitosan for Dialysis Membrane Applications. *Journal of Applied Polymer Science*, Vol. 101, No 5, (September 2006), pp 2960-2966, ISSN 1097-4628.
- Schmidt, W.F., (1998), Innovative feather utilization strategies. *Proceedings of National Poultry Waste Management conference*, pp 276-282, Springdale, Ar., October 19-22, 1998.
- Vasile, C., Bumbu, G.G., Dumitriu, R.P., Staikos, G., (2004), Comparative study of the behavior of carboxymethyl cellulose-g-poly(N-isopropylacrylamide) copolymers and their equivalent physical blends. *European polymer Journal*, Vol. 40, No. 6, (June 2004) pp 1209-1215, ISSN 0014-3057.
- Xu, X. Zhou, Z., Prum, R.O., (2001), Branched integumental structures in Sinornithosaurus and the origin of feathers. *Nature*, Vol. 410, No. 6825, pp 200-204, (March 2001), ISSN 0028-0836.
- Xu, X., Zhou, Z., Wong, X., Kuang, X. Zhang, F., Du, X., (2003), Four-winged dinosaurs from China. *Nature*, Vol. 421, No. 6921, pp 335-340, (January 2003), ISSN 0028-0836.
- Zampano, G., Bertoldo, M., Bronco, S., (2009) Poly(ethyl acrylate) surface-initiated ATRP grafting from Wood pulp cellulose fibers. *Carbohydrate Polymers*, Vol. 75, No. 1, (January 2009), pp 22-31, ISSN 0008-6215.
- Zohuriaan-Mehr, J.M., Pourjavadi, A., Sadeghi, M., (2005), Modified CMC: Part1-Optimized Synthesis of Carboxymethyl cellulose-g-Polyacrylonitrile. *Iranian Polymer Journal*, Vol. 14, No. 2, (February 2005), pp 131-138, ISSN 1026-1265.

IntechOpen



## **Infrared Spectroscopy - Materials Science, Engineering and Technology**

Edited by Prof. Theophanides Theophile

ISBN 978-953-51-0537-4

Hard cover, 510 pages

**Publisher** InTech

**Published online** 25, April, 2012

**Published in print edition** April, 2012

The present book is a definitive review in the field of Infrared (IR) and Near Infrared (NIR) Spectroscopies, which are powerful, non invasive imaging techniques. This book brings together multidisciplinary chapters written by leading authorities in the area. The book provides a thorough overview of progress in the field of applications of IR and NIR spectroscopy in Materials Science, Engineering and Technology. Through a presentation of diverse applications, this book aims at bridging various disciplines and provides a platform for collaborations among scientists.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

José Luis Rivera-Armenta, Cynthia Graciela Flores-Hernández, Ruth Zurisadai Del Angel-Aldana, Ana María Mendoza-Martínez, Carlos Velasco-Santos and Ana Laura Martínez-Hernández (2012). Evaluation of Graft Copolymerization of Acrylic Monomers Onto Natural Polymers by Means Infrared Spectroscopy, *Infrared Spectroscopy - Materials Science, Engineering and Technology*, Prof. Theophanides Theophile (Ed.), ISBN: 978-953-51-0537-4, InTech, Available from: <http://www.intechopen.com/books/infrared-spectroscopy-materials-science-engineering-and-technology/evaluation-of-graft-copolymerization-of-acrylic-monomers-onto-natural-polymers-by-means-infrared-spe>

**INTECH**  
open science | open minds

### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821