Appl Phys A (2011) 104:219–228
DOI 10.1007/s00339-010-6111-4

Applied Physics A
Materials Science & Processing

(Chicken feathers keratin)/polyurethane membranes

V. Saucedo-Rivalcoba · A.L. Martínez-Hernández · G. Martínez-Barrera · C. Velasco-Santos · V.M. Castaño

Received: 1 March 2010 / Accepted: 19 October 2010 / Published online: 4 December 2010

Abstract Actually, chicken feathers are considered as waste from the poultry industry; however, 90% of feather structure is constituted by a protein called keratin. In this research, the properties of feather keratin and polyurethane are combined in order to synthesize hybrid synthetic–natural membranes. Both polymers are linked by urethane bonds which are similar to peptide bonds found in proteins. Keratin is incorporated onto the polyurethane matrix by dissolving protein in a salt solution (urea and 2-mercaptoethanol) at different concentrations: 11, 13, 15, 17, 19, and 21% (w/w). In order to know the effect of urea on membranes, keratin is incorporated to polyurethane in two ways; as keratin salt solution and after dialyzing. Both membrane types were characterized by Scanning Electron Microscopy (SEM) to observe their morphologic changes. Fourier Transformed Infrared Spectroscopy (FT-IR), Termogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) were used to study membrane structures. Results show that keratin is grafted in polyurethane and, therefore, there is an influence of amino acids through the amino and carboxylic groups (NH and COOH) into the synthetic polymer structure. According with characterization results, the obtained membranes are functional materials that can be useful in diverse applications, among them the separation process can be emphasized.

V. Saucedo-Rivalcoba · G. Martínez-Barrera
Laboratorio de Investigación y Desarrollo de Materiales Avanzados (LIDMA), Facultad de Química, Universidad Autónoma del Estado de México, Km.12 de la carretera Toluca-Atlacomulco, San Cayetano 50200, Toluca, México

A.L. Martínez-Hernández (✉) · C. Velasco-Santos
Ingeniería en Materiales, Departamento de Metal-Mecánica, Instituto Tecnológico de Querétaro, Av. Tecnológico s/n Esq. Gral. Mariano Escobedo, Col. Centro Histórico, Querétaro 76000, México
e-mail: analaura@fata.unam.mx
Fax: +52-442-2381160

V. Saucedo-Rivalcoba · V.M. Castaño
Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, AP 1-1010, Querétaro 76000, México

List of abbreviation and symbols

%	percent(s)
% (w/w)	percent (weight/weight)
FT-IR	Fourier transform infrared
TGA	thermogravimetric analysis
DSC	differential scanning calorimetry
PU	polyurethane
TDI	Toluene diisocyanate
PPG	poly(propilenglycol)
M	molar
mM	milimolar
°C	degrees Celsius
kV	kilovolts
mBar	milibar
nm	nanometer(s)
°C/min	degrees Celsius per minute
µm	micrometer(s)
ATR	attenued total reflectance
PUcoKES	polyurethane keratin salt
PUcoKED	polyurethane dialyzed keratin

1 Introduction

Poultry feathers are considered as a worldwide waste causing serious environmental problems. The feathers, from where can be obtained fibers and also proteins, have been

considered not only a waste, but rather a complicated disposal challenge, in spite of their important characteristics. Keratin, from poultry feathers, is a fibrous protein that has high stability due to its self-assembled hierarchical structure [1]. This arrangement is formed from intra and intermolecular bonds, supported on the H-bonds, van der Waals forces, and sulfur bonds; this last is due to the cystine amino acid [2]. Keratin is composed by 18 different amino acids that forms by condensation polypeptide chains with a molecular weight in the range from 59,000 to 65,000 [3, 4]. Amino acids are the responsible compounds of protein functionality and could be able to be considering as reactive sites; such as OH, C=O, NH, S–S, S–H (Table 1), since they are touchy to be modified through functional reactions to increase their natural affinity toward metals, organic compounds, and other materials [4–6].

Different studies in keratin using natural and modified wool fibers show that the ideal grafting sites are located at thiol groups on cystine amino acid [7]. However, NH and OH groups through H-bond have also been found to act as reactive sites [8]. In general, proteins show several kinds of chemical groups that can be used as effective sites in order to hold and, therefore, remove some toxic wastes [9–12].

On the other hand, an increasing research interest in polymers containing characteristics of both natural biopolymers and synthetic chains has been developed recently [1, 4, 7, 8, 13, 14]. Among these polymers, polyurethanes (PU) are a unique class, because a large variety of them can be synthesized with a wide diversity in physical and chemical properties. Biodegradable polyurethanes are generally achieved by the incorporation of labile moieties susceptible to hydrolysis in the polymer chain. The most common method for introducing these linkages into PU has been the incorporation of hydrolysable soft segments of natural polysaccharides (chitin, starch, cellulose, and lignin) obtained from renewable sources [13, 14]. Also, lipid and proteins into a polyurethane matrix have been studied as other friendly environmental materials [15, 16].

In addition, polyurethanes have gained much attention, mainly for manufacturing membranes, taking special attention in their inherent problems, including poor heat resistance which limits their use as engineering materials [17]. Thermoplastic polyurethane elastomers are block copolymers comprising of alternating soft and hard segments, which are divided in two phases and could vary in terms of the chain extender. Different polyols are generally used as soft segments giving extensibility to the polymer, whereas diisocyanates, which belongs to chain extender, form the hard segment [18]. The latter acts as physical crosslinker and has high influence on the final mechanical performances, including toughness, elasticity and hardness. Zhang et al. [19] have studied the behavior of three diamine chain extenders and a specific hard segment, where certain bonds such as H-bond or N–H and C=O can show changes depending on diamine structure. The thermal stability is correlated to the soft-segmented molecular weight and to the polyol structure [20]. Polyurethane membranes also have been studied as interesting materials for water treatment because of the easy to forming "foam" porous. In this sense Ciobanu et al. [21], Rzeszutek et al. [22] and Das et al. [23] have developed different systems based on polyurethane membranes and apply them successfully as a separation process.

Our research group has been interested in the development of new materials that conjugate the interesting potential of keratin to attract metals or organic compounds with synthetic polymers that act as functional support for the membrane separation process. Thus, considering the amide groups present in both: keratin and nylon, Santiago-Valtierra [24] synthesized nylon-keratin membranes to remove hexavalent chromium from water. However taking into account this functional bond, not only nylon is related with proteins, but polyurethanes also present the amide bond (Fig. 1). Further polyurethane offers better characteristics than nylon to be used as structural membrane.

Table 1 Chemically reactive groups in wool and feathers (adapted from Martinez-Hernandez [4])

Reactive group*	Keratin	
	Wool	Feather
Free carboxyl	58–66	27–44
Amide	79–98	78
Carboxyl plus amide	137–164	105–122
Phenolic hydroxyl	22–36	11–12
Aliphatic hydroxyl	124–148	134–174
Amino	20–24	7–12
Aromatic	27–43	13–14
Half-disulfide	92–114	57–68
Oxidizable	526–650	309–376

*Content as gram equivalents per 10^5 g of keratin

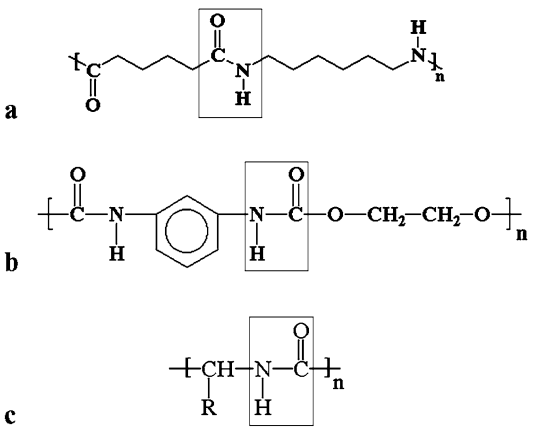

Fig. 1 Amide bonds; (**a**) nylon, (**b**) polyurethane, and (**c**) polypeptide

It is evident that polyurethane is a promising material which can be modified with natural polymer in order to increase its functionality. Keratin obtained from chicken feathers is a functional biopolymer useful to form with polyurethane novel synthetic–natural materials. This research presents a series of hybrid polyurethane–keratin membranes; the interactions between the synthetic and the natural polymer are studied. Thus, in spite of polyurethane–keratin membrane preparation method involves several stages, synthesis of these materials presents advantages such as: keratin source, water quantity employed (only few milliliters), membrane size and functional diversity. In addition, even though keratin solution preparation uses different chemical agents, the whole synthesis process is very simple. These membranes were developed taking advantage on the functionality of amino acids from protein for potential use in high flow rate waste removal, which can be the basis for future developments with this interesting material in order to introduce it in diverse material areas as a high structural and adaptable component.

2 Experimental

2.1 Materials

Commercial Toluene diisocyanate (TDI) and poly(propilenglycol) (PPG) were provided by Poliformas Plasticas (Mexico). (Ethylenedinitrilo) tetraacetic acid, disodium salt, dehydrate (EDTA) from J.T. Baker, Urea, 2-Mercaptoethanol, and Tris(hydroxymethyl)aminomethane were purchased from Sigma Aldrich. Spectra/Por dialysis membranes MWCO 6-8000 were acquired from Cole Palmer and keratin biofibers (obtained from chicken feathers) were kindly supplied by Walter Schmidt (Agricultural Research Services, USA).

2.2 Method

2.2.1 Preparation of feather keratin biofiber

The biofibers were obtained according to a patented process by Schmidt (US 5750030) [25]. The wet feathers are washed with ethanol and dried to be clean white, sanitized, and odor-free. Afterward, the feathers are cut in small pieces by a shredder, whose blades pulverize the quills. An air stream is used to separate dense quill fractions from keratin biofiber, which is constituted by barbules and some barb fragments. The keratin biofiber extracted from feathers is used in this study.

2.2.2 Keratin salt solution

Keratin was dissolved by mixing 30 g of biofiber in a solution made of Urea 8 M 98%, EDTA 3 mM 90%, 2-Mercaptoethanol 125 mM 98%, and Tris(hydroxymethyl) aminomethane 200 mM 97% in 750 ml deionized water. The mixture was stirred at room temperature for 24 hrs [26].

2.2.3 Keratin dialyzed solution

Keratin salt solution was dialyzed using a MWCO 6-8000 membrane immersed in 1 L of distilled water. The water was replaced completely after 16 and 24 hrs, and the dialysis was stopped after 48 hrs [27]. Dialyzed solution was preserved at 4°C.

2.2.4 Synthesis of polyurethane–keratin membranes

The polyurethane membranes were synthesized mixing PPG with keratin salt solution or dialyzed keratin solution. Precise volumes of the keratin solutions were added to the total mass of PU to get membranes with different weight percentages of keratin, as shown in Table 2. The keratin solution quantity was calculated according to the pure polyurethane membrane final weight of 15.4 gr. The PPG quantity added was 11 gr and 6 gr of TDI, to get a ratio of 65% to the polyol and 35% to the isocyanate, and obtain polyurethane flexible foam. After mixing PPG with keratin salt or with dialyzed keratin, the TDI phase was added. The whole solution was mixed until overcome the viscosity. The resulting mixture was poured into teflon dishes to finish the polymerization reaction and later it was placed in a closed chamber at room temperature for 24 hrs.

2.3 Characterization techniques

All synthesized membranes were analyzed by scanning electron microscopy in a JEOL model SM-6060LV microscope at 20 kV and high vacuum. Before analyzing the morphological surface, the membranes were vacuum-coated with gold at 7×10^{-2} mBar using Argon in a Sputter Coater EMS 550 with a final coat of 120 nm. The spectroscopy was performed in an Infrared spectrometer Bruker Vector 33 by the attenuated total reflectance (ATR) mode, covering a range from 400 to 4000 cm^{-1} and 32 scans at a spectral resolution

Table 2 Nomenclature of polyurethane–keratin membranes*

Keratin salt membranes nomenclature (weight percent)	Keratin salt solution weight (g)	Keratin dialyzed membranes nomenclature (weight percent)	Keratin dialyzed solution weight (g)
PUcoKES11	1.7	PUcoKED11	1.7
PUcoKES13	2.0	PUcoKED13	2.0
PUcoKES15	2.3	PUcoKED15	2.3
PUcoKES17	2.6	PUcoKED17	2.6
PUcoKES19	2.9	PUcoKED19	2.9
PUcoKES21	3.2	PUcoKED21	3.2

*Nomenclature includes weight percent of keratin solution/polyurethane. For instance: PucoKES11 is a membrane with 11 weight percent

of 1 cm^{-1}. Thermal analysis of membranes were carried out through TGA and DSC, both under nitrogen atmosphere and covering from 30 to 600°C by a heat rate of 20°C/min, in a TA model Q600-0054-SDT.

3 Results and discussion

3.1 SEM

The properties of flexible polyurethane foams are strongly influenced by their cellular structure. Cell diameters and average cell volumes are often used to characterize cell size, since a distribution in cell size is always distinguished. Another important parameter for flexible foams is cell openness degree. SEM has been used to study the detailed features of cellular structure of slabstock foams. Thus, the morphological and structural study of PU membranes obtained in this research is detailed in SEM images reproduced in Figs. 2 and 3. As it can be seen in Fig. 2, the pure polyurethane foam (none grafted) has closed-cell structure and very few opened cells. In addition, a geometrical anisotropy in the cell structure, parallel and perpendicular to the blow direction is presented (Fig. 2). This structural anisotropy is known that having effect in bulk foam properties, such as load bearing [28].

In Fig. 3, it is possible to observe that internal cell size is above the conventional filtration and microfiltration (>0.1 µm). This characteristic is formed during the first step of polyurethane reaction which involves an isocyanate group reacting with water in order to yield an unstable carbamic acid ($RNCO_2H_2$). This later moiety decomposes rapidly by an exothermic reaction to give amine and carbon dioxide (Fig. 4). The carbon dioxide is directly related to form "foam" porous and cells in polyurethane membranes and also is proportional to water quantity added in the reaction [28].

Figure 3 shows diverse morphologies in the membranes depending on the quantity and keratin type used in the synthesis. Polyurethane–keratin salt membranes are shown in Figs. 3a–c, in these images it is possible to appreciate that membranes with keratin salt have the smallest cell size, but if higher quantities of keratin salt are added homogeneous and bigger opened cells are present (Figs. 3b and 3c). On the other hand, when dialyzed keratin is used (Figs. 3d–3f), cells are opened even bigger compared with those formed by adding keratin salt. These last ones tend opening and breaking, producing important holds with cell size upper than 100 µm.

Thus, it is corroborated an important influence of keratin solution quantity in cells size in all cases, as well as the morphology of membrane is related to the treatment done to dissolved keratin: dialyzing or maintaining salt concentration.

It is important to mention that polyurethane chemical reactions are divided in two steps: "blow" and "gelation". These reactions not only help to foam expansion but also produce "hard urea segments." Gelation step links covalently polyols to hard segments. If the quantity of urea hard segments is overloaded in system (according to solubility limits), they split up and yield "urea micro-domains." At the same time when there are high water quantities at chemical polyurethane reaction, it generates high urea microdomains (aggregates) which form large urea rich regions called "urea balls" [28]. In Fig. 5, it is possible to observe both sections in the chemical structure of polyurethane: hard and soft segments. This is something to take into account, because membrane's morphology is directly affected when

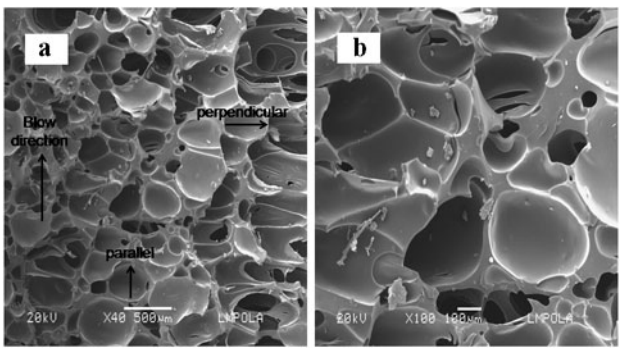

Fig. 2 SEM images of polyurethane membranes frontal view, (**a**) 40× resolution and (**b**) 100× resolution

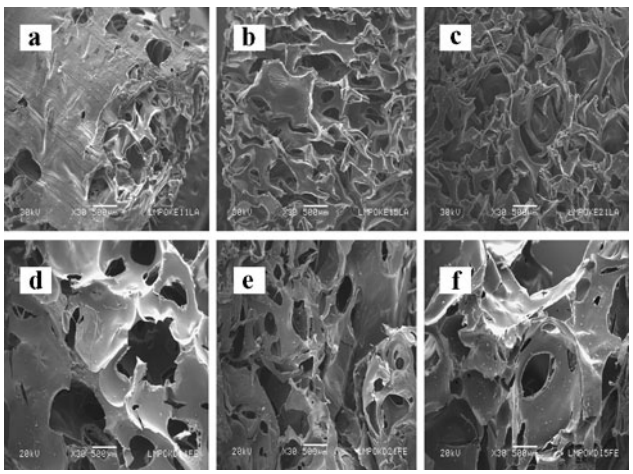

Fig. 3 SEM images of polyurethane–keratin salt membranes at 30× resolution, (**a**) PUcoKES11, (**b**) PUcoKES15, (**c**) PUcoKES21 and polyurethane–dialyzed keratin membranes at 30× resolution, (**d**) PUcoKED11, (**e**) PUcoKED15, and (**f**) PUcoKED21

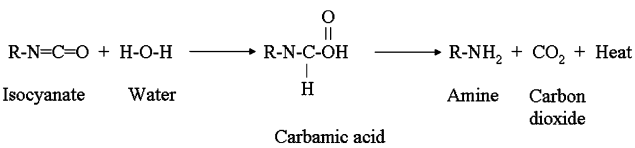

Fig. 4 Polyurethane chemical reaction, first step. Blow reaction [25]

keratin salt (high urea quantity) and dialyzed keratin (low urea quantity and high availability of amine groups) are used. Polyurethane membranes synthesized from keratin salt were more flexible than those obtained with dialyzed keratin, even thought the presence of urea groups. This fact is related with the results obtained by Coutinho and Delpech [29], who reported that diamine chain extender groups in the polyurethane chemical structure cause an increase in their rigidity and brittleness.

3.2 FT-IR

Figures 6 and 7 correspond to the FT-IR spectra of polyurethane–keratin salt membranes and polyurethane-dialyzed keratin membranes, respectively. These figures clearly show the interaction between urethane groups and keratin protein; next both spectra are discussed in order to observe resemblance and differences.

In Fig. 6, the signals at 3445 and 3340 cm^{-1} are assigned to υ(N–H) free and υ(N–H) bonded, respectively [18, 30, 31]. It is observed that sample of pure polyurethane membrane does not have these bands, but they are present in all keratin salt membranes, which indicates the presence of amine groups from keratin protein linked to urethanes and NH free groups that could work as reactive sites [4, 32]. In a similar way, a clear shoulder at 3220 cm^{-1} is observed in hybrid membranes but not in pure polyurethane. This signal is attributed to υ(N–H) related with imide groups found at allophanates formed in the crosslinking of PU [18]. The presence of this kind of moieties is attributed to the high quantity of N–H of both, urea and keratin. A small contribution of N–H groups bonded with ether oxygen in polyurethane is observed at 3312 cm^{-1} (polyether soft segment in PU) [18, 33] confirming urethane linkage. Also, the complete reaction of isocyanate and hydroxyl groups in all polyurethane membranes can be corroborated by the lack of a signal around 2275 cm^{-1} related with υ_{as} (CN) [34].

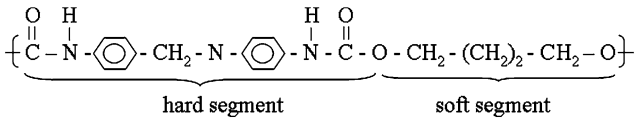

Fig. 5 Chemical polyurethane zones, soft and hard segments

The bands at 2971 cm^{-1} $\upsilon_{as}(CH_3)$, 2933 $\upsilon_{as}(CH_2)$ and 2862 $\upsilon_s(CH_3)$ cm^{-1} increase in all spectra of hybrid membranes with respect to PU spectrum; this is due to the existence of aliphatic chains from proteins, [35]. The signal at 1731 cm^{-1} corresponding to υ(C=O) from free urethane shows clear differences in the spectra of membranes in comparison with PU. These changes are related with the broad signal at 1601 cm^{-1} υ(C=O) that is affected by the H-bonded urea due to NH in the urethane and urea group from membranes with keratin salt [18], but also by the presence of keratin structure with the same vibration υ(C=O) [36]. The grafting of keratin in polyurethane is corroborated with the shift from 1220 cm^{-1} in PU to 1235 cm^{-1} for hybrid membranes. This signal is associated to υ(C=N) Amide III of urethane and keratin protein [19, 37, 38]. These signals increase their intensity with the concentration of keratin salt solution.

The bands at 1710 cm^{-1} υ(C=O) and 1531 cm^{-1} δ(N–H) are classical from polyurethane/polyether, as well as 1084 cm^{-1} υ(C–O–C); these bands suggest that hard and

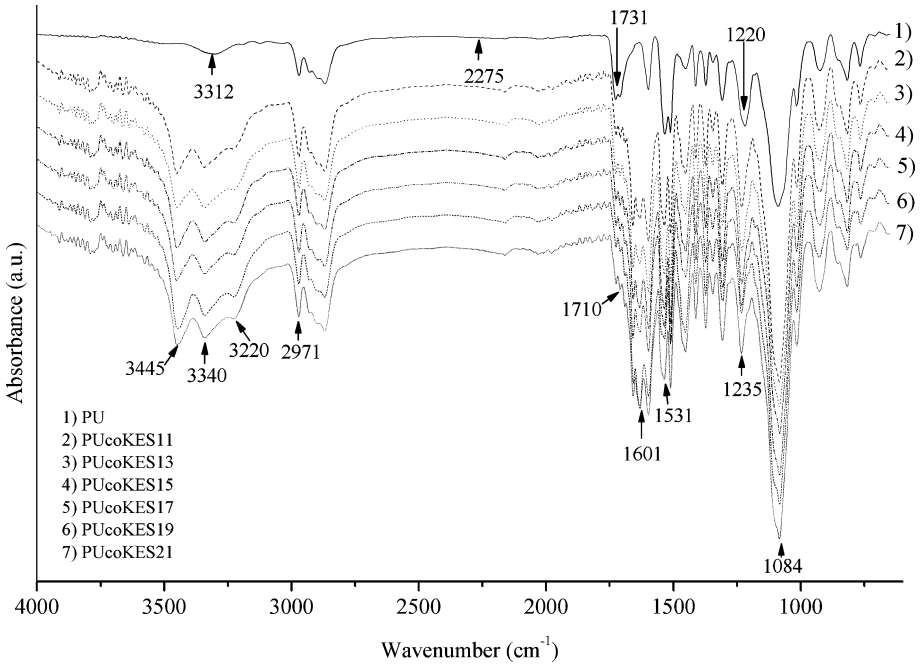

Fig. 6 FTIR spectra of polyurethane–keratin salt membranes

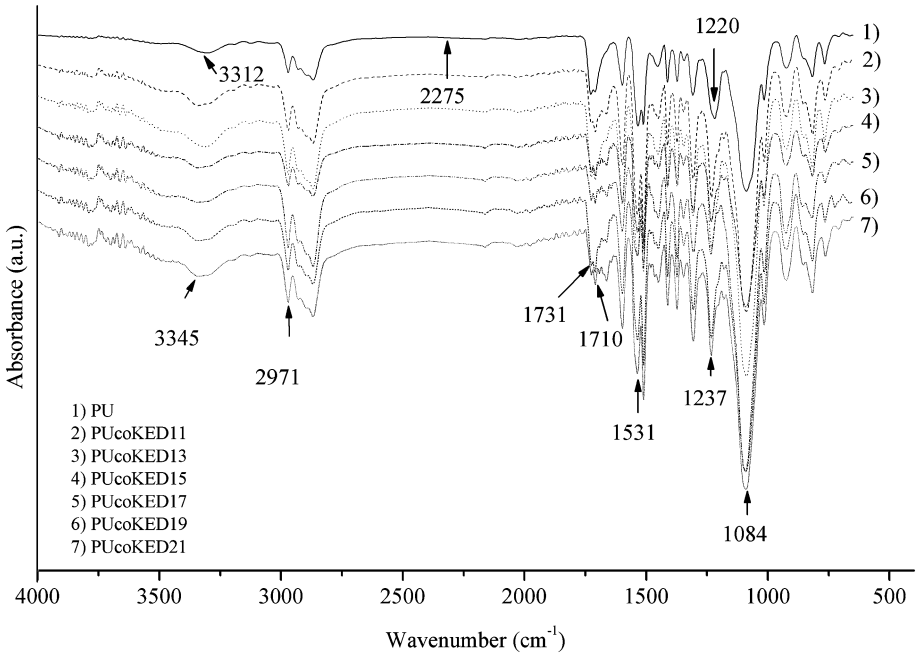

Fig. 7 FT-IR spectra of polyurethane–dialyzed keratin membranes

soft segments are linked via ether bonds [18] and this happens in both, pure polyurethane and polyurethane–keratin copolymer, since these signals appear in all spectra. In addition, the last signal is clearly increased by the presence of keratin salt.

Figure 7 shows spectra of the polyurethane-dialyzed keratin membranes and pure polyurethane. Here, it is observed that the band at 3312 cm^{-1} from PU shifts at 3345 cm^{-1} in the membrane spectra; this suggests that only υ(N–H) bonded is present, compared with spectra of polyurethane–keratin salt. Thus, not only the urethane linkage is confirmed, but also the keratin grafting in PU is evident. In addition, there is no signal at 2275 cm^{-1} υ_{as}(CN) confirming the complete PU reaction.

The bands at 2971 cm^{-1} $\upsilon_{as}(CH_3)$, 2933 $\upsilon_{as}(CH_2)$, and 2862 $\upsilon_s(CH_3)$ cm^{-1} show the same effect than polyurethane–keratin salt membranes, since these are increased by the presence of aliphatic groups due to protein chain.

On the other hand, when the dialyzed keratin is present, the band at 1731 cm^{-1} υ(C=O) undergoes just an expansion of the peak, indicating that dialysis process eliminates urea salts in this kind of membranes [19, 29].

The bands at 1710 cm^{-1} υ(C=O), 1531 cm^{-1} δ(N–H) and 1084 cm^{-1} υ(C–O–C), classical from polyurethane/polyether [18], show the same behavior than PU-keratin salt membranes, inasmuch as they increase their intensity with keratin concentration.

It is important to notice that in both Figs. 6 and 7, proteins confer high content of alifatic and shown in bands at 1457, 1411, 1374, 1307, and 1235 cm^{-1} and aromatic groups observed in a pair of bands at 860 + 814 cm^{-1} and 768 + 720 cm^{-1} whom correspond to the aromatic ring bi and mono substituted, respectively; also, a signal at 757 cm^{-1} related with υ(CC) skeletal [39]. All of them increase their intensity because of keratin's amino acids contribution.

3.3 TGA

The thermogravimetric analysis of polyurethane–keratin salt membranes is shown at Fig. 8. In these thermograms, two phases and the start on the phase's degradation (*Tonset*) are observed, and are related to hard and soft segments. The first phase occurs from 123 to 147°C with a weight loss of 6–8%. Thermogravimetric curves of membranes have a decrement of weight at lower temperature compared with pure polyurethane whose T_{onset} is 240°C and weight loss is around 1%. In PU, this degradation phase is caused by the breaking at the hard segments, seen in Fig. 5, mostly influenced by chemical structure of the components and the NCO/OH ratio [14, 31]. The behavior is explained by the presence of high oxygen content and the dehydration reaction. Also, Herrera et al. [40], reported that carbon dioxide; one of the most abundant products is observed during the first phase of degradation, indicating the scission of urethane bond. It is evident that premature degradation in membranes is influenced by the presence of urea. As well, this indicates that keratin salt is bonded to polyurethane segments and promotes the early degradation in this stage.

The second phase of degradation is more notorious in weight loss compared with the first phase. Here, the temperature range varies from 418 to 424°C with a weight loss between 80 and 88% for PU–keratin salt membranes, and

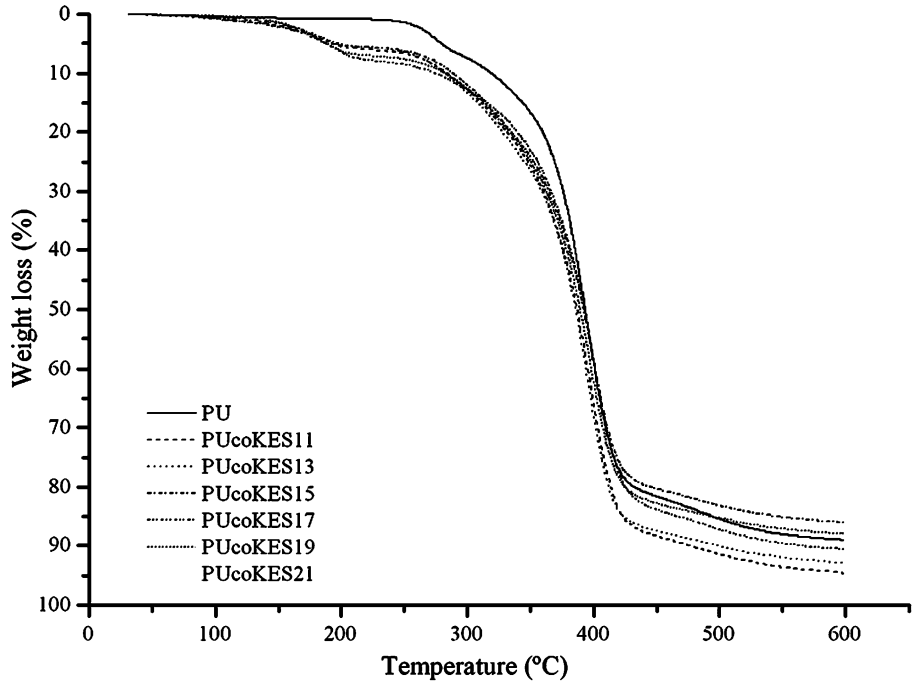

Fig. 8 TG curves of polyurethane–keratin salt membranes at different concentrations membranes

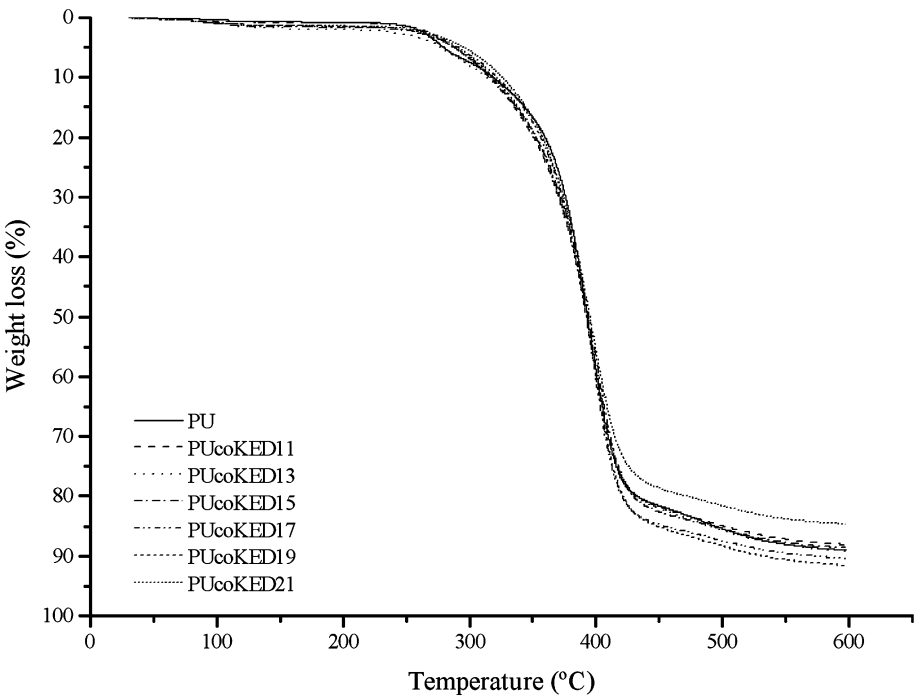

Fig. 9 TG curves of polyurethane–dialyzed keratin membranes at different concentrations

422°C for PU. This phase is a complex mixture of products most probably due to polyol segments, and also more carbon dioxide is presented [40]. The initial degradation of this stage is also affected by the presence of keratin-salt.

Figure 9 shows the thermogravimetric analysis of polyurethane–dialyzed keratin membranes. In these materials, the first step occurs from 236 to 263°C related with the free water found in dialyzed keratin with a weight loss of 1–2%. This step is not presented by pure polyurethane and verifies the fact that the dialysis process eliminates the urea from the solution; inasmuch as, the behavior of these thermogravimetric curves is very different in comparison with the polyurethane–keratin salt membranes (Fig. 8). Also, these samples show a second stage that begin around 418 to 424°C and finish at the same time that PU (which thermal behav-

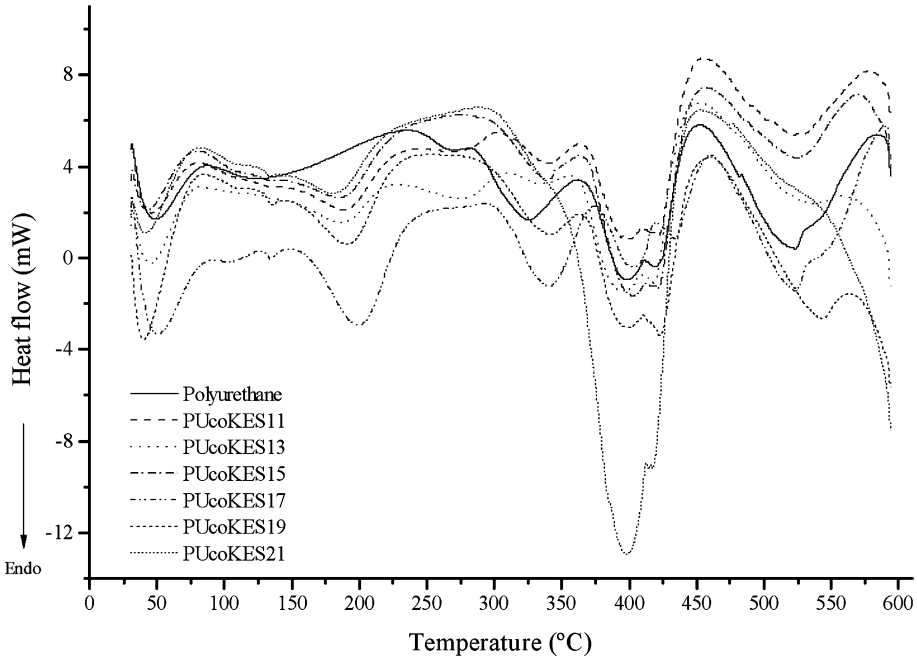

Fig. 10 DSC curves of polyurethane–keratin salt membranes at different concentrations

Table 3 Thermogravimetric analysis of polyurethane–keratin membranes

Membrane	1° phase		2° phase	
	T_{onset} (°C)	Loss weight (%)	T_{onset} (°C)	Loss weight (%)
Keratin salt				
PUcoKES11	135	6	421	88
PUcoKES13	130	6	421	86
PUcoKES15	142	6	425	80
PUcoKES17	123	8	424	83
PUcoKES19	138	7	421	82
PUcoKES21	147	7	418	85
Keratin dialyzed				
PUcoKED11	236	1	421	81
PUcoKED13	259	2	424	81
PUcoKED15	260	1	423	81
PUcoKED17	263	1	418	83
PUcoKED19	262	1	418	84
PUcoKED21	260	1	423	77
Polyurethane	240	1	422	81

ior was explained before). It is possible observe that keratin in polyurethane–dialyzed keratin membranes is integrated into the synthetic polymer and promotes a second degradation large stage. Table 3 presents information related with the thermogravimetric analysis of the membranes. The results corroborate the different thermal behavior due to the grafting of two polymers, the synthetic polyurethane and biological protein (keratin).

3.4 DSC

Figure 10 shows the curves obtained in Differential Scanning Calorimetry (DSC) for polyurethane–keratin salt membranes. The influence of keratin and its concentration into synthesized polyurethane hybrid materials is evident. The curves of polyurethane–keratin salt membranes show endothermic events. The first peak corresponds to the dissociation of short and long hard segment domains [41] at 50°C, for polyurethane, and $40 < T < 52$°C to polyurethane keratin salt membranes. Also, the melting of urea at 133°C and decomposition of urea at 183–200°C for polyurethane–keratin salt membranes are presented [42]. The most abundant product in the degradation stage is carbon dioxide [40, 43], its production can be observed at $338 < T < 342$°C for both polyurethane and polyurethane–keratin salt membranes. At 397°C, a dehydration process occurs, due to high quantities of oxygen for both polyurethane and polyurethane–keratin salt membranes. The components formed at previous steps are burned at 521°C for polyurethane and $522 < T < 539$°C to polyurethane–keratin salt membranes [40]. Grassie et al. [44] proposed a mechanism based on purely hard segment, where urethane groups first undergo depolycondensation, resulting in individual monomers, which further react to produce carbon dioxide, followed by the subsequent reaction of these monomers to form volatile products and a dehydration reactions promote char yield (500–600°C).

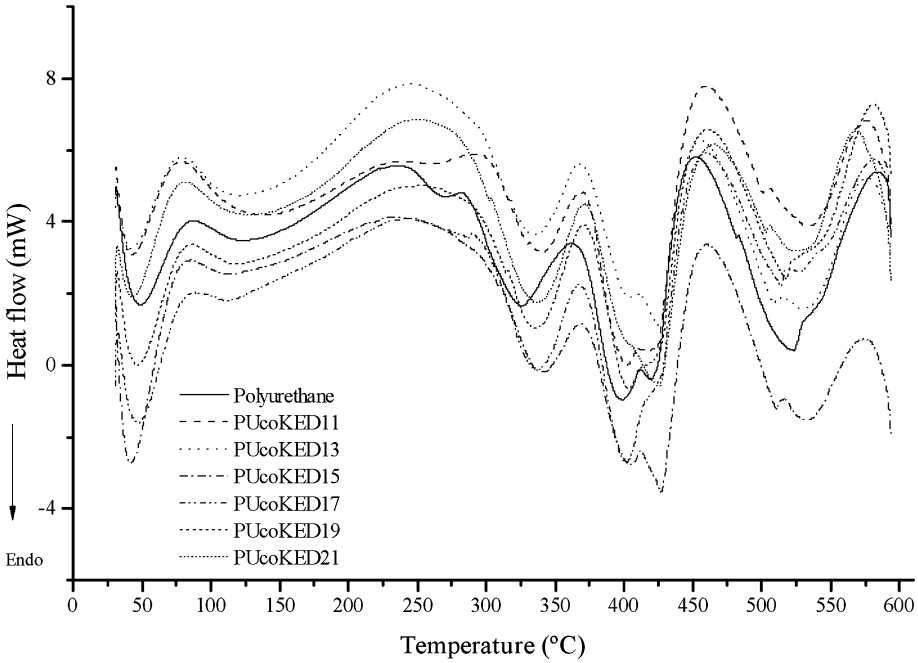

Fig. 11 DSC curves of polyurethane–dialyzed keratin membranes at different concentrations

Figure 11 shows DSC curves for polyurethane-dialyzed keratin membranes. In these thermograms, it can be observed endothermic peaks (as well as for polyurethane–keratin salt membranes). The first transition related with dissociation of short and long hard segments domains is presented from 42 to 48°C. This thermal behavior is a little different from the behavior observed at Fig. 10. The changes between both thermograms are due to urea is extracted from keratin salt solution during dialysis process and the presence of protein take part in thermal transitions at polyurethane–dialyzed keratin membranes. Also, removal of urea was confirmed due to the peak of degradation of urea at $133 < T < 200$°C (melting and decomposition of urea) is not present in Fig. 11. Dialyzed keratin solution and the type of polyol used in these membranes also bring about a complex thermal behavior; DSC curves shown a pair of endothermic peaks related with dehydration process at $402 < T < 426$°C and the other related with char products at $510 < T < 533$°C [40, 43]. It possibly suggests that maybe a homogeneous graft copolymer is formed with dialyzed keratin, inasmuch as all endothermic peaks coincide in temperature. This effect is not presented in polyurethane keratin-salt membranes.

4 Conclusions

A series of graft copolymer polyurethane–keratin membranes were synthesized. Protein into the structure of polyurethane causes cells and an opening of cell size due to the presence of water, amino, and carboxylic groups from the keratin solutions (salt and dialyzed). This produces so novel hybrid membranes formed of synthetic and natural polymers.

According to the characterization by FTIR spectroscopy, two different types of membranes are developed. Polyurethane–keratin salt membranes present groups and bonds that are not found in polyurethane–dialyzed keratin membranes. The presence of a high amount of NH and COOH as well as aliphatic and aromatic groups from proteins plays a key role on the graft linkage. The incorporation of dialyzed keratin into PU brings about an increase in thermal stability of these materials. The presence of keratin salt solution decreases thermal degradation of the grafted polymer observed in TGA analysis. These materials present different thermal transition observed in DSC. The different endothermic peaks obtained by this technique corroborate that not only there exist urea linkages to polyurethane matrix, but also there are other interactions of amino and carboxylic bonds to the synthetic polymer from amino acids of protein when it was dialyzed.

The results show that a synthetic polyurethane can be joined to a natural protein due to similar peptide and urethane bonds and functional groups. In addition, the protein in PU generates possible reactive sites from amino acids and increases their probable uses. Polyurethane–keratin membranes synthesized from a waste like chicken feathers can be used to remove toxic residues or pollutants from waters, air, and sludge. Inasmuch as keratin protein extracted from chicken feathers has been studied as a new biosorbent material to remove heavy metals from wastewater [26, 45, 46]. Thus, these membranes can be applied in this context, allowing getting a functional material with reactive sites found in keratin. Therefore, a complete understanding on how keratin

affects polyurethane characteristics is needed and reported here as the principal aim of this article.

Acknowledgements The authors are grateful to Ms. Alicia del Real-López for her assistance in SEM, to Dr. Genoveva Hernández-Padron for IR analysis, and Dr. Susana Hernandez-Lopez for her technical assistance in the thermal analysis. Also, V. Saucedo-Rivalcoba gives thanks to Consejo Nacional de Ciencia y Tecnologia (CONACyT), Mexico, for the financial support through the Ph.D. scholarship. A.L. Martinez-Hernandez thanks the economical support of LOREAL-Mexico under the program "*For Women in Science*" and DGEST Mexico.

References

1. A.L. Martínez-Hernández, C. Velasco Santos, M. de Icaza, V.M. Castaño, Compos. Part B Eng. **38**, 405 (2007)
2. M. Feughelman, Keratin, in *Encyclopedia of Polymer Science and Engineering*, vol. 8, ed. by H. Mark, N. Bikales, C. Overberger, C. Menges, J.I. Kroschwitz (Wiley, New York, 1987)
3. E.H. Mercer, *Keratin and Keratinization, an Essay in Molecular Biology* (Pergamon, Oxford, 1961)
4. A.L. Martínez-Hernández, A.L. Santiago-Valtierra, M.J. Alvarez-Ponce, Mater. Res. Innov. **12**, 184 (2008)
5. S.A. Sayed, S.S. Saleh, E.E. Hasan, Desalinaton **181**, 243 (2005)
6. F.A. Banat, S. Al-Asheh, Environ. Eng. Policy **2**, 85 (2000)
7. M. Tsukada, H. Shiozaki, G. Freddi, J.S. Crighton, J. Appl. Polym. Sci. **64**, 343 (1997)
8. G. Freddi, M. Tsukada, H. Shiosaki, J. Appl. Polym. Sci. **71**, 1563 (1999)
9. M. Kruppa, D. Frank, H. Leffler-Schuster, B. König, Inorg. Chim. Acta **359**, 1159 (2006)
10. E. Farkas, I. Sóvágó, Metal complexes of amino acids and peptides, in *Amino Acids, Peptides and Proteins*, vol. 33, ed. by G.C. Barrett, J.S. Davies (Royal Society of Chemistry Publishing, Cambridge, 2002)
11. S. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, Water Res. **33**, 2469 (1999)
12. S.M.C. Ritchie, L.G. Bachas, T. Olin, S.K. Sikdar, D. Bhattacharyya, Lagmuir **15**, 6346 (1999)
13. K.M. Zia, M. Barikani, I.A. Bhatti, M. Zuber, H.N. Bhatti, J. Appl. Polym. Sci. **110**, 769 (2008)
14. C. Ciobanu, M. Ungureanu, L. Ignat, D.D. Ungureanu, V.I. Popa, Ind. Crops Prod. **20**, 231 (2004)
15. H. Tian, Y. Wang, L. Zhang, C. Quan, X. Zhang, Ind. Crops Prod. **32**, 13 (2010)
16. W. Wang, Y. Guo, J.U. Otaigbe, Polymer **51**, 5448 (2010)
17. J. Liu, D. Ma, Z. Li, Eur. Polym. J. **38**, 661 (2002)
18. A.K. Mishra, D.K. Chattopadhyay, B. Sreedhar, K.V.S.N. Raju, J. Appl. Polym. Sci. **102**, 3158 (2006)
19. S. Zhang, Z. Ren, S. He, Y. Zhu, C. Zhu, Spectrochim. Acta A **66**, 188 (2007)
20. T.L. Wang, T.H. Hsieh, Polym. Degrad. Stab. **55**, 95 (1997)
21. G. Ciobanu, G. Carja, O. Ciobanu, Desalination **222**, 197 (2008)
22. K. Rzeszutek, A. Chow, J. Membr. Sci. **181**, 265 (2001)
23. S. Das, A.K. Banthia, B. Adhikari, Chem. Eng. J. **138**, 215 (2008)
24. A.L. Santiago-Valtierra, Utilización de un residuo avícola para generar materiales de queratina aplicados a la eliminación de cromo VI como contaminante en el agua. Master Degree Thesis, Instituto Tecnológico de Aguascalientes, México, Junio 2005 (in Spanish)
25. W.F. Schmidt, Innovative feather utilization strategies, in *Proceedings of the 1998 National Poultry Waste Management Symposium*, Springdale, USA (1998)
26. P.M.M. Schrooyen, P.J. Dijkstra, R.C. Oberthür, A. Bantajes, J. Feijen, J. Agric. Food Chem. **48**, 4326 (2000)
27. P.M.M. Schrooyen, P.J. Dijkstra, R.C. Oberthür, A. Bantajes, J. Feijen, J. Agric. Food Chem. **49**, 221 (2001)
28. A. Aneja, Structure-property relationships of flexible polyurethane foams. PhD Thesis, Department of Chemical Engineering, Virginia Polytechnic Institute and State University, USA (2005)
29. F.M.B. Coutinho, M.C. Delpech, Polym. Degrad. Stab. **70**, 49 (2000)
30. P.S. Wang, W.Y. Chiu, L.W. Chen, B.L. Denq, T.M. Don, Y.S. Chiu, Polym. Degrad. Stab. **66**, 307 (1999)
31. B. Ravat, R. Gschwind, M. Grivet, E. Duverger, A. Chambaudet, L. Makovicka, Nucl. Instrum. Methods B **160**, 499 (2000)
32. A.L. Martínez-Hernández, C. Velasco-Santos, M. de Icaza, V.M. Castaño, e-Polymers, No. 016 (2003)
33. A.M. Issam, Eur. Polym. J. **43**, 214 (2007)
34. B.F. d'Arlas, L. Rueda, P.M. Stefani, K. de la Caba, I. Mondragón, A. Eceiza, Thermochim. Acta **459**, 94 (2007)
35. E.A. Moawed, Anal. Chim. Acta **580**, 263 (2006)
36. M. Jackson, H.H. Mantsch, Crit. Rev. Biochem. Mol. **30**, 95 (1995)
37. A.L. Martínez-Hernández, C. Velasco Santos, M. de Icaza, V.M. Castaño, Int. J. Environ. Pollut. **23**, 162 (2005)
38. C.R. Jacob, S. Luber, M. Reiher, J. Phys. Chem. B **113**, 6558 (2009)
39. H.G.M. Edwards, D.E. Hunt, M.G. Sibley, Spectrochim. Acta A **54**, 745 (1998)
40. M. Herrera, G. Matuschek, A. Kettrup, Polym. Degrad. Stab. **78**, 323 (2002)
41. D. Sarkar, J.-C. Yang, A.S. Gupta, S.T. Lopina, J. Biomed. Mater. Res. A **90**, 263 (2009)
42. A. Lundström, B. Andersson, L. Olsson, Chem. Eng. J. **150**, 544 (2009)
43. N. Yoshitake, M. Furukawa, J. Anal. Appl. Pyrolysis **33**, 269 (1995)
44. N. Grassie, M. Zulfiqar, J. Polym. Sci. Polym. Chem. **16**, 1563 (1978)
45. G. de la Rosa, H.E. Reynel-Avila, A. Bonilla-Petriciolet, I. Cano-Rodríguez, C. Velasco-Santos, A.L. Martínez-Hernández, Int. J. Chem. Biol. Eng. **1**, 185 (2008)
46. V. Saucedo-Rivalcoba, A.L. Martínez-Hernández, G. Martínez-Barrera, C. Velasco-Santos, J.L. Rivera-Armenta, V.M. Castaño, Water Air Soil Pollut. (2010). doi:10.1007/s11270-010-0668-6