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Polydimethylsiloxane Modified Chitosan IV. Preparation and Characterization of Porous Hybrid Membranes

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Polydimethylsiloxane Modified Chitosan IV. Preparation and Characterization of Porous Hybrid Membranes

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This paper deals with the synthesis of organic-inorganic hybrid membranes prepared by modified chitosan with epoxy terminated polydimethylsiloxane and γ–glycidoxypropyltrimetoxysilane as cross-linking agents. The transformation of amino groups of chitosan through the reaction with epoxy groups was confirmed by FT-IR analysis. As proved by electron and atomic force microscopy, the hybrid membrane are phase segregated materials with spherical domains of silica core covered by hydrophobic siloxane in a hydrophilic chitosan matrix. The water contact angles of hybrid membranes (85°–96°) and pure chitosan membranes (72°) indicated a lower hydrophilic character of modified chitosan. As a result of the crosslinking and of increased hydrophobicity, the hybrid membranes were characterized by a smaller water swelling degree (about 30%) as compared to pure chitosan membrane (700%). However, the presence of the pores in hybrid membranes determined an increase of the water adsorption (maximum swelling degree, about 200%). The hybrid membranes possess a higher thermal stability as compared to chitosan, but a lower one as compared to polydimethylsiloxane.

Keywords: chitosan, γ-glycidoxypropyltrimetoxysilane, polydimethylsiloxane, organic-inorganic hybrids

1 Introduction

In separation technology and replacing medicine, the *renewable native polymers* such as chitin -(poly[β-(1–4)-2-acetamido-2-deoxy-D-glucopyranose]) are continually of great interest because its nontoxicity, biodegradability, commercially availability and, easiness of modification of hydroxyl and deacetylated amino groups. This is why the need of chitin/chitosan-based derivatives, micro- and macroporous films, membranes and scaffolds with advanced functionality and morphology are constantly growing.

Chitin, a naturally occurring polysaccharide, is found in the shells of crustaceans such as crab and shrimp, the cuticles of insects, and the cell walls of fungi. It is the second most abundant organic resource next to cellulose on Earth. Deacetylation of chitin with a degree of deacetylation more than 50% gives chitosan, (poly[β-(1–4)-2-amino-2-deoxy-D-glucopyranose]), which is soluble in organic acids such as acetic or formic acid, and it has been more widely used than chitin as films (1–3), membranes (4, 5), fibers (6, 7) and particles (8, 9). Chitosan, as a functional material, offers a special set of characteristics: biocompatibility, biodegradability, and anti-bacterial properties. Chemical modification of chitosan through graft copolymerization has shown to be a promising method for the preparation of new materials, which enables to introduce special properties into these abundant biopolymers and enlarge their fields of potential applications (10, 11).

The polysiloxane displays a unique combination of characteristics which includes high flexibility of the siloxane backbone, low glass transition temperature, thermal stability, and hydrophobicity (12, 13). It is widely used in medical applications owing to its biocompatibility, high oxygen permeability, good oxidative stability (14). Kim et al. (2002) prepared pH-sensitive hydrogels by the crosslinking of chitosan with epoxy-terminated polydimethylsiloxane using the UV irradiation technique (10). Another research group obtained graft copolymers by the condensation of the amino groups of chitosan with carboxylic functionalities of poly(ethylene glycol)-polydimethylsiloxane copolymers and investigated the swelling mechanism of the resulting copolymers (14). Similar approaches have been also reported by Shin et al. (2002) on semi-interpenetrating polymer network hydrogels prepared by crosslinking poly(vinyl alcohol)-polydimethylsiloxane copolymers with chitosan under UV irradiation (15). These photocrosslinked hydrogels exhibited equilibrium water content (EWC) in the range of 65–95%. In addition, polysiloxanes may lead to surface

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modifications, due to their surface energy lower than most of other materials. The incorporation of polyorganosiloxane as "soft" segments into chitosan can improve its physical and mechanical properties for practical uses.

Previously we reported the preparation of graft and crosslinked poydimethylsiloxane-chitosan copolymers (16) and their ability to complex divalent metal cations (17). This paper deals with the synthesis of organic-inorganic hybrid membranes obtained by simultaneous grafting and crosslinking of chitosan with mono epoxy-terminated polydimethylsiloxane and γ–glycidoxypropyltrimethoxysilane which were than treated with calcium chloride. The chemical structure of the crosslinked materials was elucidated by FT-IR spectroscopy. The swelling behavior, water contact angles, morphological and thermal properties were also investigated.

2 Experimental

2.1 Materials

Low molecular weight of chitosan, (CS), with a degree of deacetylation (DD) of 75–85%, was used as received (Aldrich). The precise value of the deacetylation degree was found to be about 80%, as determined from nitrogen content of the sample (8.23%). The intrinsic viscosity of CS sample was determined in 0.25 M acetic acid/0.25 M sodium acetate aqueous solution using an Ubbelohde viscometer, at 25°C. The viscosity molecular weight was found to be approximately 380 KDa by using the Mark-Houwink-Sakurada equation (MHS): $[\eta] = \mathrm{K} \times \mathrm{M}^{\alpha}$ where: $[\eta]$ is the intrinsic viscosity and the empirical constants for the MHS equation were: $k = 1.81 \times 10^{-3}$ (dl/g), $\alpha = 0.93$ (18). γ–Glycidoxypropyltrimetoxysilane (GP-TMS, 98%; Aldrich.), calcium chloride ($CaCl_2$, Aldrich) were used as received.

2.2 Synthesis

2.2.1. *Glycidoxypropyl-terminated PDMS (GP-PDMS)*

Epoxy-terminated PDMS was synthesized according to a procedure previous by described (19).

2.2.2. *Preparation of hybrid membranes*

The hybrid membranes were obtained by simultaneous grafting and crosslinking of chitosan with epoxy terminated polydimethylsiloxane and γ-glycidoxypropyltrimetoxysilane. The method is outlined as follows (Hy_1): chitosan was dissolved in 0.25 M acetic acid aqueous solution to attain a concentration of 2% (w/v). The solution was stirred at room temperature for 24 h, filtered to remove the insoluble material, and then treated in an ultrasonic bath for 20 min. Then, 0.5 g

γ–glycidoxypropyltrimethoxysilane (GP-TMS), 1 g epoxy-terminated PDMS (GP-PDMS) and 0.1 ml isopropyl alcohol were added to the chitosan solution. The reaction mixture was treated in an ultrasonic bath for 1 h and then let under stirring for 24 h. Half of the resulted solution was poured onto a polystyrene Petri dish and dried at 40°C for 48 h. The dry film was washed with deionized water and with acetone to remove any unreacted materials that were not incorporated into the film and dried at 40°C for 4 days under vacuum.

Elemental analysis (%): Hy_1 (Calculated: Si: 10.9; found: Si: 8.06); Hy_2 (Calculated: Si: 16.36; Found: Si: 15.98); Hy_3 (Calculated: Si:17.56; Found: Si: 17.03).

The hybrid membranes treated with $CaCl_2$(Hy_1Ca) were conducted as follows: half of the copolymer solution was mixed with $CaCl_2$(0.25 g), treated in an ultrasonic bath for 15 min and stirred for 2 h. The reaction mixture was poured into a glass mold and was dried at 40°C under vacuum up to 48 h. The membrane obtained was washed with acetone, and then washed with deionized water and dried at 40°C for 4 days under vacuum. The hybrid membranes (Hy_2, Hy_2Ca and Hy_3, Hy_3Ca) were obtained by the same procedure (Table 1).

Unmodified chitosan membranes (CS) was prepared in a similar manner by drying the chitosan solution prepared as described above in a glass Petri.

2.3 Measurements

Fourier transform infrared (FT-IR) spectra were obtained by using a Specord M 80 under dry air at room temperature on KBr pellets in the range of 4000–500 cm^{-1}.

Nitrogen content of CS and of hybrid materials was obtained on a Perkin-Elmer elemental analyzer.

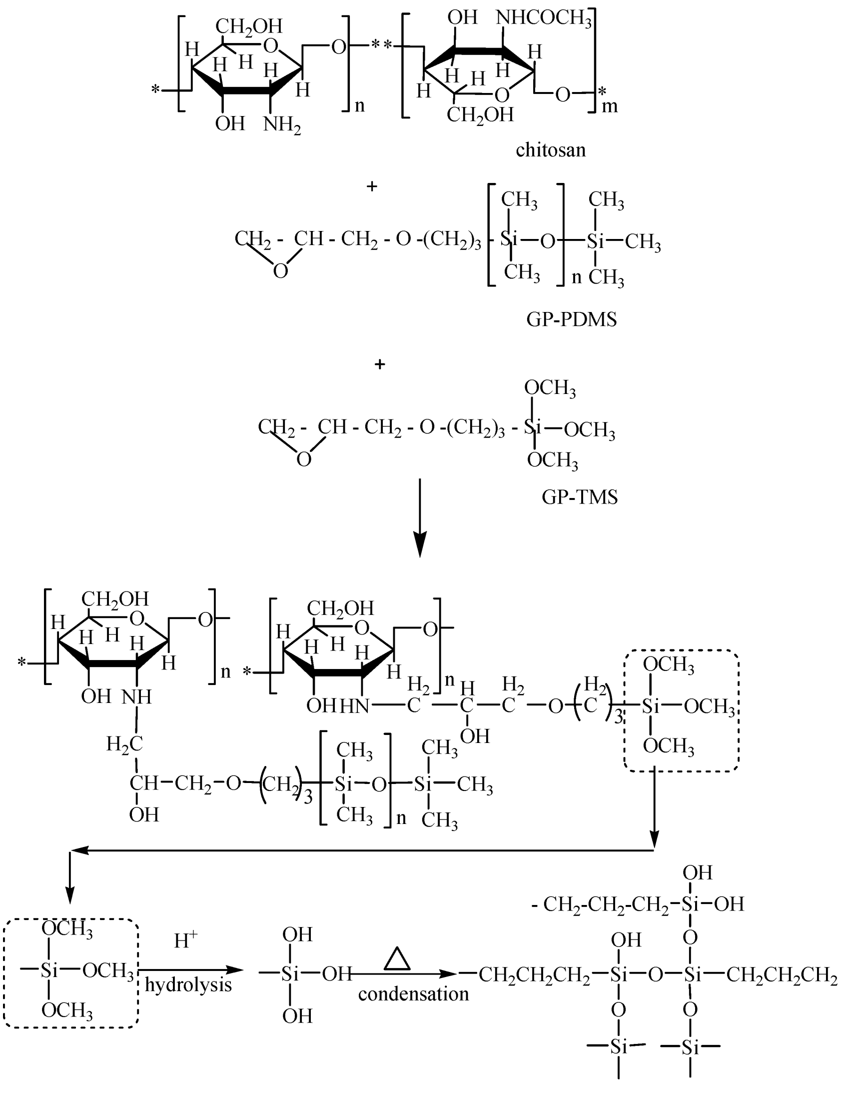
The surface morphology of membranes was investigated with a Tesla BS 301 scanning electron microscope (SEM) with an accelerating voltage of 10 KV and on a Solver PRO-M atomic force microscope (AFM). AFM measurements were done in air using the tapping mode and employing NSG10/Au Silicon cantilevers of typical force constant $K_N = 11.5$ N/m.

The membrane swelling behavior was determined by equilibrium swelling studies, according to a recently published procedure (20). The dried samples were cut into small pieces of 1 cm × 1 cm precisely weighed (mg) and

Table 1. Synthesis* of hybrid membranes

Sample	*Chitosan (g)*	*GP-PDMS (g)*	*GP-TMS (g)*	*$CaCl_2$ (g)*
CS	2	—	—	—
Hy_1	2	0.5	1	—
Hy_2	2	1	1.5	—
Hy_3	2	1	2	—
Hy_1Ca				0.25
Hy_2Ca				0.25
Hy_3Ca				0.25

*Synthesis conditions: 2 % w/v CS solution in 0.25 M aqueous acetic acid; isopropyl alcohol, 1% by weight against the sum of GP-PDMS and GP-TMS amount; at room temperature; duration, 24 h.



Sch. 1. Synthesis of hybrid membranes.

submerged into distilled water for different times at room temperature until equilibrium was reached. At each immersion interval, the swollen samples were removed from the water, excess water on surface with filler paper was wiped off and immediately weighed at room temperature on an electronic balance. The initial sample weight before immersion was recorded as W_d and the sample weight after each immersion interval was recorded as W_s. The percent swelling at equilibrium E_{sw} was calculated according to the swelling formula:

$$E_{SW}(\%) = (W_s - W_d)/W_d \times 100$$

The contact angle toward distilled water was measured with a Contact Angle Meter, at room temperature by the sessile drop method (21).

Themogravimetric analysis (TGA) was conducted with a Q-1500 D, MOM Budapest derivatograph system at the heating rate of 10°C/min under air atmosphere.

3 Results and Discussion

3.1 Membrane Synthesis

Hydrophobically modified CS was prepared by simultaneous grafting and crosslinking of CS with GP-PDMS and GP-TMS according to Scheme 1. Three different compositions of copolymers were prepared as shown in Table 1. It is well known that the primary amine groups quickly undergo nucleophilic substitution with epoxy rings. In a first step, secondary amino groups are formed; they further undergo a second substitution yielding tertiary amines. The reaction of amine groups of CS with epoxy rings linked to siloxane or silane moieties is quite difficult due to the very different solubility parameters of the mentioned reaction partners. In fact, the reaction takes place in a heterogeneous system, at the interface between CS aqueous solution and oil siloxane phase. However, in the mentioned reaction conditions, about two thirds of the GP-PDMS/GP-TMS mixture was linked to CS, according to silicon elemental analysis of the sample.

3.2 Membrane Structure

The chemical structure of hybrid membranes was proved by FT-IR analysis. The FT-IR spectrum (Figure 1) presents the characteristic absorption of both precursors. Figure 1 shows the basic characteristics of chitosan at: 3429 cm^{-1} (O-H stretch), 2924 cm^{-1} (C-H stretch), 1596 cm^{-1} (N-H bend), 1157 cm^{-1} (bridge-O-stretch), and 1087 cm^{-1}(C-O stretch) (22). The strong peak around 3429 cm^{-1} could be assigned to the axial stretching vibration of O-H superposed to the N-H stretching band, and inter hydrogen bonds of the polysaccharide. Following the chemical modification of chitosan primary amine groups through their reaction with GP-PDMS and GPTMS epoxy rings, the absorption band at 1596 cm^{-1}(NH bending of the primary amine salt) (Figure 1. CS) is moved to 1557 cm^{-1} (Figure 1. Hy$_1$). The $\nu_{C-O-C,}\nu_{simC-OH,}and\nu_{asC-OH}$ bands appearing at 1157, 1087, 1026 cm^{-1} in CS are superposed on $\nu_{Si-O-Si}$ strong band in membranes. IR spectrum also evidenced Si-CH$_3$ characteristic bands at 1259 and 797 cm^{-1} from siloxane chain. Chitosan forms amino groups-Ca^{2+} complexes according to Yamaguchi et al. (23). The hybrid with CaCl$_2$ showed a different FT-IR peak profile (in the 1600–1400 cm^{-1}region of amino groups) from the hybrid without CaCl$_2$.

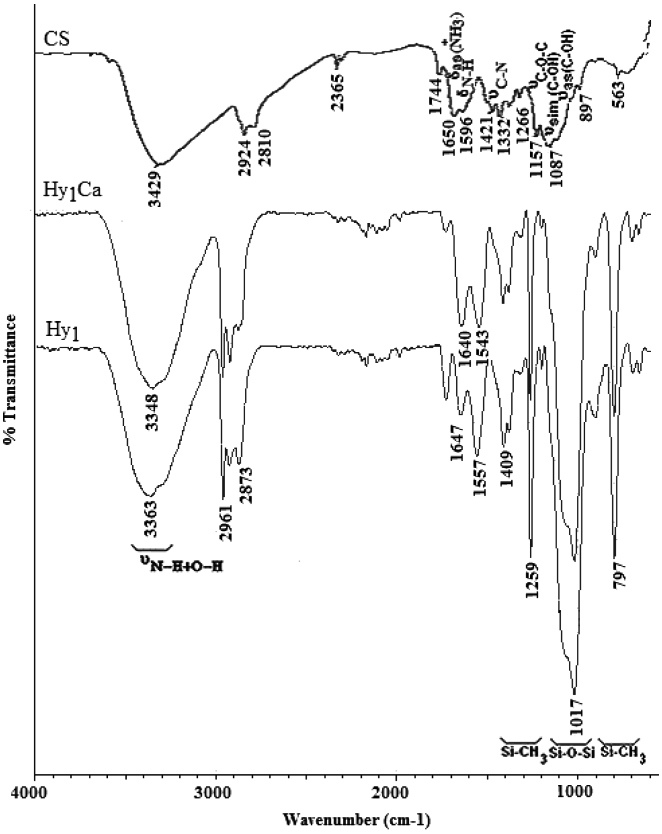


Fig. 1. FT-IR spectra of chitosan, hybrid membranes and hybrid membranes treated with CaCl$_2$.

3.3 Surface Morphology

The prepared non-porous and porous hybrid membranes are three-component systems containing chitosan, polydimethylsiloxane (PDMS) and silica. Silica was *in situ* generated and should form tight domains distributed in a phase segregated crosslinked copolymer matrix, owing the strong difference in the solubilities of chitosan (soluble in acidic water) and PDMS (soluble in non-polar solvents).

To observe morphological properties such as surface porosity, texture and roughness, SEM e and AFM micrographs of pure chitosan membranes and hybrid membranes were registered (Figures 2 and 3).

3.4 Scanning Electron Microscopy (SEM)

The SEM observations of native chitosan revealed a uniform and dense surface microstructure (Figure 2a). The structure of CS was totally modified in the crosslinked materials, wherein distinct morphological differences were discernible in their surface topography. The hybrid membrane not treated with calcium chloride (Figures 2b, 2d, and 2g) showed spherical domains of silica core covered by hydrophobic siloxane in hydrophilic chitosan matrix, a normal disposal of hydrophobic-hydrophilic segments considering the polar character of the separation medium (water-acetic acid solution). The membranes obtained in the presence of CaCl$_2$ (Figure. 2c, 2e and 2h) present a porous structure with pore dimensions depending on membrane composition.

3.5 Atomic Force Microscopy (AFM)

Tapping mode AFM images yielded information about the surface features of the unmodified CS membrane and of the hybrid membranes at three different concentration (Hy$_1$, Hy$_2$, Hy$_3$) (Figs. 3a, 3e, 3i and 3m). The roughness of the surface, S$_{a,}$measured on scanning areas of 5.00 × 5.00 μm^2 indicated values of 2.99 and 2.32, 2.24, 0.638 nm for pure CS and Hy$_1$, Hy$_2$, Hy$_3$membranes, respectively. The roughness of the surface (S$_a$) decrease with the increase concentration of siloxane sequence. The height profiles (Figs. 3c, 3g, 3k and 3o) generated along the horizontal lines (Figs. 3a, 3e, 3i, 3m) indicate a more compact structure of CS membranes and a nanoporous structure of hybrid membranes. The difference between CS and hybrid membranes can be also seen in 3D images (Figs. 3b, 3f, 3j and 3n). The highest majority of height population is situated around 14 and 10, 35, 7 nm for CS and Hy$_1$, Hy$_2$ and Hy$_3$ membranes, respectively (Figures 3d, 3h, 3e and 3p). No reliable results in AFM experiments were obtained on hybrid membranes treated with CaCl$_2$.

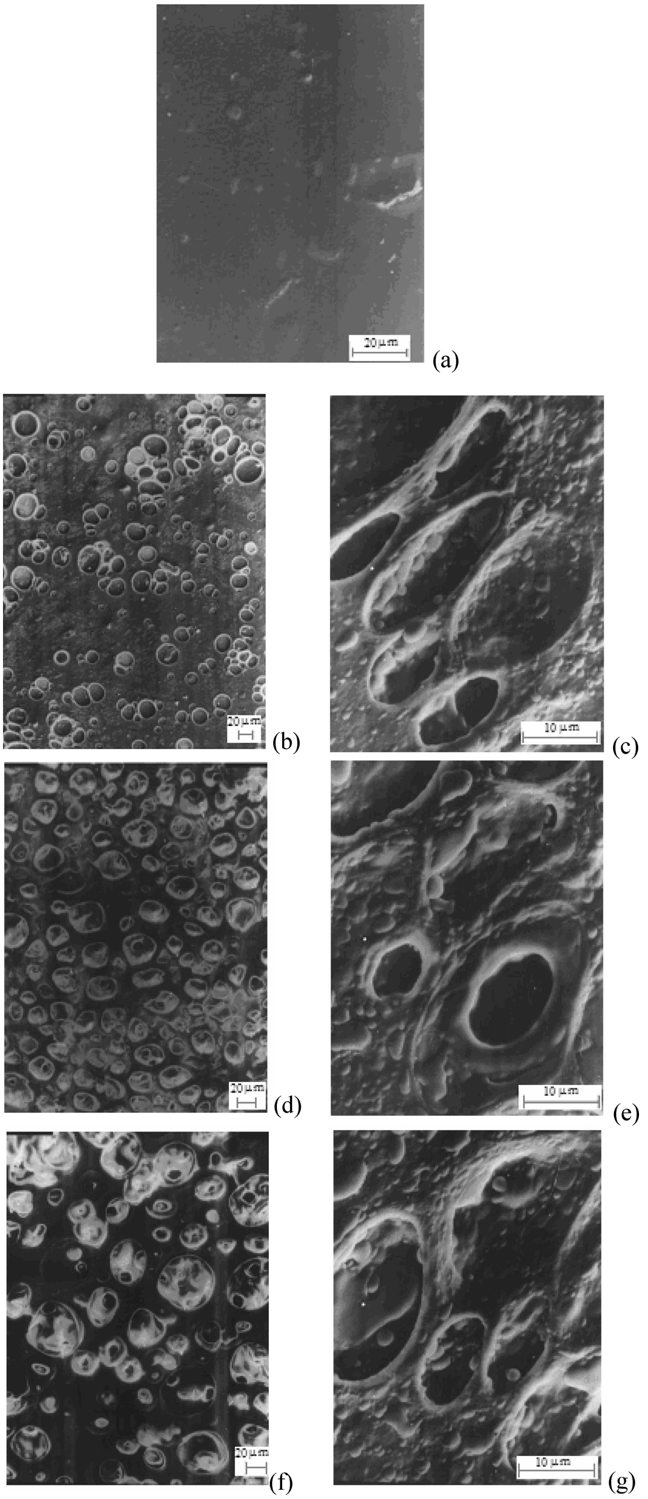


Fig. 2. Scanning electron micrographs (SEM) of (a), CS; (b), Hy$_1$; (d), Hy$_2$; (g), Hy$_3$and (c), Hy$_1$Ca; (e), Hy$_2$Ca; (h), Hy$_3$Ca.

3.6 Swelling Behavior

The degree of swelling of pure chitosan membrane and hybrid membranes was calculated by applying conventional swelling formula (Figures 4a and 4b). The unmodified CS membrane (Figure 4a) achieved equilibrium after immersion about 6–7 h in distillate water and the maximum degree of swelling was about 700%. The hybrid membranes reached the equilibrium much easier, after immersion for 10 min in distillate water (Figure 4b) in the case of Hy$_3$ and 20 min for Hy$_1$, Hy$_2$, demonstrating the disturbing of the tight, more ordered package of the pure biopolymer, but the maximum degree of swelling was low (about 30%). The curves corresponding to the porous membranes obtained in the presence of CaCl$_2$showed a maximum degree of swelling as high as 200 %, more than six times higher as compared to that corresponding to non-porous hybrid membrane, due to the presence of the pores.

The lower maximum degree of swelling for all hybrid membranes as compared to chitosan is the effect of crosslinking and enhanced surface hydrophobicity of the materials. PDMS acts both as a crosslinker and as a surface modifier for chitosan and the obtained materials could be good candidates in applications that require more hydrophobic surfaces.

3.7 Surface Characterization

3.7.1. *Contact angle*

The surface properties of the pure chitosan, the hybrid membranes and hybrid membranes treated with CaCl$_2$were investigated by contact angle analysis. To compare the wettability of hybrid membranes to the unmodified CS membrane, contact angle (θ) between samples surface and water were measured in air using the sessile drop method (Table 2). Water was carefully dropped on films and contact angles were quickly determinate before the membranes start to swell. The reported values are the average of three different measurements. The water contact angle of the unmodified CS membrane was: 72°±2°, which is significantly lower than those of the hybrid membrane ranging from 85° to 96°, meaning that incorporation of PDMS rendered the surface less water wettable. The decrease in the contact angle with

Table 2. Water contact angle of pure chitosan, hybrid membranes and hybrid membranes treated with CaCl$_2$

Sample	*Contact angle (degree)*
CS	72°± 2°
Hy$_1$	85°± 1°
Hy$_2$	82°± 4°
Hy$_3$	96°± 1°
Hy$_1$Ca	65°± 1°
Hy$_2$Ca	67°± 2°
Hy$_3$Ca	68°± 1°

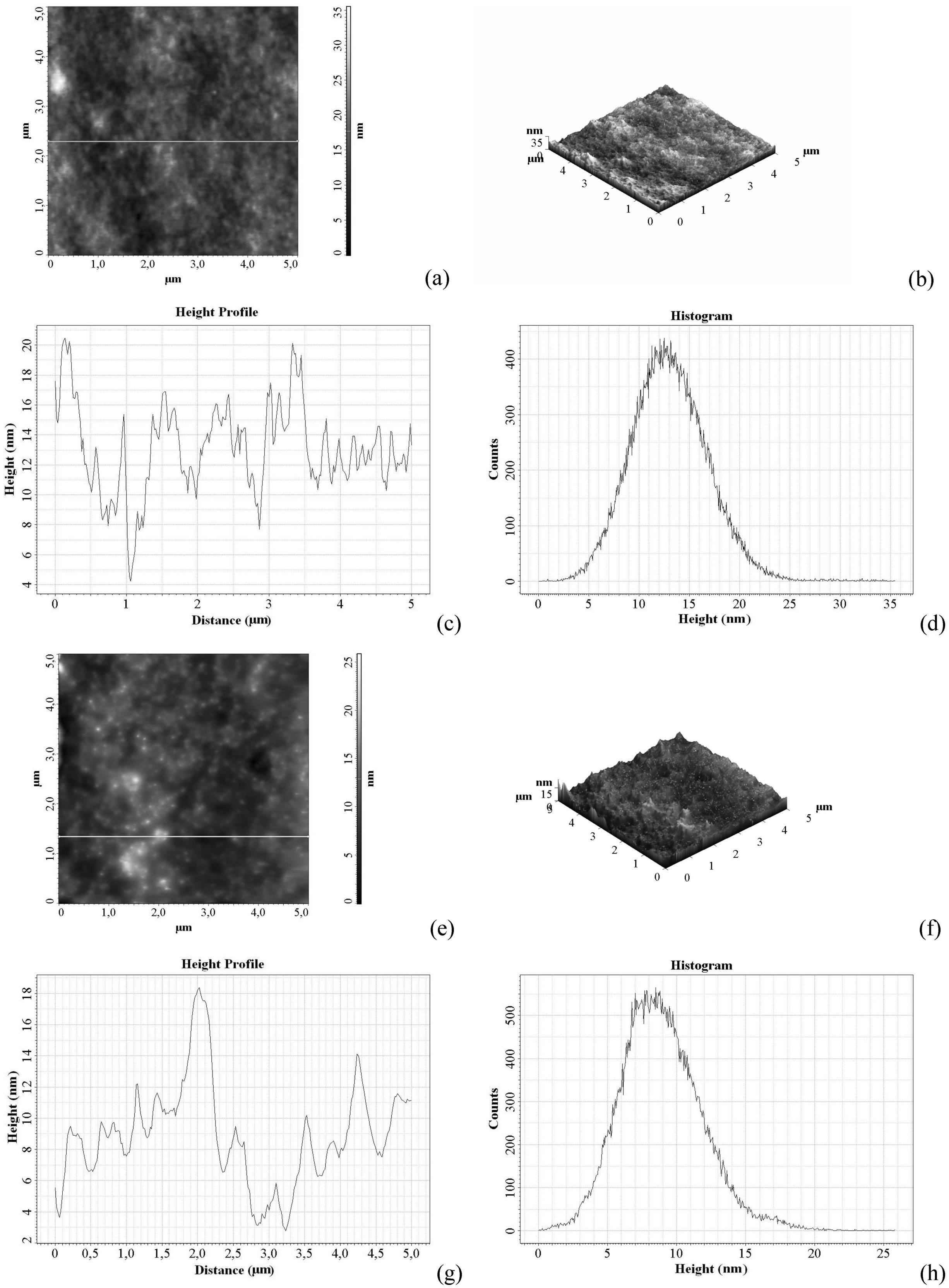


Fig. 3. AFM topographic images of samples surface: two-dimensional images (2D) of (a), CS and (e), Hy$_1$; (i), Hy$_2$; (m), Hy$_3$; three-dimensional images (3D) of (b), CS and (f), Hy$_1$; (j), Hy$_2$; (n) Hy$_3$; the height profile for (c), CS and (g), Hy$_1$; (k), Hy$_2$; (o) Hy$_3$; the height histograms for (d), CS and (h), Hy$_1$; (e), Hy$_2$; (p) Hy$_3$. (Continued)

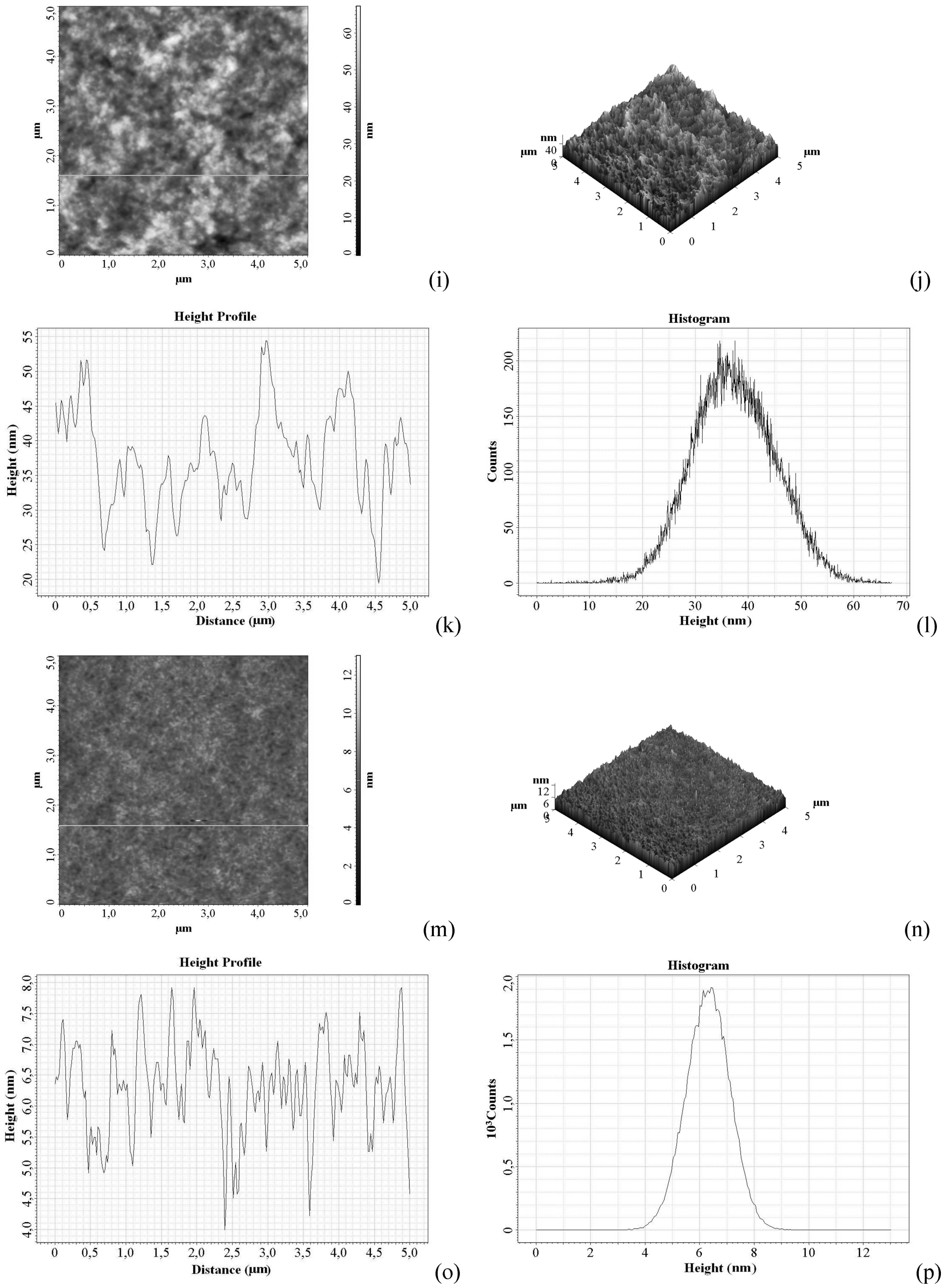
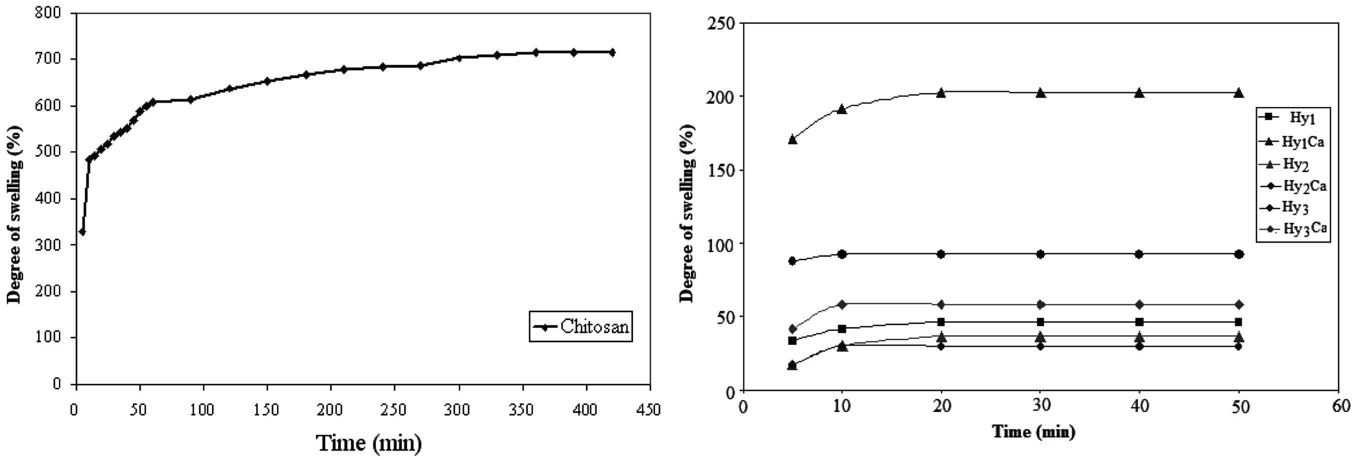


Fig. 3. (Continued)



(a) (b)

Fig. 4. Swelling behavior of (a), pure CS and (b) hybrid membranes and hybrid membranes treated with $CaCl_2$.

the addition of $CaCl_2$ to the hybrid indicates that the incorporation of Ca (II) into the crosslinked polysaccharide can effectively improving the wettability of hybrids.

3.7.2. *Thermal stability*

The thermal stability of the pure chitosan, the hybrid membranes and hybrid membranes treated with $CaCl_2$was evaluated by thermogravimetric (TGA) analysis under air atmosphere. The weight loss with a temperature under 100°C was attributed to the evaporation of absorbed water. Taking the temperature at various % weight losses (T_d) to evaluate the thermal stability of the hybrid materials, it can be seen from Table 3 (TG curves in Figure 5) that the hybrids exhibited better thermal stability than the pure chitosan membrane. The increase in the thermal stability of modified CS samples can be attributed to the high thermal stability of siloxane phase and to the protection of CS domains.

4 Conclusions

Novel chitosan-inorganic hybrids were synthesized by using epoxy terminated polydimethylsiloxane and $\gamma-$glycidoxypropyltrimetoxysilane as cross-linking agent. Fourier transform infrared analysis confirmed that interaction were present between the amino groups of chitosan

Table 3. TGA analysis of pure chitosan, hybrid membranes and hybrid membranes treated with $CaCl_2$

	Temperature (°C) for various % decompositions					
Sample	*5 %*	*10 %*	*20 %*	*30 %*	*40 %*	*50 %*
CS	110	140	210	250	270	310
Hy_1	120	135	260	295	330	410
Hy_2	120	170	265	300	355	435
Hy_3	125	170	270	300	360	440
Hy_1Ca	120	150	245	250	305	410
Hy_2Ca	115	175	245	260	335	485
Hy_3Ca	115	175	245	270	335	455

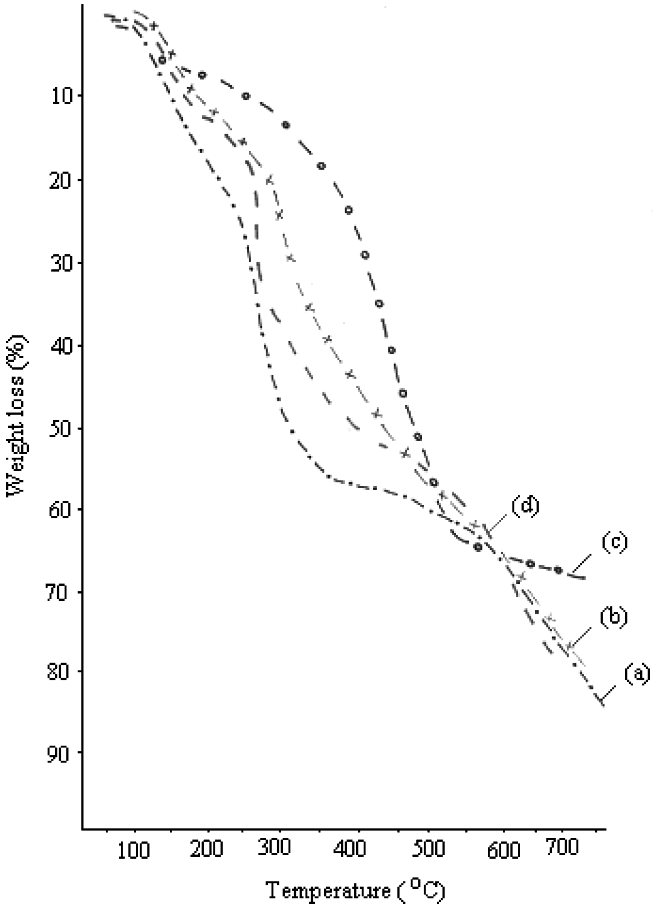


Fig. 5. ATG thermograms obtained under air atmosphere at a heating rate of 10°C/min: (a), CS (b), Hy_1; (c), GP-PDMS; (d) Hy_1Ca.

and epoxy groups. Scanning electron microscopy (SEM) observations indicated that the non-porous membrane is a phase segregated material with spherical domains of silica core covered by hydrophobic siloxane in a hydrophilic chitosan matrix, while the hybrid membranes obtained in the presence of $CaCl_2$ present irregular pores. Atomic force microscopy (AFM) studies, revealed that chitosan membranes are relatively smooth and homogeneous, while the hybrid membranes present nanoporous structure. The hybrid membranes were characterized by an expected reducing of water sorption ability due to both the crosslinked structure and the increased hydrophobicity induced by the siloxane grafts. As expected from the low surface tension of siloxane polymers, the modification of chitosan with polysiloxane enhances the surface hydrophobicity of the materials, as indicated by the increase of water contact angles. Higher thermal decomposition temperatures of hybrid membranes as compared to pure chitosan were evidenced by thermogravimetric analysis.

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