Carbohydrate Polymers 76 (2009) 268–278

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Polydimethylsiloxane modified chitosan. Part III: Preparation and characterization of hybrid membranes

Daniela Enescu [a,b,1], Viorica Hamciuc [b], Rodinel Ardeleanu [b], Mariana Cristea [b,1], Aurelia Ioanid [b], Valeria Harabagiu [b,*,1], Bogdan C. Simionescu [a,b,1]

[a] Departament of Macromolecules, "Gh. Asachi" Technical University, 700050 Iasi, Romania
[b] "Petru Poni" Institute of Macromolecular Chemistry, Department of Inorganic Polymers, 41A Aleea Grigore Ghica Voda, 700487 Iasi, Romania

ARTICLE INFO

Article history:
Received 5 March 2008
Received in revised form 20 September 2008
Accepted 20 October 2008
Available online 6 November 2008

Keywords:
Chitosan
Polydimethylsiloxane
γ-Glycidoxypropyltrimethoxysilane
Organic–inorganic hybrid

ABSTRACT

The paper deals with the synthesis of organic–inorganic hybrid membranes, Hy, obtained by simultaneous grafting and crosslinking of chitosan with epoxy-terminated polydimethylsiloxane and γ-glycidoxypropyltrimethoxysilane. Porous membranes, HyP, were also obtained by acid decomposition, at different temperatures (25 and 50 °C), of calcium carbonate porogenic agent trapped inside the material. As proved by electron and atomic force microscopy, the non-porous membrane is a phase segregated material with spherical domains (10–40 μm) of silica core covered by hydrophobic siloxane in a hydrophilic chitosan matrix. The porous membranes showed different morphologies with irregular circular pores of 10–30 μm diameters for the membranes obtained at lower temperature, while the membranes prepared at 50 °C tend to adopt a plan-parallel porosity. The water contact angles of hybrid membranes (78°) 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 HyP membranes determined an increase of the water adsorption (maximum swelling degree, about 100%). The hybrid membranes possess a slightly higher thermal stability as compared to chitosan (first initial decomposition temperature, 147 and 175 °C for chitosan and hybrid membranes, respectively), but a lower one as compared to pure polydimethylsiloxane. The high storage modulus of chitosan (about 5.1×10^9 Pa at 20 °C) is decreased by about one order of magnitude by the introduction of the highly flexible polysiloxane and the hybrid membranes are more flexible.

1. Introduction

Natural polymers (polysaccharides, proteins and their derivatives) represent a promising alternative as biodegradable and renewable materials having in mind the increased environmental constraints and the strong requirements for an economy independent on fossil resources (Arvanityannis, 1999; Krochta & De Mulder-Johnston, 1997). Among them, chitosan (poly[β-(1-4)-2-amino-2-deoxy-D-glucopyranose]) is one of the most studied materials for use in drug delivery systems (Park, You, Park, Haam, & Kim, 2001; Hu, Li, Wang, & Shen, 2004; Peniche, Feranadez, Gallardo, Lopez-Barvo, & Roman, 2003), as membranes for ultrafiltration, pervaporation and reverse osmosis (Chanachai et al., 2000; Ge, Cui, Yan, & Jiang, 2000) or as solid polyelectrolytes (Gandini, Hariri, & Nest, 2003; Wan, Creber, Peppley, & Bui, 2003) and surfactants (Ngimhuang, Furukawa, Satoh, Furuike, & Sakairi, 2004). It is a nontoxic, biodegradable, and biocompatible cationic polysaccharide, produced by partial deacetylation of chitin, isolated from naturally occurring crustacean shells (Wong, Gastineau, Gregorski, Tillin, & Pavlath, 1992). Chitin, in fact, is one of the most abundant polysaccharides found in nature, making chitosan a plentiful and relatively inexpensive product. However, some unsatisfactory mechanical properties, such as severe shrinkage, deformation after drying, low solubility in acidic media, and compressibility at high operating pressure, as well as the inherent brittleness and stiffness limit its application and processing convenience (Francis & Matthew, 2000; Hirano, Yamaguchi, & Kamiya, 2003; Rabea, Badaway, Stevens, Smagghe, & Meysteurbaut, 2003; Sashiwa, Yamamori, Ichinose, Sunamoto, & Aiba, 2003; Tolaimate, Desbrires, Rhazi, & Alagui, 2003; Zeng & Ruckenstein, 1998; Zhou, Yang, Wang, & Liu, 2003). To improve the end use properties of chitosan-based materials, different approaches, such as processing techniques, blending, chemical modification, etc. have been proposed. For instance, chitosan-based packaging films were prepared by drying at ambient temperature and also by oven drying and infrared (IR) drying (Srinivasa, Ramesh,

---

* Corresponding author. Tel.: +40 232 217454; fax: +40 232 211299.
E-mail address: hvaleria@icmpp.ro (V. Harabagiu).

[1] Member of the European Polysaccharide Network of Excellence (EPNOE), http://www.epnoe.eu.

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.10.026

Kumar, & Tharanathan, 2004). It was found that the films prepared by IR drying are superior in preserving desirable functional characteristics of chitosan. The gas permeation properties of chitosan–gelatin blends appropriate for edible films were found to increase with the total plasticizer (water, polyols) content (Arvanityannis, Nakayama, & Aiba, 1998). Keratin–chitosan composite films were showed to support fibroblast attachment and proliferation, demonstrating to be a good substrate for mammalian cell culture (Tanabe, Okitsu, Tachibana, & Yamauchi, 2002). Another approach to improve the physicochemical properties of chitosan and other biomaterials is through the formation of organic–inorganic hybrids (Liu, Su, & Lai, 2004).

The chemical modification of natural polymers is another promising method for the preparation of new materials. It enables one to introduce special properties and enlarge the field of the potential applications of biopolymers. Considerable efforts are especially directed at modifying chitosan to improve its solubility in water (Hirano et al., 2003; Sashiwa et al., 2003; Zhou et al., 2003) and other physicochemical properties (Francis & Matthew, 2000; Tolaimate et al., 2003; Zeng & Ruckenstein, 1998). One of the most convenient and effective approaches to modify the properties of chitosan consists in its crosslinking. The hydroxyl and amino groups on glucosamine units of chitosan provide the reactive sites for crosslinking reactions. Various reagents, including glutaraldehyde (Goissis et al., 1999), epoxy compounds (Wei, Hudson, Mayer, & Kaplan, 1992), and nontoxic natural agents (Jin, Song, & Hourston, 2004; Kuboe, Tonegawa, Ohkawa, & Yamamoto, 2004; Mi, Sung, Shyu, Su, & Peng, 2003), etc., have been used as crosslinkers for chitosan.

The incorporation of polyorganosiloxanes as "soft" segments into chitosan-based materials is expected to improve the physical and mechanical properties for practical uses. PDMS is a highly flexible polymer showing a very low glass transition temperature (about −123 °C). It is widely used in medical applications owing to its biocompatibility, high oxygen permeability, good oxidative stability (Rutnakornpituk, Ngamdee, & Phinyocheep, 2005). Kim et al. (2002) prepared pH-sensitive hydrogels by the crosslinking of chitosan with epoxy-terminated polydimethylsiloxane using the UV irradiation technique. 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 resulted copolymers (Rutnakornpituk, Ngamdee, & Phinyocheep, 2005). 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 (Shin et al., 2002). These photocrosslinked hydrogels exhibited equilibrium water content (EWC) in the range of 65–95%.

Previously, we reported the preparation of graft and crosslinked polydimethylsiloxane–chitosan copolymers (Enescu et al., in press) and their ability to complex divalent metal cations (Enescu, Hamciuc, Harabagiu, Tampu, & Simionescu, 2008). 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. The chemical structure of the crosslinked materials was elucidated by FT-IR spectroscopy. The swelling behavior, water contact angles, morphological, thermal, and dynamical mechanical properties were also investigated.

2. Experimental

2.1. Materials

Low molecular weight 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 measured in 0.25 M acetic acid/0.25 M sodium acetate aqueous solution using an Ubbelohde viscometer kept in a constant temperature bath at 25 °C. The viscosity molecular weight was found to be approximately 380 kDa by using the Mark–Houwink–Sakurada equation (MHS), $[\eta] = K \times M^{\alpha}$, where $[\eta]$ is the intrinsic viscosity and the empirical constants for the MHS equation were $K = 1.81 \times 10^{-3}$ dl/g and $\alpha = 0.93$ (Kassai, Arul, & Charlet, 2000). Hexamethylcyclotrisiloxane (D_3, 98%; Fluka), *n*-butyllithium (BuLi, Aldrich) dimethylchlorosilane (DMCS, 97%; Aldrich), calcium carbonate, hexachloroplatinic acid monohydrate (Aldrich), allyl glycidyl ether (AGE, 99%; Aldrich), γ-glycidoxypropyltrimethoxysilane (GP-TMS, 98%; Aldrich) were used as received. All solvents (cyclohexane, tetrahydrofuran, and toluene) were purified according to standard methods.

2.2. Synthesis

2.2.1. Hydro-terminated polydimethylsiloxane (H-PDMS)

Monofunctional H-PDMS was synthesized by anionic polymerization of D_3 in the presence of *n*-butyllithium initiator and tetrahydrofuran promoter and stopping the polymer chain growth with DMCS, as previously reported (Rosati et al., 1998). A polymer with an average number molecular weight of 1910 g/mol was obtained.

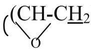
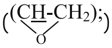
FT-IR: (KBr), cm^{-1}: 2963–2905 (CH_3); 2120 (Si–H); 1261, 841, and 800 (–Si–CH_3); 1094–1024 (Si–O–Si).

^{1}H NMR: ($CDCl_3$), δ (ppm): 0.06–0.11 (Si $(CH_3)_2$); 0.08–0.10 (CH_3Si H); 4.74 (Si–*H*).

2.2.2. Glycidoxypropyl-terminated PDMS (GP-PDMS)

Mono epoxy-terminated PDMS was synthesized by the hydrosilation of allyl glycidyl ether with H-PDMS in toluene, in the presence of hexachloroplatinic acid 2% solution in isopropanol, according to a procedure previously described (Simionescu, Harabagiu, Giurgiu, & Hamciuc, 1990). The complete conversion of H–Si groups to Si–C units was monitored by the IR spectra of the reaction mixture through the disappearance of Si–H characteristic band at 2120 cm^{-1}.

FT-IR: cm^{-1}: 2963–2905 (CH_2, CH_3); 1261, 841, 800 (Si–CH_3); 1094–1024 (CH_2–O–CH_2 and Si–O–Si); 905 (epoxy).

^{1}H NMR: $CDCl_3$, δ (pmm): 0.014 (Si$(CH_3)_2$); 0.46–0.54 (Si–CH_2); 1.55–1.65 (CH_2–CH_2–CH_2), 2.57–2.60 and 2.76–2.79 ( $(\mathrm{CH{-}C\underline{H}_2});$); 3.12–3.13 ( $(\mathrm{C\underline{H}{-}CH_2});$); 3.36–3.50 and 3.67–3.71 (CH_2–O–CH_2–).

2.2.3. Preparation of hybrid membranes

The hybrid membranes were obtained by simultaneous grafting and crosslinking of chitosan with GP-PDMS and GP-TMS. The method is outlined as follows. 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. To 100 ml of chitosan solution, 1.5 g GP-TMS, 0.5 g GP-PDMS and 0.1 ml isopropyl alcohol were added. 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 exposed to UV irradiation for 1 h at room temperature. The sample was dried at 40 °C for 4 days. The dry film was washed with deionized water and with acetone to remove any unreacted materials that were not incorporated into the hybrid membrane (Hy).

Elemental analysis (%): calculated: Si: 12.75; found: Si: 8.98.

To obtain porous hybrid membranes (HyP) according to a procedure described by Chow and Khor (2000), half of the copolymer solution was mixed with calcium carbonate ($CaCO_3$) (1 g), treated in an ultrasonic bath for 15 min and stirred overnight. The reaction mixture was poured into a glass mould and exposed to UV irradiation for 1 h. The obtained gel was dried at 40 °C under vacuum up to a constant weight to obtain a film. The decomposition of calcium carbonate was performed at two different temperatures, i.e., 25 °C or 50 °C, by soaking the dried film in 0.1 N HCl solution for 4 h. The resulting porous membranes (HyP_{25} and HyP_{50}) were immersed first in deionized water (to ensure a complete removal of HCl, and calcium residues), then in acetone (to remove the non-reacted PDMS) and dried at 40 °C under vacuum for 4 days.

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

2.3. Spectral analysis: IR, NMR

Fourrier transform-infrared (FT-IR) spectra were obtained by using a Nicolet 60 SX FT-IR apparatus under dry air at room temperature on KBr pellets in the range of 4000–500 cm^{-1}. ^1H NMR spectra were registered on a Bruker Avance 400 spectrometer in $CDCl_3$.

2.4. Chemical analysis

Active hydrogen in hydro-terminated PDMS (H-PDMS) and epoxy groups content in glycidoxypropyl-terminated PDMS (GP-PDMS) precursors were determined by modified Zerewitinoff method (McHard, 1959, chap. XIV) and from the integral ratio of the specific protons in ^1H NMR spectra, respectively.

Silicon content of hybrid materials was obtained by sample decomposition in the presence of conc. H_2SO_4 (Smith, 1974).

2.5. Morphology: SEM, AFM, WAXD

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.

Wide angle X-ray diffraction (WAXD) patterns were recorded on a Bruker AXS D8 Advance X-ray diffractometer with scanning scope of 0°–60°, scanning speed of 4°/min, using Cu Kα radiation.

2.6. Density and porosity

A method used for chitosan–poly(ethylene glycol) membranes (Zeng & Fang, 2004) was applied to roughly estimate the porosity of HyP membranes. The densities of the non-porous (Hy: density, 1.081 g/cm^3) and porous membranes (HyP_{25}: density, 0.825 g/cm^3; HyP_{50}: density, 0.831 g/cm^3) were calculated based on the measurements of their dimensions and weights. For both HyP membranes, a porosity of about 23–24% was then estimated with the formula

$$\epsilon = V_p/V_t \times 100 = (1 - \rho_2/\rho_1) \times 100,$$

where V_p and V_t are the pore and the total volumes, respectively; ρ_1 and ρ_2 are the densities of the non-porous and porous membranes, respectively.

2.7. Swelling behavior

The membrane swelling behavior was determined by equilibrium swelling studies, according to a recently published procedure (Shanmugasundaram et al., 2001). The dried samples were cut into small pieces of 1 cm × 1 cm, precisely weighed and submerged into distilled water for different periods of time at room temperature until equilibrium was reached. At each immersion interval, the swollen samples were removed from water, wiped off excess water on surface with filter paper and immediately weighed. 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:

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

2.8. Contact angle

The contact angle toward distilled water was measured with a Contact Angle Meter, at room temperature, by the sessile drop method (Ioanid, 2007).

2.9. Thermo-mechanical analysis: ATG, DMTA

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

Dynamic mechanical thermal analysis (DMTA) was performed on a Diamond Perkin Elmer apparatus, in tension mode, at a frequency of 1 Hz. In a first experiment, the samples were cooled at -150 °C and the temperature scan was performed between -150 and 150 °C, with a heating rate of 4 °C/min, under nitrogen atmosphere. Additionally, in a second experiment, the CS and Hy membranes were subjected to the following heating–cooling cycle: heating between 20 and 110 °C (4 °C/min), isothermal treatment at 110 °C for 15 min, cooling (110–0 °C; 4 °C/min), heating (0–175 °C; 4 °C/min). The films (10 × 9.52 × 0.17 mm) were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The values of the storage modulus (E') and tension loss tangent ($\tan \delta = E''/E'$) were obtained as a function of temperature.

3. Results and discussion

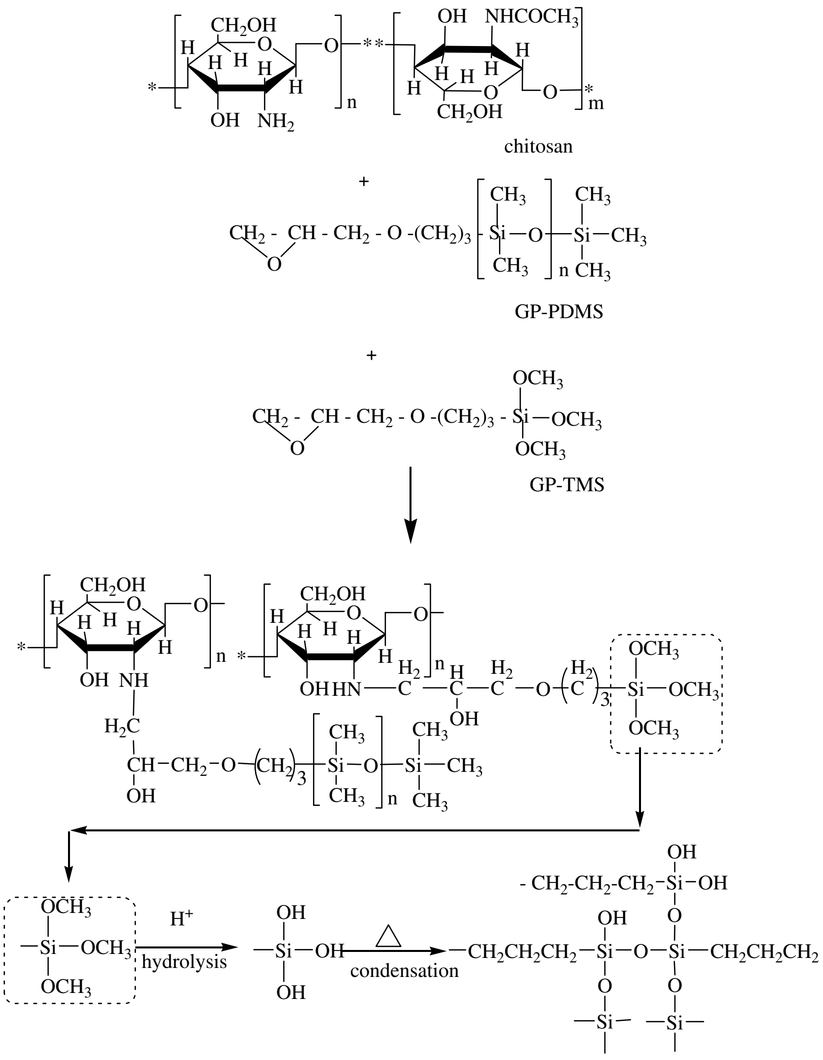
3.1. Membrane synthesis

Hydrophobically modified CS was prepared by simultaneous grafting and crosslinking of CS with GP-PDMS and GP-TMS (Scheme 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.

The hybrid membrane (Hy) was prepared from the modified chitosan by drying the copolymer solution and purifying the obtained film. To obtain porous hybrid membranes (HyP), calcium carbonate was incorporated into copolymer solution and, after drying, the film was decomposed by treating with HCl solution. The texture and physical properties of the membranes depend on the temperature of carbonate decomposition, as can be seen from the next paragraphs.

3.2. Membrane structure

The structure of hybrid membranes was proved by FT-IR analysis. The FT-IR spectra (Fig. 1) of membranes present the character-



Scheme 1. Synthesis of hybrid membranes.

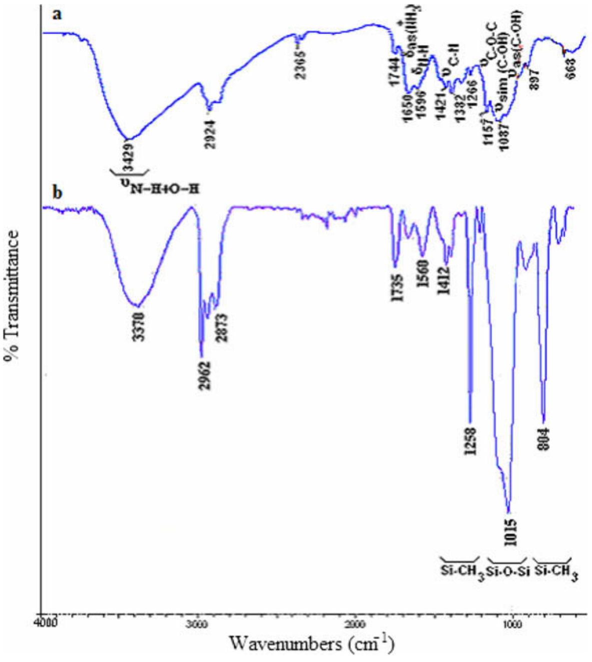


Fig. 1. FT-IR spectra of (a), CS and of (b), Hy membranes.

istic absorption bands of both precursors. Fig. 1a 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), 1158 cm^{-1} (bridge-O-stretch), and 1087 cm^{-1} (C–O stretch) (Brugnerotto et al., 2001). 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 to 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} is moved to 1560 cm^{-1} (Fig. 1b). The ν_{C-O-C}, $\nu_{sim\ C-OH}$, and $\nu_{as\ C-OH}$ 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 at 1258 and 804 cm^{-1} the Si–CH$_3$ characteristic bands of the siloxane chain.

3.3. Surface and bulk 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). The surface and bulk morphologies of hybrid membranes were determined by SEM, AFM, and WAXD and compared to that of chitosan membrane.

3.3.1. Microscopy (SEM and AFM)

To observe morphological properties such as surface porosity, texture and roughness, SEM micrographs of the surface and cross-section and AFM micrographs of the pure chitosan membrane and hybrid membranes were registered (Figs. 2 and 3).

The SEM images of pure CS membrane revealed a uniform and dense surface microstructure (not shown) and a fibrous non-porous structure in cross-section (Fig. 2a). The hybrid membrane (Hy) not treated with calcium carbonate (Fig. 2b) showed a surface with spherical domains (10–40 μm) of silica core covered by hydrophobic siloxane in a hydrophilic chitosan matrix, a normal disposal of hydrophobic–hydrophilic segments considering the polar character of the separation medium (water–acetic acid solution). Irregular phase segregated domains (black regions) are also observed in chitosan rich phase (detail, Fig. 2b′). The cross-section image of Hy membrane (Fig. 2b″) revealed irregular ellipsoid segregated domains, while the fibrous crystallites in chitosan domains

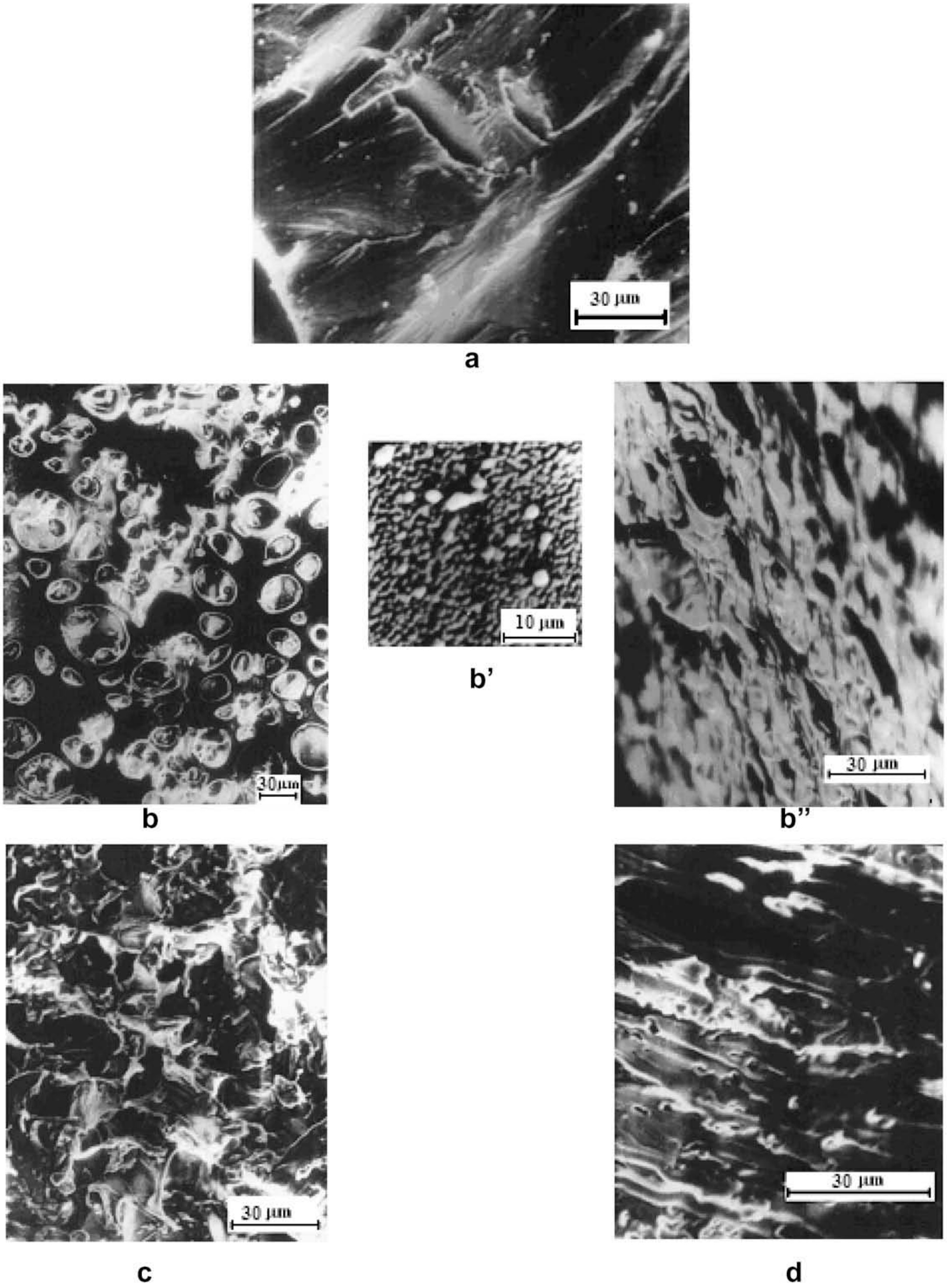


Fig. 2. Scanning electron micrographs (SEM) of membranes: (a), CS surface; (b, b′), Hy surface; (b″), Hy cross-section; (c), HyP_{25} cross-section; (d), HyP_{50} cross-section.

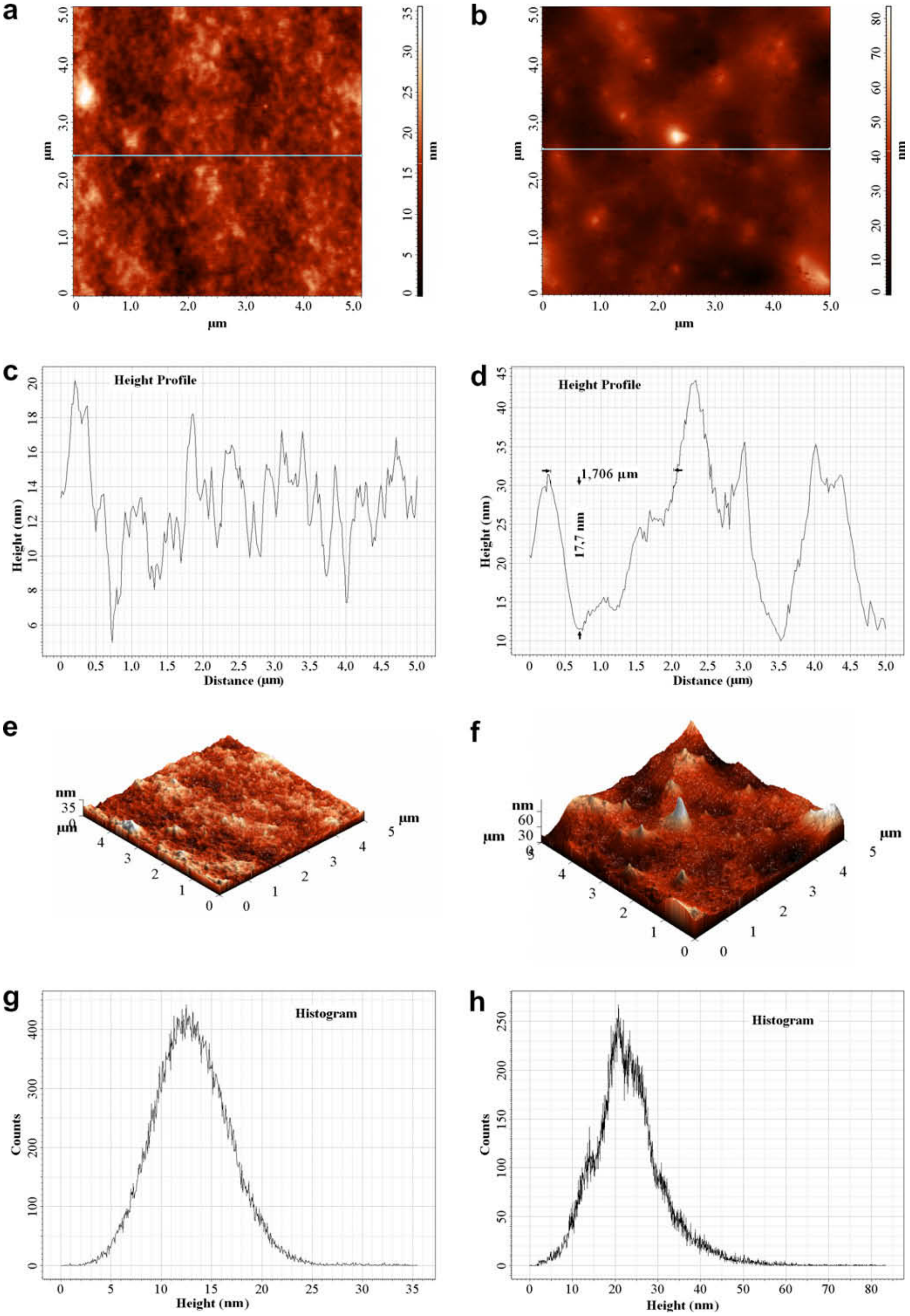


Fig. 3. AFM topographic images of membranes surface: two-dimensional images (2D) of (a), CS; (b), Hy; the height profiles were generated along the horizontal lines of (c), CS and (d), Hy; three-dimensional images (3D) of (e), CS and (f), Hy; the height histograms of (g), CS and (h), Hy.

are no more evidenced. The porous membranes (HyP) prepared by the decomposition of calcium carbonate trapped inside the material at 25 and 50 °C show similar irregularly layered surface morphologies (not shown). However, the cross-sections of the porous membranes showed different morphologies with irregular circular pores of 10–30 µm diameters for the membranes obtained at lower temperature (Fig. 2c), while the membranes prepared at 50 °C tend to adopt a plan-parallel porosity (Placenov & Koisenkov, 1988) (Fig. 2d).

Fig. 3a and b shows the morphology of unmodified CS and Hy membranes investigated by atomic force microscopy. CS membrane presents quite homogeneous surfaces while the Hy membrane reveals a predominantly hill-valley-structured surface with irregular pores of nanoscale topography, in agreement with other reports (Huang, Moon, & Pal, 2001). The surface roughness, S_a, measured on scanning areas of $5.00 \times 5.00\ \mu m^2$, indicated values of 2.99 and 6.24 nm for pure CS membrane and Hy membrane, respectively. The height profiles (Fig. 3c and d) generated along

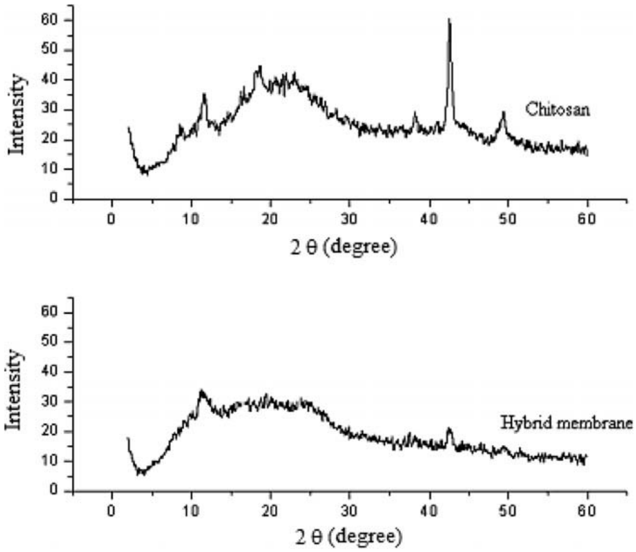


Fig. 4. X-ray diffractograms of CS and Hy membranes.

the horizontal lines (Fig. 3a and b) indicate a more compact structure of CS membrane as compared to Hy membrane. The last one showed a hilly surface with vertical irregularities of tens of nm horizontally disposed at distances of microns. The differences between CS and Hy membranes can be also seen in 3D images (Fig. 3e and f). The major population of heights is situated around 14 and 25 nm for CS and Hy membranes, respectively (Fig. 3g and h). No reliable results in AFM experiments were obtained on porous membranes.

3.3.2. X-ray diffraction (XRD)

The X-ray diffraction patterns (XRD) of pure CS and Hy membranes are compared in Fig. 4. As one can see from the figure, CS sample is a partially crystalline material. The peaks of CS practically disappeared in the XRD diffraction pattern of Hy membrane, showing that the introduction of PDMS into chitosan induces the decrease of the crystallinity.

3.4. Porosity

The treatment with calcium carbonate and hydrochloric acid is expected to introduce pores in HyP membranes through the production of carbon dioxide. The porosity of the prepared porous membranes was roughly estimated by comparing their densities (volumes) with that of the non-porous Hy membrane. As expected, the Hy_{25} and HyP_{50} membranes obtained by the decomposition of calcium carbonate at 25 and 50 °C, respectively, were found to have the same porosity of about 23–24% because they contained the same amount of porogenic agent. However, as revealed by TEM, the preparation conditions are influencing the shape and the disposal of the pores.

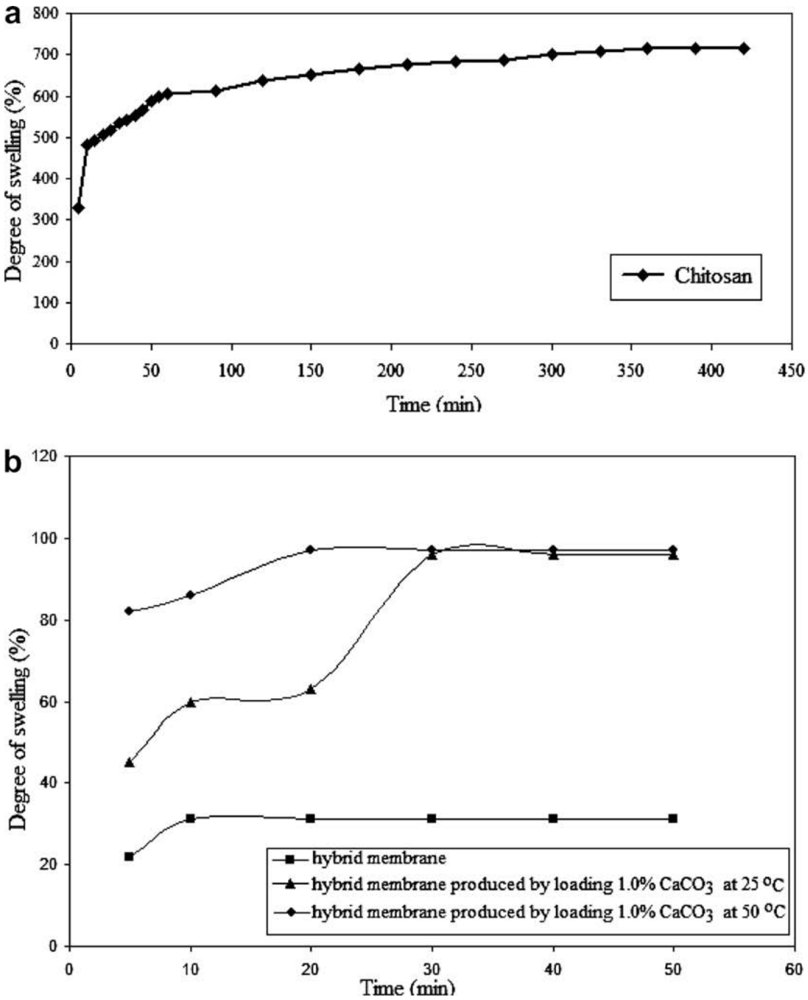


Fig. 5. Swelling behavior of (a), CS and (b), Hy membranes.

Table 1
Water contact angle of pure chitosan and hybrid membranes.

Sample	Contact angle (degree)
Chitosan	72° ± 2°
Hybrid membrane	78° ± 2°

3.5. Swelling behavior

The degree of swelling of unmodified CS membrane and Hy membranes in water was calculated by applying the conventional swelling formula. Fig. 5a and b presents the swelling equilibrium results. The pure CS membrane achieved equilibrium after immersion for about 6–7 h in distilled water and the maximum degree of swelling was about 700%. The hybrid membrane reached the equilibrium much easier, after immersion for 10 min in distilled water, demonstrating the disturbing of the tight, more ordered package of the pure biopolymer, as already evidenced by morphological investigation, but the maximum degree of swelling was low (about 30%).

The curves corresponding to HyP porous membranes obtained in the presence of $CaCO_3$ showed a maximum degree of swelling as high as 100%, more than three times higher as compared to that corresponding to Hy non-porous membrane, due to the presence of the pores. The temperature of preparation of porous membranes influences the swelling rate but has no influence on the maximum degree of swelling. This observation is in accordance with porosity measurements, i.e., HyP_{25} and HyP_{50} membranes have similar porosity; the difference in the rates of swelling should be induced by the pore shape and distribution as evidenced by SEM.

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.

3.6. Surface characterization

3.6.1. Contact angle

Contact angle measurements of water droplets on material surfaces are used to characterize surface properties of hybrid membranes. The contact angle is defined as the angle between the substrate surface and the tangent line at the point of contact of the liquid droplet with the substrate. To compare the wettability of hybrid membranes to the unmodified chitosan, contact angle (θ) between samples surface and water were measured in air using the sessile drop method. Water was carefully dropped on films and contact angles were quickly measured before the beginning of the swelling. The reported values (Table 1) are the average of three different measurements.

As one can see from Table 1, the water contact angles of hybrid membranes are ranging from 75° to 80°. The contact angle of unmodified chitosan is significantly lower than those of the hybrid membranes, meaning that the incorporation of PDMS rendered the surface less water wettable. The result is in agreement with SEM images (Fig. 2b), showing a PDMS-enriched surface.

3.7. Thermo-mechanical properties

3.7.1. TGA analysis

The thermal stability of pure chitosan and hybrid membranes was evaluated by thermogravimetric (TGA) analysis under air atmosphere. Fig. 6 presents the weight loss of Hy and HyP membranes as compared to CS and epoxy-terminated PDMS precursors. As one can see, CS (12%) and Hy (HyP) membranes (8%) showed weight losses up to 150 °C (loss of adsorbed and complexed water and of acetic acid used for membrane preparation). Their purification by heating at 50 °C (to avoid degradation) under vacuum was not sufficient to completely remove the solvents. The initial thermal decomposition is located at 247 and 275 °C for CS and Hy (HyP) membranes, respectively. Both Hy and HyP membranes possess thermal stabilities situated between the less stable CS and the more stable PDMS in the whole range of investigated temperatures. This is in accordance with the generally observed stabilizing effect of the incorporation of inorganic components into organic materials. 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.

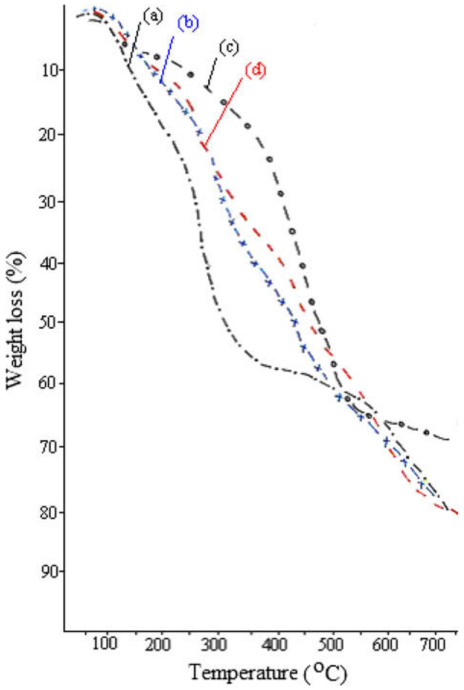


Fig. 6. Membranes weight loss (under air atmosphere at a heating rate of 10 °C/min): (a), CS; (b), Hy; (c), GP-PDMS; (d), HyP_{25}.

3.7.2. Dynamic mechanical thermal analysis (DMTA)

Chitosan and hybrid membranes have been studied by DMTA. Fig. 7 shows the storage modulus E′ and tan δ for CS, Hy and HyP membranes. CS was analysed in the $-110 \div 150$ °C temperature range, while Hy and HyP membranes were investigated between −150 and 150 °C. It is to mention that, from visual observation, CS membrane is fragile, while the hybrid membranes are much more flexible. However, as one can see from Fig. 7a, at low temperatures, all samples show a plateau of storage modulus, E', with a magnitude over 10^9 Pa, typical for glassy polymers. Thus, according to E' values, the increased flexibility of modified CS membranes is not accompanied by an important loss of the mechanical properties.

Reports on CS thermal transitions demonstrate a large diversity of the glass transition intervals (Cho, Grant, Miller, & Allen, 2006; Garrido, Gonzalez, & Arechederra, 2007; Toffely & Glasser, 2001; Wan, Wu, Yu, & Wen, 2006; Wu, Wan, Cao, & Wu, 2008; Wu et al., 2006) depending on CS origin, molecular weight, deacetylation degree. Moreover, the history of the sample preparation greatly influences both the formation of hydrogen bonds and its thermomechanical properties. For CS membrane, a large relaxation was noticed between −50 and 30 °C. This thermal transition could include the β relaxation (found by Neto et al. (2005) at −20 °C) associated to local motions of side groups in CS superposed on other non-identified transitions. As no γ relaxation at around -75 °C was seen, it is also possible that this relaxation is occurring at higher temperature, in the interval mentioned above. A sharp decrease of E' till 4.6×10^7 Pa at 73 °C starts at 40 °C. The evolution of E' then consists in an important increase till 1.65×10^8 Pa followed by a small and large drop till 1×10^8 Pa at 120 °C. As already mentioned, according to TGA analysis, the membrane samples are still containing water (12 and 8% in CS and Hy membranes, respectively). Thus, the variations of E' in the $-40 \div 120$ °C interval could be associated to a superposition of α relaxation on solvent loss. Other transitions which can occur in this temperature interval and explain the complex shape of E' and tan δ variation (Fig. 7b) could be related either to the reorganisation of packing of CS chains due to an increase of water mobility (Mucha & Pawlak, 2005) or to a local molecular motion in a pseudo-stable state in the presence of water, as stated by Sakurai, Maegawa, and Takahashi (2000). To check the influence of the solvent traces on DMA results, a heating-isothermal treatment at 110 °C-cooling–heating experiment between 20 and 110 °C (Fig. 8) was performed. It showed the disappearance of the variation of E' associated to the solvent loss in the second heating step. Both CS and Hy membranes presented higher values of the storage modulus in the second heating step due to solvent removal and the shift of the E' drop to higher temperatures (140 and 110 °C, respectively). According to Neto et al. (2005) the decrease of the glass transition of CS as compared to the values between 156 and 170 °C reported by Mucha and Pawlak (2005) could be explained by the plasticizer effect of the water present in the sample. Thus, in the used experimental conditions, not all water plastifier was removed. A third heating experiment was not possible due to experimental difficulties (the samples became thinner and slipped from the device attachment). In these experimental conditions the high storage modulus of chitosan (about 5.1×10^9 Pa at 20 °C) is decreased by about one order of magnitude by the introduction of the highly flexible polysiloxane and the hybrid membranes are more flexible.

Hy membranes are phase segregated materials (see Fig. 2b and b″) where silica like spherical domains surrounded by siloxane shells in a CS rich matrix are present. As a consequence, the above described relaxation phenomena of CS domains are also present in Hy copolymers. They are more or less shifted to higher or lower temperatures as compared to CS. The glass relaxations at very

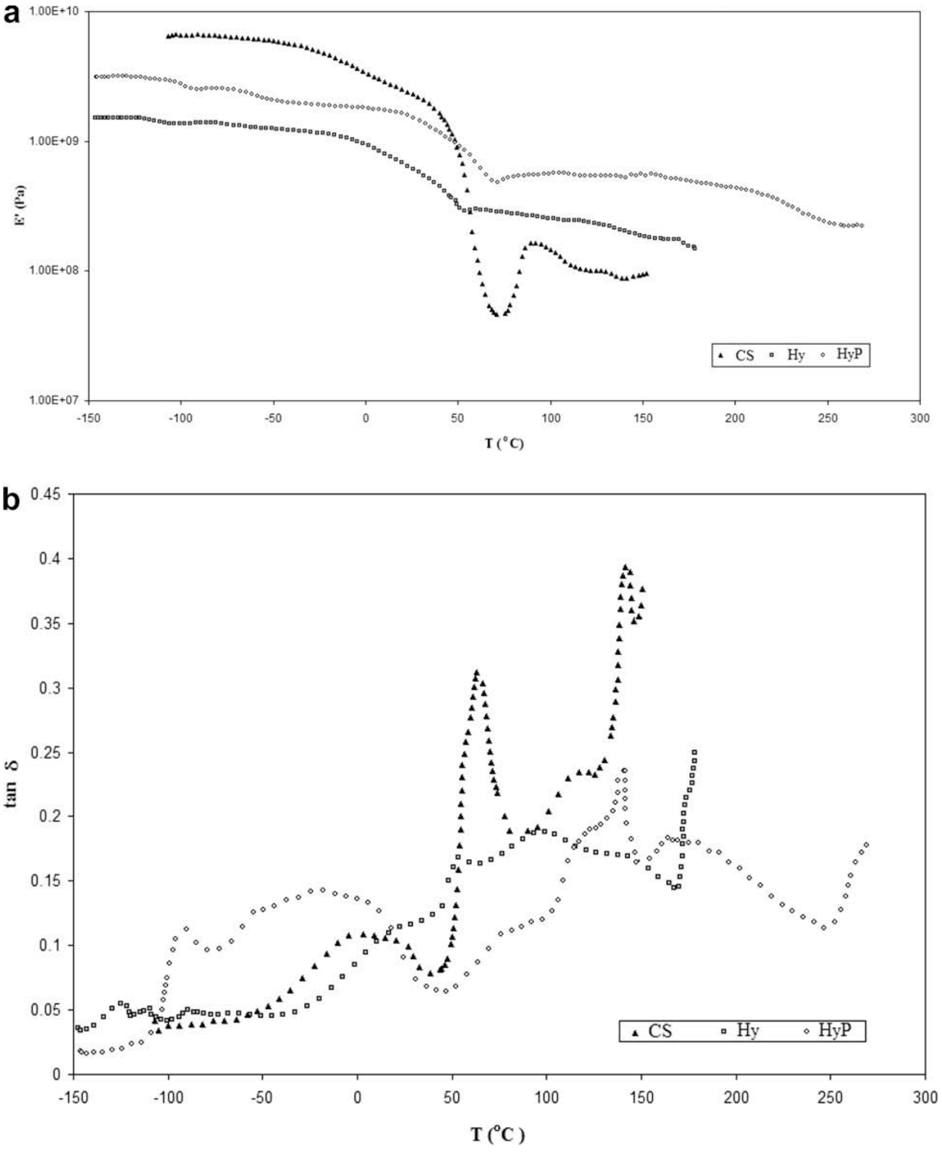


Fig. 7. Dynamic thermo-mechanical analysis (first heating) of (a), variation of storage modulus; (b) variation of tan δ.

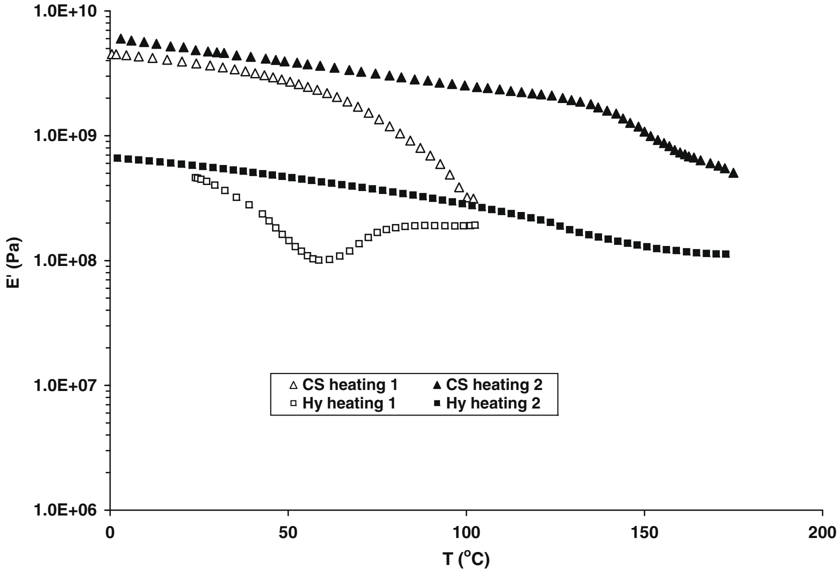


Fig. 8. Dynamic thermo-mechanical analysis of CS and Hy membranes in two heating runs.

low temperature, characteristic to siloxane domains, are more complex as compared to pure polysiloxane (one single Tg at about −123 °C). Three relaxations at −120, −115, and −95 °C were identified (Fig. 7b). They could be assigned to the glass transition of siloxane domains having different neighbourhoods. No melting of siloxane rich domains was observed at around −47 °C in Hy and HyP samples.

4. Conclusions

This study evaluated the properties of the novel hybrid membranes, Hy, obtained by simultaneous grafting and crosslinking of chitosan with epoxy-terminated polydimethylsiloxane and γ-glycidoxypropyltrimetoxysilane. Porous membranes, HyP, were also prepared by the decomposition, at different temperatures (25 and 50 °C), of calcium carbonate porogenic agent trapped inside the material. Fourier transform-infrared analysis confirmed the transformation of amino groups of chitosan through the reaction with epoxy groups, while the X-ray diffraction (XRD) studies revealed that the hybrid membrane exhibits an amorphous character. Scanning electron microscopy (SEM) observations indicated that the non-porous membrane is a phase segregated material with spherical domains (10–40 μm) of silica core covered by hydrophobic siloxane in a hydrophilic chitosan matrix, while the hybrid membranes obtained in the presence of $CaCO_3$ present irregular pores with shapes and dimensions depending on the temperature of decomposition of the porogenic agent. Atomic force microscopy (AFM) studies, possible on non-porous CS and Hy membranes only, revealed that chitosan membranes are relatively smooth and homogeneous, while the hybrid membranes present a predominantly hill-valley-structured surface of nanoscale topography. 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. Higher thermal decomposition temperatures of hybrid membranes (175 °C) as compared to pure chitosan (147 °C) were evidenced by thermogravimetric analysis. 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. The good mechanical properties of chitosan (storage modulus of 3.7×10^9 Pa) were not affected by its chemical modification, while, by the contrary, its fragility was diminished.

Acknowledgments

This work was financially supported by EC project NMP3-CT-2005-500375 – POLYSACHARIDES, by the CNCSIS grant 1431 and by the CEEx MATNANTECH project 40(510). The authors acknowledge the useful comments and suggestions of the reviewers.

References

Arvanityannis, I. S. (1999). Totally and partially biodegradable polymer blends based on natural and synthetic macromolecules: Preparation and physical properties and potential as food packaging materials. *Journal of Macromolecular Science – Reviews of Macromolecular Chemistry and Physics, C39*, 205–271.

Arvanityannis, I. S., Nakayama, A., & Aiba, S. (1998). Chitosan and gelatin based edible films: state diagrams, mechanical and permeation properties. *Carbohydrate Polymers, 37*, 371–382.

Brugnerotto, J., Lizardi, J., Goycoolea, F. M., Arguelles-Monal, W., Desbrieres, J., & Rinaudo, M. (2001). An infrared investigation in relation with chitin and chitosan characterization. *Polymer, 42*, 3569–3580.

Chanachai, A., Jiraratananon, R., Uttapap, D., Moon, G. Y., Anderson, W. A., & Huang, R. Y. M. (2000). Pervaporation with chitosan/hydroxyethylcellulose (CS/HEC) blended membranes. *Journal of Membrane Science, 166*, 271–280.

Cho, J., Grant, J., Miller, M. P., & Allen, C. (2006). Synthesis and physicochemical and dynamic mechanical properties of a water-soluble chitosan derivative as a biomaterial. *Biomacromolecules, 7*, 2845–2855.

Chow, K. S., & Khor, E. (2000). Novel fabrication of open-pore chitin matrixes. *Biomacromolecules, 1*, 61–67.

Enescu, D., Hamciuc, V., Pricop, L., Hamaide, T., Harabagiu, V., & Simionescu, B.C. (in press). Polydimethylsiloxane modified chitosan I. Synthesis and structural characterization of graft and crosslinked copolymers. *Journal of Polymer Research*, doi: 10.1007/s10965-008-9204-4.

Enescu, D., Hamciuc, V., Harabagiu, V., Tampu, D., & Simionescu, B. C. (2008). Copper (II), nickel (II), cobalt (II)/chitosan–polydimethylsiloxane complexes. *Journal of Optoelectronic and Advances Materials, 10*, 1473–1477.

Francis, S. J. K., & Matthew, H. W. T. (2000). Application of chitosan-based polysaccharide biomaterials in cartilage tissue engineering: A review. *Biomaterials, 21*, 2589–2598.

Gandini, A., Hariri, S., & Nest, J. F. L. (2003). Furan-polyether-modified chitosans as photosensitive polymer electrolytes. *Polymer, 44*, 7565–7572.

Garrido, Q., Gonzalez, I. V., & Arechederra, M. J. M. (2007). The role played by the interactions of small molecules with chitosan and their transition temperatures. Glass-forming liquids: 1, 2, 3-Propantriol (glycerol). *Carbohydrate Polymers, 68*, 173–186.

Ge, J., Cui, Y., Yan, Y., & Jiang, W. (2000). The effect of structure on pervaporation of chitosan membrane. *Journal of Membrane Science, 165*, 75–81.

Goissis, G., Junior, E. M., Marcantonio, R. A. C., Lai, R. C. C., Cancian, D. C. J., & De Caevallho, W. M. (1999). Biocompatibility studies of anionic collagen membranes with different degree of glutaraldehyde cross-linking. *Biomaterials, 20*, 27–34.

Hirano, S., Yamaguchi, Y., & Kamiya, M. (2003). Water-soluble *N*-(*n*-fatty acyl) chitosans. *Macromolecular Bioscience, 3*, 629–631.

Hu, Q., Li, B., Wang, M., & Shen, J. (2004). Preparation and characterization of biodegradable chitosan/hydroxyapatite nanocomposite rods via in situ hybridization: A potential material as internal fixation of bone fracture. *Biomaterials, 25*, 779–785.

Huang, R. Y. M., Moon, G. Y., & Pal, R. (2001). Chitosan/anionic surfactant complex membranes for the pervaporation separation of methanol/MTBE and characterization of the polymer/surfactant system. *Journal of Membrane Science, 184*, 1–15.

Ioanid, G.E. (2007). Contact angle meter, Patent Ro. 120384, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania.

Jin, J., Song, M., & Hourston, D. J. (2004). Novel chitosan-based films cross-linked by genipin with improved physical properties. *Biomacromolecules, 5*, 162–168.

Kassai, R., Arul, J., & Charlet, G. (2000). Intrinsic viscosity-molecular weight relationship for chitosan. *Journal of Polymer Science. Part B: Polymer Physics, 38*, 2591–2598.

Kim, I. Y., Kim, S. J., Shin, M., Lee, Y. M., Shin, D., & Kim, K. J. (2002). PH and thermal characteristics of graft hydrogels based on chitosan and poly(dimehylsiloxane). *Journal of Applied Polymer Science, 85*, 2661–2666.

Krochta, J. M., & De Mulder-Johnston, C. (1997). Edible and biodegradable polymer films: Challenges and opportunities. *Food Technology, 51*, 61–74.

Kuboe, Y., Tonegawa, H., Ohkawa, K., & Yamamoto, H. (2004). Quinone cross-linked polysaccharide hybrid fiber. *Biomacromolecules, 5*, 348–357.

Liu, Y. L., Su, Y. H., & Lai, J. Y. (2004). In situ crosslinking of chitosan and formation of chitosan–silica hybrid membranes with using γ-glycidoxypropyltrimethoxysilane as a crosslinking agent. *Polymer, 45*, 6831–6837.

McHard, J. A. (1959). In G. M. Kline (Ed.). *Analytical chemistry of polymers* (Vol. 13, pp. 374). New York: Interscience. part. I.

Mi, F. L., Sung, H. W., Shyu, S. S., Su, C. C., & Peng, C. K. (2003). Synthesis and characterization of biodegradable TPP/genipin crosslinked chitosan gel beads. *Polymer, 44*, 6521–6530.

Mucha, M., & Pawlak, A. (2005). Thermal analysis of chitosan and its blends. *Thermochimica Acta, 427*(1–2), 64–67.

Neto, C. G. T., Giacometti, J. A., Job, A. E., Ferreira, F. C., Fonseca, J. L. C., & Pereira, M. R. (2005). Thermal analysis of chitosan based networks. *Carbohydrate Polymers, 62*, 97–103.

Ngimhuang, J., Furukawa, J., Satoh, T., Furuike, T., & Sakairi, N. (2004). Synthesis of a novel polymeric surfactant by reductive *N*-alkylation of chitosan with 3-*O*-dodecyl-D-glucose. *Polymer, 45*, 837–841.

Park, S. B., You, J. O., Park, H. J., Haam, S. J., & Kim, W. S. (2001). A novel pH sensitive membrane from chitosan-TEOS IPN: Preparation and its drug permeation characteristics. *Biomaterials, 22*, 323–330.

Peniche, C., Feranadez, M., Gallardo, A., Lopez-Barvo, A., & Roman, J. S. (2003). Drug delivery systems based on porous chitosan/polyacrylic acid microspheres. *Macromolecular Bioscience, 3*, 540–545.

Placenov, T.G., & Koisenkov, S. (1988). *Parometria*, Leningrad Himia.

Rabea, E. I., Badaway, M. E. T., Stevens, C. V., Smagghe, G., & Meysteurbaut, W. (2003). Chitosan as antimicrobial agent: Applications and mode of action. *Biomacromolecules, 4*, 1457–1465.

Rosati, D., Perrin, M., Navard, P., Harabagiu, V., Pinteala, M., & Simionescu, B. C. (1998). Synthesis of poly(styrene-dimethylsiloxane) block copolymers: Influence of the phase separated morphologies on the thermal behavior. *Macromolecules, 31*(13), 4301–4308.

Rutnakornpituk, M., Ngamdee, P., & Phinyocheep, P. (2005). Synthesis, characterization and properties of chitosan modified with poly (ethylene glycol)-polydimethylsiloxane amphiphilic block copolymers. *Polymer, 46*, 9742–9752.

Sakurai, K., Maegawa, T. T., & Takahashi, T. (2000). Glass transition temperature of chitosan and miscibility of chitosan/poly(*N*-vinyl pyrrolidone) blends. *Polymer, 41*, 7051–7056.

Sashiwa, H., Yamamori, N., Ichinose, Y., Sunamoto, J., & Aiba, S. (2003). Chemical modification of chitosan. 17a. Michael reaction of chitosan with acrylic acid in water. *Macromolecular Bioscience, 3*, 231–233.

Shanmugasundaram, N., Ravichandran, P., Reddy, P. N., Ramamurty, N., Pal, S., & Rao, K. P. (2001). Collagen-chitosan polymeric scaffolds for the in vitro culture of human epidermoid carcinoma cells. *Biomaterials, 22*, 1943–1952.

Shin, M., Kim, S. I., Kim, I. Y., Kim, N. G., Song, C. G., & Kim, S. J. (2002). Characterization of hydrogels based on chitosan and copolymer of poly(dimethylsiloxane) and poly(vinyl alcohol). *Journal of Applied Polymer Science, 84*, 2591–2596.

Simionescu, C. I., Harabagiu, V., Giurgiu, D., & Hamciuc, V. (1990). Hydrophobic–hydrophilic copolymers from functional organosiloxane oligomers. *Bulletin des Sociétés Chimiques Belges, 99*, 11–12.

Smith, A. L. (1974). *Analysis of silicones* (Vol. 41). J. Wiley & Sons eds. p. 120.

Srinivasa, P. C., Ramesh, M. N., Kumar, K. R., & Tharanathan, R. N. (2004). Properties of chitosan films prepared under different drying conditions. *Journal of Food Engineering, 63*, 79–85.

Tanabe, T., Okitsu, N., Tachibana, A., & Yamauchi, K. (2002). Preparation and characterization of keratin–chitosan composite film. *Biomaterials, 23*, 817–825.

Toffely, A., & Glasser, G. W. (2001). Chitin derivatives III. Formation of amidized homologues of chitosan. *Cellulose, 8*, 35–47.

Tolaimate, A., Desbrieres, J., Rhazi, M., & Alagui, A. (2003). Contribution to the preparation of chitins and chitosans with controlled physico-chemical properties. *Polymer, 44*, 7939–7952.

Wan, Y., Creber, K. A. M., Peppley, B., & Bui, C. T. (2003). Ionic conductivity of chitosan membranes. *Polymer, 44*, 1057–1065.

Wan, Y., Wu, H., Yu, A., & Wen, D. (2006). Biodegradable polylactide/chitosan blend membranes. *Biomacromolecules, 7*, 1362–1372.

Wei, Y. C., Hudson, S. M., Mayer, J. M., & Kaplan, D. L. (1992). The crosslinking of chitosan fibers. *Journal of Polymer Science. Part A: Polymer Chemistry, 30*, 2187–2193.

Wong, D. W. S., Gastineau, F. A., Gregorski, K. S., Tillin, S. J., & Pavlath, A. E. (1992). Chitosan–lipid films: Microstructure and surface energy. *Journal of Agricultural and Food Chemistry, 40*, 540–544.

Wu, H., Wan, Y., Cao, X., & Wu, Q. (2008). Interlocked chitosan/poly(DL-lactide) blends. *Materials Letters, 62*, 330–334.

Wu, B. Y., Yu, S. H., Mi, L. F., Wu, W. C., Shyu, S. S., Peng, K. C., et al. (2006). Preparation and characterization of mechanical and antibacterial properties of chitosan/cellulose blends. *Carbohydrate Polymers, 57*, 435–440.

Zeng, M., & Fang, Z. (2004). Preparation of sub-micrometer porous membrane from chitosan/polyethylene glycol semi-IPN. *Journal of Membrane Science, 245*, 95–102.

Zeng, X., & Ruckenstein, E. (1998). Cross-linked macroporous chitosan anion-exchange membranes for protein separations. *Journal of Membrane Science, 148*, 195–205.

Zhou, Y., Yang, Y., Wang, D., & Liu, X. (2003). Preparation and characterization of 6-carboxychitosan. *Chemistry Letters, 32*, 682–683.