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Effect of sonic treatment on the permeation performance of cellulose acetate membranes modified by n-SiO_2

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Abstract: Cellulose acetate (CA) membranes were modified by nano-silicon dioxide (n-SiO_2), and they were exposed to ultrasonic waves at a frequency of 35 kHz. The effect of sonication on their water sorption tendency and permeation capability was investigated. The characterization of the membranes was done by FTIR and SEM analysis, and the hydrophilic character of the membranes was deduced by swelling studies and contact angle (CAn) measurements. Permeation studies of the membranes were performed by using the diffusion method and theophylline was used as a model chemical in the permeation studies. The results indicated that beside the high hygroscopic property of n-SiO_2, the presence of n-SiO_2 in CA membranes did not significantly improve their hydrophilicity; however, when they were exposed to sonic waves, it was determined that the sonication effectively enhanced their water sorption capacity and permeability.

Key words: Ultrasonic wave, cellulose acetate, membrane, nano-filler, theophylline

1. Introduction

Cellulose acetate (CA) is one of the best membrane materials in the field of membrane processes such as reverse osmosis, ultrafiltration, and gas permeation.[1] Among the many polymeric membranes, CA membranes are widely used and investigated; they have broad applications mainly in the areas of wastewater treatment[1,2] and especially in pharmacology.[3,4] CA is used in osmotic release systems,[5,6] transdermal release systems,[7,8] and polymeric matrix systems,[9] and as a covering material of drug cores.[10,11] However, CA as a rate controlling membrane material for transdermal drug delivery systems generally requires plasticizers and needs some modifications to improve its permeation performances.[12,13]

Filling fine inorganic particles, such as silica, activated carbon, zeolites, titanium oxide, silicon carbide, zirconium oxide, and aluminum oxide, in polymeric membranes is one way to improve the diffusive, transport, surface, and some of the mechanical properties of the membranes as well as their hydrophilicity.[14–17] Watanabe et al.[16] studied nafion/SiO_2 composite membranes and they indicated that the nafion/SiO_2 membranes showed the best water sorption qualities of SiO_2 above the other hygroscopic oxides such as TiO_2. Bi et al.[17] reported that SiO_2 containing nafion membranes showed good water balance.

Sonication is a new applicable modification processes and it appears as a new branch of chemistry.[18] It is commonly preferred in the synthesis and modification of both organic and inorganic materials. The physical

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effects of high-intensity ultrasound have some chemical consequences: enhanced mass transport, emulsification, bulk thermal heating, modification of particle size of polymer powders, various effects on solids, etc.[19] It has also proved to be a very advantageous method for the depolymerization of macromolecules without a change in chemical nature, simply reducing the molecular weight by splitting the most susceptible chemical bonds.[18,20,21] Most of the ultrasonic studies, however, have been concentrated on polymer solutions,[18,20,22–26] but the effect of sonication on solid polymeric membranes has not been well studied.

In the present study, since nano-silicon dioxide (n-SiO_2) is known to be the best hygroscopic oxide,[17] it was used as a filler to increase the hydrophilic character of CA membranes in order to compare and determine the effect of sonic treatment on the water sorption capacity and permeability of sonically treated CA membranes. Since CA is frequently used in drug release studies, theophylline was used as a model chemical for the permeation studies. The characterization of the membranes was done by FTIR and SEM analysis, and the hydrophilic character of the membranes was deduced by swelling studies and contact angle (CAn) measurements. The effects of the presence of n-SiO_2 and sonic waves on the sorption capacity and the theophylline permeability of the CA and SiO_2/CA membranes were investigated. The amount of n-SiO_2 on the permeation of theophylline through sonically treated SiO_2/CA membranes was also investigated.

2. Results and discussion

2.1. Theophylline permeation through CA and SiO_2/CA membranes

CA and SiO_2/CA membranes were placed into Franz diffusion cells. The permeation of theophylline solution (5 mg/mL) was performed against the phosphate buffer solution of pH 7.40, at constant temperature (32 $\pm$ 1 °C, which is the skin's surface temperature). After a total permeation period of 24 h, the quantity of the permeated amount of theophylline, Q_t, was calculated by using Eq. (1):

$$Q_t = \frac{M_t}{A.t}, \tag{1}$$

where M_t is the mass (kg) of the theophylline permeated across an area of A (m^2) at time t (s). Swelling percentages, $S\%$, of the membranes for water ($S_w\%$) and buffer solutions ($S_B\%$) were also calculated by using Eq. (2):

$$S\% = \frac{W - W_0}{W_0}, \tag{2}$$

where W and W_0 are the wet and dry mass of the membranes, respectively. The results of the permeation are given in Table 1 together with the swelling percentage values of the membranes and the percentage amount of theophylline permeated through the membranes at the end of a permeation period of 24 h. As seen from the table, the presence of n-SiO_2 in the CA membranes only increased the permeation from 2.40 $\times$ 10^{-7} kg/m^2 s to 6.75 $\times$ 10^{-7} kg/m^2 s, and permeation percentage was only increased to 3.50% from 1.25%. Furthermore, the $S\%$ values of CA membranes were slightly changed by the addition of n-SiO_2, although it is known as a strongly hygroscopic compound.[17] This most probably resulted from the strong intermolecular attractive forces between the CA chains.[27] In our previous study[27] we tried to modify CA membranes by using a water soluble plasticizing and pore forming agent poly (ethylene glycol) (PEG), which has also high hydrophilicity. In that study, it was determined that although the removal of PEG from a polymeric material generally leads to a porous structure in polymeric membranes, in the case of CA membranes the porosity was not changed. CA

is one of the esters of cellulose, which is a polysaccharide composed of glucosidic rings linked through oxygen bridges with repeating units that have three hydroxyl groups and acetal linkages. Strong hydrogen bonding between the hydroxyl groups makes cellulose a highly crystalline polymer.[27,28] Therefore, as stated in Table 1, the swelling of the membranes and the permeation of theophylline were not high as expected, and this led to the less free volume for diffusion. From these results, it can be said that although n-SiO_2 is hygroscopic, the presence of n-SiO_2 in CA membranes is insufficient to improve their sorption and permeation capability efficiently.

Table 1. Swelling and permeation behaviors of the unsonicated membranes.

Membrane	S_w%	S_B%	Q (kg/m^2 s) $\times$ 10^{+7}	Permeated amount of theophylline % (m/m)
CA	10	8	2.40	1.25
SiO_2/CA	13	11	6.75	3.50

2.2. Theophylline permeation through sonicated CA and SiO_2/CA membranes

The theophylline permeation performance of the sonicated membranes was studied against pH 7.4 buffer solution at constant temperature. The results of the permeation of theophylline through sonically treated CA and SiO_2/CA (US-CA and US-SiO_2/CA) membranes are given in Figure 1. As seen from the figure, US-SiO_2/CA membranes have much greater theophylline permeation than US-CA membranes. To compare the permeation performance of the sonicated membranes with the unsonicated, corresponding Q_t values of US-CA and US-SiO_2/CA membranes were calculated for the total permeation period of 24 h as 401 $\times$ 10^{-7} kg/m^2 s and 579 $\times$ 10^{-7} kg/m^2 s, respectively. When these values are compared with the Q_t value of the CA and SiO_2/CA membranes (given in Table 1), it can be clearly seen that sonication has a remarkable effect on the increase in the permeation of theophylline through the membranes and US-SiO_2/CA membranes show greater permeation than the other membranes. Since porosity percentages (ε%) of the membranes give an idea about the volume available for permeation, ε% values of the sonicated and unsonicated membranes were calculated by using Eq. (3):[27–29]

$$\varepsilon\% = \frac{(W_1 - W_2)/D_w}{(W_1 - W_2)/D_w + W_2/D_p}, \tag{3}$$

where W_1 and W_2 are the wet and dry weight of the membranes, respectively; D_W and D_P correspond to the density of water and polymer, respectively. The results of the calculation are given in Table 2, together with the swelling percentages and water contact angle values of the membranes. As seen from the table, the sonically treated US-CA and US-SiO_2/CA membranes have much greater percentage porosity and water swelling percentage than unsonicated CA and SiO_2/CA membranes. This result is also satisfied by the lower water-contact angle values of US-CA and US-SiO_2/CA membranes (as given in Table 2) than both CA and SiO_2/CA membranes, since the lower CAn indicates the greater interaction between two phases,[30] i.e. membrane surface and water.

To determine the effect of sound waves on the chemical nature of the membranes, FTIR analysis of the CA and US-SiO_2/CA membranes were studied by using a Mattson 1000 FTIR (Unicam Co.) spectrometer and the results are given in Figure 2. In the figure, stretching vibration peaks at $\sim$3487.43 cm^{-1}, $\sim$2944.16 cm^{-1},

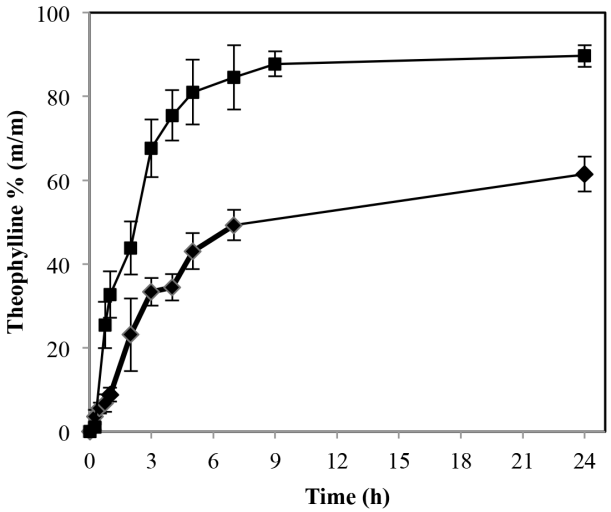

Figure 1. Permeation of theophylline through US-CA and US-SiO_2/CA membranes.

Table 2. Percent swelling, contact angle, and free volume percentages of the membranes.

Membrane	S_w%	ε%	CAn (°)
CA	10*	9	54.14 ± 0.61
SiO_2/CA	13*	11	41.61 ± 1.41
US-CA	66	41	36.30 ± 1.21
US-SiO_2/CA	91	54	32.10 ± 1.31

*values (as given in Table 1) used again here for the integrity of the data comparison

and ∼1737.27 cm^{-1} correspond to O–H, C–H, and C=O groups present in CA. As seen from comparison of the spectra of CA and US-SiO_2/CA, the intensity of the C–H and C=O peak in the spectrum of the US-SiO_2/CA membranes is lower than that of CA membranes. Such an intensity decrease most probably results from the removal of some polymeric material from the membrane by sonication, which probably should lead to a greater free volume, i.e. greater porosity and greater permeation. Ultrasound represents a high-frequency pressure wave. As this pressure wave passes through the medium, regions of high and low pressure are created. This pressure is known as acoustic pressure and it is directly proportional to the energy applied to the system. It causes cavitation and bubbling in viscous systems, e.g., aqueous systems. During the collapse of a bubble or repetitive transient cavitation, extremely high pressures can be generated (∼70–100 MPa), which result in outward propagating shockwaves. Contrary to all chemical or thermal decomposition reactions, ultrasonic depolymerization is a random process that produces fragments of definite molecular size.[31] In aqueous systems, it is known that the chain cleavage occurs preferentially near the mid-point, at the end point, or in any bond in the chain.[32] However, details of the degradation process, which is commonly observed for polymer solutions,[33] are still obscure and little information has been published on polydispersity, which is a useful quantity to show the degradation mechanism.

Similar results related to the effect of ultrasonic waves were reported in the literature; Julian and Zentner[34] studied the ultrasonically mediated solute permeation through cellulose and poly (dimethyl siloxane) films by using hydrocortisone and benzoic acid as permeants. They observed that ultrasonic irradiation increased the permeability coefficients of the films. Grönroos et al.[35] studied the effect of ultrasonic input power

and ultrasonic frequency on the degradation of PVA solutions and they confirmed that the most extensive degradation took place at an ultrasonic frequency of 23 Hz without causing any changes in the chemical nature of the polymer. Price et al.[36] subjected powders of polyethylene, polypropylene, poly (vinyl chloride), and poly (methyl methacrylate) polymers, which were suspended in water, to the irradiation of high intensity ultrasound. They reported that ultrasound changes the particle sizes and surface morphology of the materials. They also reported that the sonication deforms the polymer and removes some of the material in the case of polyethylene film.

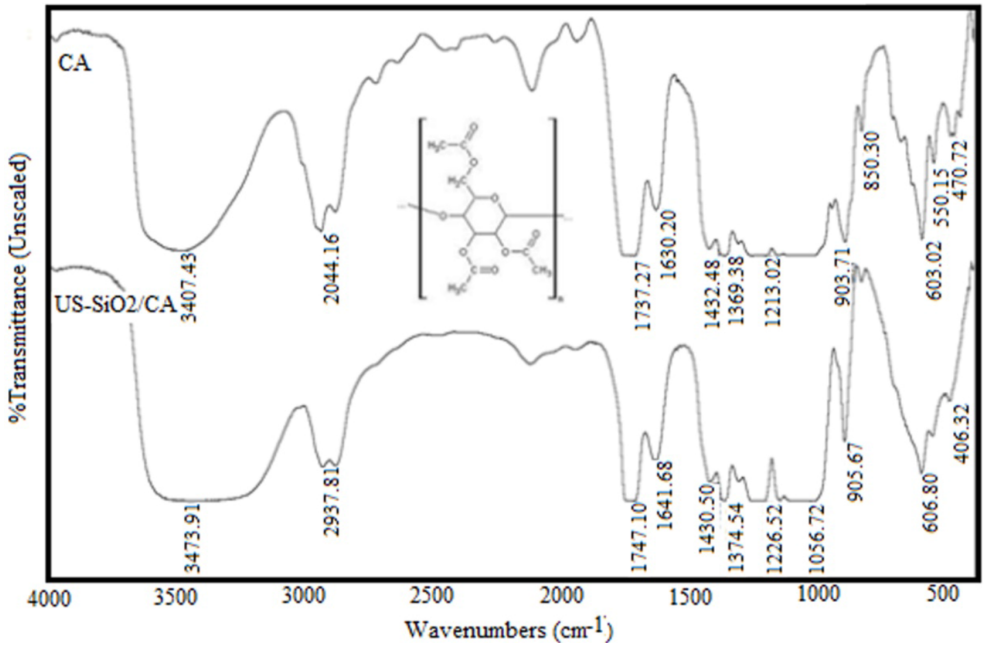

Figure 2. FTIR spectrum of CA and US-SiO_2/CA membranes.

To get an idea about the morphologies of the membranes, they were placed into an electron microscope and their surface and interior images were recorded (Figure 3a) and the SEM image of the swollen US-CA membrane is given in Figure 3b. As reflected in Figure 3a, the inner part of the US-SiO_2/CA membranes has randomly distributed large pores, in addition to smaller pores, and as seen from Figure 3b, a micro-sized porous structure was obtained after ultrasonic treatment of CA membranes.

These results also explain the higher permeation tendency of US-SiO_2/CA membranes than CA, US-CA, and SiO_2/CA membranes.

2.3. Effect of the amount of n-SiO_2 on the permeation of theophylline through US-SiO_2/CA membranes

Since US-SiO_2/CA membranes showed greater permeation among the others, in this part of the study, to determine the amount of SiO_2 on the permeation of theophylline through US-SiO_2/CA membranes, casting solution was prepared by an increment of 5% from 10% to 35% by mass of the dry polymer content of 6% CA (m/v) solution. The results of the permeation are shown in Figure 4. It is explicitly seen that theophylline permeation is not significantly affected by the change in the n-SiO_2 used in the membrane material.

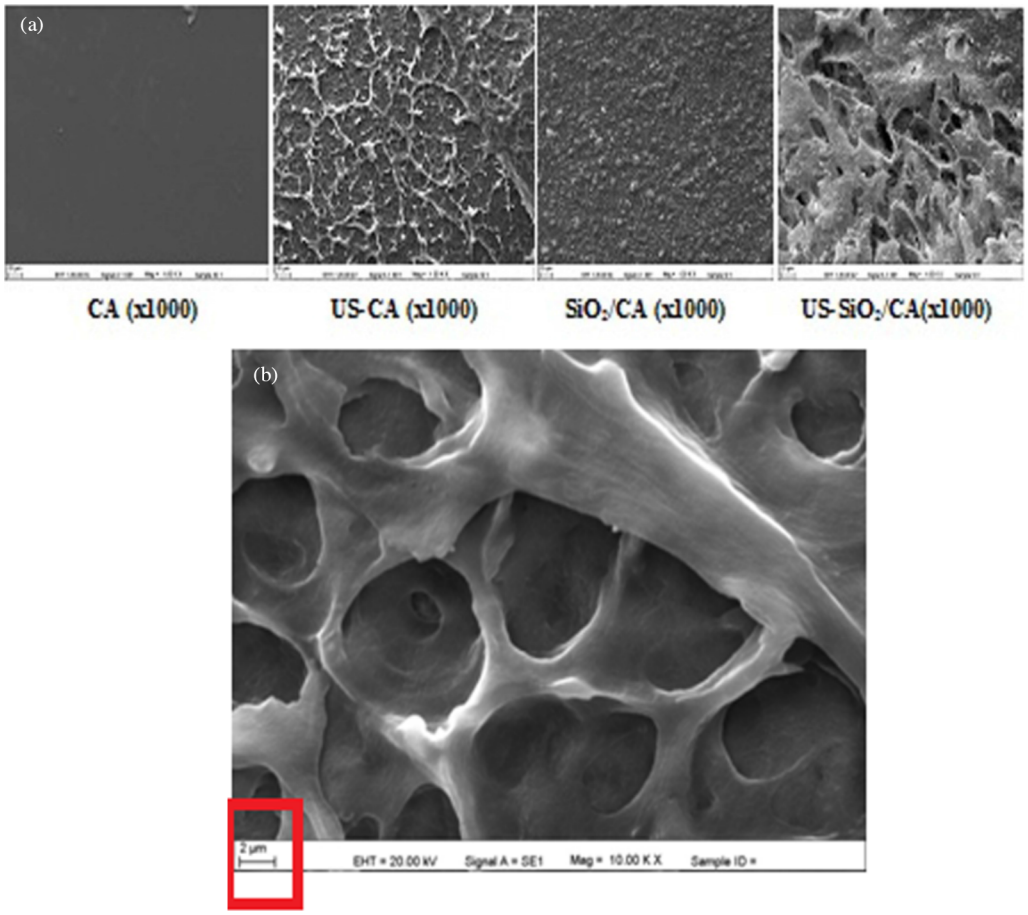

Figure 3. a) SEM images of CA, US-CA, SiO_2/CA, and US-SiO_2/CA membranes. b) SEM image of US-CA membrane swollen in buffer solution.

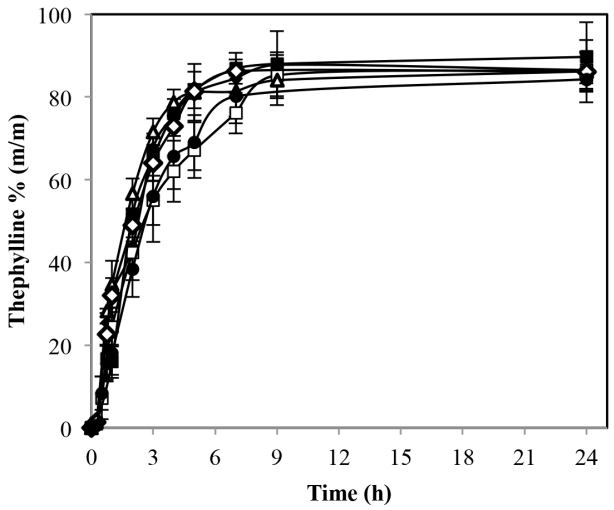

Figure 4. Effect of the amount of n-SiO_2 on the permeation of theophylline through US-SiO_2/CA membranes.

3. Experimental

3.1. Materials

CA (50,000 g/mol, 39.7% acetyl content) and anhydrous theophylline (180.16 g/mol) were supplied by Sigma-Aldrich Co. LLC (Germany). n-SiO_2 (10 nm) was purchased from Aldrich, and it was used without any further process. Acetone (C_3H_6O) (58.08 g/mol; d = 0.79 kg/L), disodium hydrogen phosphate ($Na_2HPO_4.2H_2O$) (141.96 g/mol), and sodium dihydrogen phosphate ($NaH_2PO_4.2H_2O$) (119.98 g/mol) were supplied by Merck Chemicals Ltd.

A contact angle micrometer (Surface Electro Optics PHX 150) was used to determine the interaction of the outer layer of the membrane surface with water. The measured contact angles were the average values of at least five CAn measurements. Surface micrographs of the membranes were obtained by Quanta 200 FEG SEM-FEI Instrument. In order to prepare the samples for the SEM analysis, firstly, they were swollen in a buffer solution of pH 7.4 for 48 h, and then quickly frozen below their freezing point using liquid nitrogen. The sample container was then transferred to a freeze dryer (Labconco, Freezone 6 Stopperin Tray Dryer model) and freeze-dried until the samples were completely dried; then the samples were sputtered with Au/Pd and placed into a microscope.

3.2. Procedure

3.2.1. Preparation of the membranes

CA and SiO_2/CA membranes were prepared by dry-casting method. CA solution was prepared at a concentration of 6% CA (m/v) and acetone was used as a solvent. In order to prepare SiO_2/CA membranes, a homogeneous solution of 6% CA (m/v) in acetone, containing 10% n-SiO_2 by mass, was used as casting solution. A predetermined amount of casting solution was poured into petri dishes and the solvent was allowed to evaporate until complete dryness at constant temperature (40 °C) was obtained. Dried membranes were removed and preserved in a buffer solution of pH 7.4. The thickness of the membranes (l) was determined using a precision micrometer (Aldrich, Germany) by taking the average of at least ten point measurements. For the sonication process, dry-cast CA and SiO_2/CA membranes were immersed in 6 M HCl solution and were placed in a sonicator (Elmasonic X-tra 50 H model). Then the membranes were subjected to sonic waves at a frequency of 35 kHz for definite time intervals. After the sonication process, the membranes were removed and rinsed with water until neutral pH was obtained, and preserved in buffer solutions at pH 7.4. They were called US-CA and US-SiO_2/CA membranes, respectively, after the sonication process. Since sonication affected the physical resistance of the membranes, membrane thickness was optimized in the first part of the study[37] and the suitable thickness for the membranes was determined as 70 μm.

3.2.2. Permeation studies

Permeation studies were carried out in a thermostated water bath, by using a Franz diffusion cell,[38] which consists of a donor compartment and an acceptor compartment separated by the membrane. The donor compartment holds theophylline solution (5 mg/mL) and acceptor compartment was filled with buffer solution at a pH of 7.4. pH adjustments of the solutions were done using a Hanna pH211 model pH meter. The receiver part of the diffusion cell was stirred by a magnetic stirrer operating at constant rotation rate (200 rpm) to obtain uniform composition during the permeation. The receiver solution was sampled periodically and samples were replaced with equal volumes of fresh buffer solution. The concentrations of theophylline solution were determined spectrophotometrically at 272 nm by using a Unicam 4802 UV/VIS double beam spectrometer.

4. Conclusion

The hydrophilicity of CA membranes could only be improved very slightly by using n-SiO_2 as a hygroscopic additive. However, the application of sonic waves to CA and SiO_2/CA membranes enhanced their water sorption tendency and permeation capacity. Therefore, it is confirmed that sonic treatment was an effective, useful method to obtain permeable CA-based membranes.

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