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# Diffusion permeability of hybrid chitosan/polyhedral oligomeric silsesquioxanes (POSS$^{TM}$) membranes to amino acids

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## Abstract

Hybrid membranes of chitosan (Chi), hydrophilic polyhedral oligomeric silsesquioxanes (POSS$^{TM}$, 2.5 mol%) and ethylene glycol diglycidyl ether (EGDGE, 75 mol%) as a crosslinker were prepared by casting the blends onto nonwoven microporous polymer support, drying at 70 °C and treating with 0.5% sodium hydroxide solution. The POSS differed by the tether used: {[3-(2,3-Dihydroxypropoxy)propyl]dimethylsilyloxy}in DL-POSS, 3-aminopropyl in OA-POSS and (tetramethylammonio)oxy in TMA-POSS. The diffusion permeability of the hybrid membranes both to hydrophobic (alanine, tryptophane) and hydrophilic (glutamic acid, lysine) amino acids was investigated to elucidate the effect of POSS on the membrane transport properties. The experiments were carried out at pH 3 and 11, i.e., with the chitosan amino groups fully protonated or deprotonated. Diffusion transport of amino acids was affected by their p*I*, hydrophilic indexes and molecular sizes. Membrane permeability was indirectly affected by the POSS tethers due to changes in the morphology of the hybrid membranes on nanoscale. The longer the tether used, the higher the packing density of chitosan chains in the membrane and the lower its diffusion permeability to amino acids. The TMA-POSS, undergoing hydrolytic-condensation in acidic chitosan solution during membrane preparation, formed large silica segments, which caused the largest morphological disorder in Chi/TMA-POSS membranes and, as result, their highest permeability to all amino acids studied. The contribution of incorporated POSS to transport of amino acids is discussed.

*Keywords:* Chitosan; Polyhedral oligomeric silsesquioxanes; POSS; Organic–inorganic hybrid membranes; Amino acids; Diffusion

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## 1. Introduction

Hybrid polymers with incorporated organosiloxane compounds have been intensively studied in recent decades because fine control of the polymer morphology on nanoscale gives great opportunities for design of new materials, including membranes, with improved performance [1–3].

From the preparation methods of hybrids based on conventional organic polymers and inorganic compounds, the most versatile ones are the *in situ* sol–gel condensation of organosilanes [1–2], incorporation of polyhedral oligomeric silsesquioxanes (POSS) in a host polymer, and polymerization of POSS [3]. Rapid development of the methods is promoted by a large variety of available organosiloxane precursors [4–7].

As far as the morphology of polymer–inorganic hybrids is concerned, polyhedral oligomeric silsesquioxanes, if compared with organosilanes, enable better control of the distribution of inorganic phase in a host polymer [3,8] because of the presence of various polymer-compatible groups (tethers) such as amines, epoxides, esters, halides, olefins, nitriles, phosphines, norbornenes, methacrylates, chlorosilanes, alkoxysilanes, alcohols and phenols, silanols and styrenes [9–10]. Therefore, the morphology of the POSS-based hybrids is more reproducible than that of organosilane hybrids, which form *in situ* inorganic networks with virtually uncontrollable and unpredictable structure [3], distribution and effect on the morphology of a host polymer [7]. Aggregation of POSS in polymers could be minimized

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by adjusting conditions of preparation and using a suitable tether. The effect of tethers on the morphology of an organic network can be predicted by the Monte Carlo simulation; the agreement between the predictions and experiment in polymerization of functionalized POSS is good [11]. The specific surface, pore volume, pore size distribution and degree of crosslinking of a network of functionalized POSS was dependent on the length of tethers. The modeling studies on assembled POSS-polymer networks that are currently underway are expected to open the exciting avenues [11] for creating new polymer–inorganic hybrids with directed morphology.

Excellent polymer–POSS compatibility is given by the formation of covalent and noncovalent bonds between tethers and polymer chains [9]. Due to the rigidity of the $Si_8O_{12}$ cage and flexibility of tethers [12], the POSS molecules act as well-dispersed nanofillers, affecting the morphology and mechanical stability of POSS-reinforced polymer matrices under elevated temperature and deformation.

In our study, hydrophilic POSS$^{TM}$ derivatives with different type of tethers were used to modify the morphology of chitosan (Chi) membranes and consequently their permeability. The use of chitosan, the deacetylated natural polysaccharide—chitin, as a film and membrane material is constantly growing because of high concentration of easily modifiable amino groups, excellent film-forming properties, high hydrophilicity and commercial availability. Chitin is produced mainly from crustaceans and as a by-product of the seafood industry it is cheap [13].

Balanced transport and mechanical properties (sufficient elasticity and small compressibility) are general requirements for chitosan films, coatings and membranes in many applications. Chitosan films and membranes could be used for removal of heavy metal ions (Cu, Ni, Zn, Mn, Pb, Co, Cd, Ag, Mg, Ca, Ba [14]) by coordination with the chitosan amino groups. Highly hydrophilic membranes based on chitosan and its derivatives have shown selective water permeability in pervaporation of organic solvents [15,16]. Chi/$SiO_2$ membranes were already prepared by sol–gel polymerization of tetraethoxysilane in acid chitosan solution [17]. In our previous study, it was shown that the tether type, the Chi/POSS ratio in blends and the method of preparation affect interactions of chitosan with tethers resulting in variation of structural and mechanical stability of the hybrid membranes [18].

The aim of this study is to evaluate the effect of an incorporated POSS, octakis(tetramethylammonio)-POSS$^{TM}$, octakis(3-aminopropyl)-POSS$^{TM}$ and octakis{[3-(2,3-dihydroxypropoxy)propyl]dimethylsilyloxy}-POSS$^{TM}$, on transport of amino acids through the hybrid Chi/POSS membranes. The membranes with the same Chi/POSS ratio and amino acids of different size, isoelectric point (p*I*) and hydrophilicity were used. The contribution of POSS tethers to transport of amino acids through Chi/POSS membranes was evaluated from diffusion, permeability and solubility coefficients.

## 2. Experimental

### 2.1. Preparation of Chi/POSS hybrid membranes

The preparation of Chi/POSS hybrid membranes has been described in detail in [18]. Briefly, 1.5 g of chitosan (MW ~750,000, 4.3 mmol $NH_2$ groups/g, Aldrich, Germany) was dissolved in 100 ml of 1% (v/v) acetic acid and filtered through a glass filter. A POSS$^{TM}$ derivative (Hybrid Plastics$^{TM}$, Fountain Valley, CA, USA) was dissolved in water (TMA-POSS, OA-POSS) or in alcohol (DL-POSS) and centrifuged at 6000 rpm for 10 min to clarify the solutions. POSS solution (2.5 mol% relative to $NH_2$–Chi groups) and then crosslinker (ethylene glycol diglycidyl ether, EGDGE, 75 mol%) were added dropwise to a vigorously stirred chitosan solution. The mixture was evacuated to remove air bubbles, cast on nonwoven tissue and dried at 70 °C for 2 h. The membranes were treated with 0.5% sodium hydroxide solution and thoroughly washed with distilled water.

### 2.2. SEM of Chi/POSS hybrid membranes

A JSM 6400 JEOL scanning electron microscope (SEM) was used for characterization of the membrane surface and fracture covered with a thin platinum-sputtering layer (4 nm). The fractures of the membranes were obtained in liquid nitrogen.

### 2.3. Permeability of Chi/POSS hybrid membranes

Permeability of Chi/POSS hybrid membranes to amino acids (L-tryptophane (Trp), Fluka, Germany, L-alanine (Ala), L-lysine (Lys) and L-glutamic acid (Glu), Wako Pure Chemical Industries Ltd., Japan) was investigated using a two-compartment membrane cell separated by a vertically positioned membrane with a window diameter of 2 cm. Stirred solutions in the cell compartments were kept at $25 \pm 0.1$ °C. Initially, both cell compartments were filled with 47 $cm^3$ of 0.14 mol/$dm^3$ universal buffer solution (0.04 mol/$dm^3$ amounts of acetic, phosphoric and boric acids) adjusted to pH 3 or 11 with 0.2 mol/$dm^3$ sodium hydroxide solution. The solution from the receiving compartment was circulated through the cell of a RIDK-102 differential refractometer (Labio, Czech Republic) connected to a REC 101 recorder (Pharmacia, Sweden). After 30 min (needed for establishing of the baseline), the buffer solution in the feed compartment was replaced with a solution (47 $cm^3$) of an amino acid dissolved in the buffer used and the experiment started. Values of the refractive index in the receiving solution were recorded and converted to the concentration of an amino acid using a calibration curve. The initial concentration in the feed solution was 0.1 mol/$dm^3$ for Ala and Lys but lower for Trp and Glu (0.05 and 0.08 mol/$dm^3$, respectively) because of their lower solubility. Each permeability experiment was repeated with the same membrane after its washing with alkaline and acid buffers and equilibration with