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# THE INFLUENCE OF THE HYDROPHOBIC COMPONENT CONTENT ON THE PROPERTIES OF HYBRID POLYMER-INORGANIC MEMBRANES

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**Abstract.** Hybrid polymer-inorganic membranes with varied composition of polymeric matrix were synthesized by UV-curing of a mixture of acrylic monomers with simultaneous formation of inorganic network *via* sol-gel reaction of tetraethoxysilane. Composition of polymeric counterpart was varied by changing the ratio of hydrophilic and hydrophobic monomers, whereas the content of inorganic counterpart was maintained constant. Morphology, thermal behavior and water uptake of membranes were investigated.

**Keywords:** polymer-inorganic membrane, UV-curing, sol-gel process, acrylate, tetraethoxysilane.

## 1. Introduction

Membrane technology has been widely applied in many fields such as wastewater treatment, seawater desalination, protein purification, gas separation, *etc*. [1] Most specifically, ion-transport across the polymer ion-exchange membranes plays important role in performance of the electrochemical devices such as fuel cell, batteries and electrolyzers [2, 3]. However, for most of the membranes it is difficult to meet the requirements for mechanical strength, separation efficiency, functionality, and cost at the same time. Therefore, it is necessary to synthesize novel materials, develop facile modification strategies, and design more reasonable membrane structures to fulfill optimal properties [4].

Amphiphilic polymer network (APN) is a kind of cross-linked polymer made up of hydrophobic polymeric chains as well as hydrophilic ones via covalent bonding [5]. It can be swollen in water as well as in non-polar solvents. However, the sole hydrophobic or hydrophilic polymer chains in APN will be self-congregated. As a result, microscopic phase separation will take place such that hydrophilic and hydrophobic components will form individual domains. In particular, the authors [6] found that hydrophobic/hydrophilic macromolecular chains retain their own physical and chemical character, respectively. The degree of separation will greatly affect the resulting morphology, which can have adverse effects on the mechanical and transport properties of the resulting membrane. Therefore, for particular application a compromise needs to be found to balance hydrophilicity and hydrophobicity.

One way to achieve such balance is to co-polymerize hydrophilic and hydrophobic monomers simultaneously [7]. Direct copolymerization of suitable functional monomers is, in many instances, also the best route for the design of various functional materials. For example, potassium 3-sulphopropyl acrylate (SPAK) is one of such functional monomers which can be used to introduce proton conductivity to the polymer membrane. Membranes functionalized with sulfonic groups have potential application as proton conductive, ion exchange or water purification materials.

However, in many cases it is necessary to copolymerize SPAK with other monomer(s) in order to improve mechanical characteristics of the membrane and control swelling. Among various monomers which can be copolymerized with SPAK, acrylonitrile is one of the most suitable candidates. It was previously shown that membranes containing acrylonitrile units in their structure exhibit superior inherent ultraviolet (UV) and chemical resistances, thermal stability, and mechanical properties. Also, copolymerization of hydrophilic monomers with acrylonitrile significantly improves mechanical stability of the resulting membrane and reduces its swelling upon exposure to water [8].

Hybrid polymer-inorganic composites have attracted much attention because they often combine both properties of polymers and inorganic components. For instance, by filling polymer with inorganic particles one can introduce optical, magnetic or electrical response;

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improve mechanical and thermal stability, *etc*. Furthermore, combining polymer and inorganic components provides excellent opportunity to promote unique properties, which are not accessible by either of the components alone [9, 10]. Recently, a sol-gel reaction was used to prepare hybrid polymer-inorganic membranes [11].

The aim of this study was investigation of the influence of hydrophobic-to-hydrophilic monomer ratio on the properties and characteristics of the hybrid polymer-inorganic membranes. Since the system chosen for the synthesis of the membranes consists of several components, it is important to study the influence of each component on the characteristics of the obtained material. To achieve this aim, we synthesized series of hybrid membranes by varying the content of hydrophilic and hydrophobic monomers. Membranes were synthesized using *in situ* polymerization method that is simultaneous UV-curing of monomers and formation of inorganic network *via* sol-gel process.

## 2. Experimental

All reagents used for membrane preparation – acrylonitrile (AN), acrylamide (AAm), potassium 3-sulfopropyl acrylate (SPAK), tetraethylorthosilicate (TEOS), *N,N*-methylenebis-(acrylamide) (MBA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), and phosphoric acid (85 wt %) were purchased from Sigma-Aldrich and used as received. Milli-Q® water, absolute ethanol (VWR) and acetone were used as solvents.

The polymeric parts of the membranes were prepared by polymerizing AN, AAm, and SPAK monomers. The feed compositions of monomers used for the preparation of hybrid membranes are summarized in Table 1. Apart of monomers, all compositions contained also 1.0 wt % MBA as a cross-linker. To initiate polymerization, 2.0 wt % of DMPA photo-initiator was used.

Following synthetic protocol was used to prepare hybrid membranes. The aqueous solution containing water-soluble reagents (AAm, SPAK and MBA) was mixed with and appropriate amount of AN containing DMPA photo-initiator for 35 min at 500 rpm. Sol-gel precursor solution was prepared separately by mixing of TEOS, ethanol, water, and phosphoric acid with respective ratio 1:4:2:1.8 mol/mol and continuously stirred at 500 rpm in 323 K water bath for 22 min. Then, sol-gel precursor solution (20 wt % with respect to the total mass of monomers) was added to the monomer mixture before gelation point.

The mixtures containing monomers, MBA, DMPA, and sol-gel precursor were transferred to special glass form (50×20×0.15 mm) and covered with glass slide to prevent the inhibiting effect of oxygen. The formulations were exposed to UV light (365 nm, 15 $J\cdot cm^{-2}$ radiation power) using a multi-lamp BIO-LINK® cross-linker (BLX-365, Witec AG, Switzerland) equipped with five UV lamps (8W, output 0.8W). After UV exposure, the obtained membranes with the average thickness of 100–150 μm were washed with a large excess of acetone and water to remove unreacted monomers and initiator. Finally, membrane samples were dried in an oven at 323 K until constant weight was obtained.

To determine the content of gel-fraction in the synthesized membranes the samples were extracted with methanol for 1 day in a Soxhlet extraction apparatus.

The composition and chemical structure of membranes were analyzed by ATR-FTIR spectroscopy. FTIR spectra of hybrid membranes were recorded using the FTIR Microscope Hyperion 2000 (Bruker, Germany) equipped with both MCT detector and ATR objective coupled to FTIR spectrometer Vertex 70 (Bruker, Germany) in 600–4000 $cm^{-1}$ range with the resolution of 4 $cm^{-1}$. To analyze and compare the data, spectra were normalized with respect to the band of constant component (1183 $cm^{-1}$, stretching vibration of S–O, internal reference approach) [12]. TGA analysis was done using TA Instruments Q5000 (USA). The samples were heated at the rate of 10 K/min from the room temperature to 1073 K under nitrogen atmosphere.

The morphology of polymer-inorganic membranes was investigated by scanning electron microscopy (SEM) using NEON 40 FIB-SEM workstation (Carl Zeiss AG, Germany) operated at 5 kV. For cross-sectional imaging, dehydrated samples were fractioned upon being immersed in liquid nitrogen. Before imaging, the samples were coated with 3 nm of Pt layer.

*Table 1*

**Monomer feed compositions used for the preparation of hybrid membranes**

| Sample | SPAK, wt % | AAm, wt % | AN, wt % |
|---|---|---|---|
| PS1 | 25.2 | 66.6 | 8.2 |
| PS2 | 25.2 | 50.2 | 24.6 |
| PS3 | 25.2 | 33.9 | 40.9 |
| PS4 | 25.2 | 17.6 | 57.2 |

Water uptake of the composite membranes was determined by measuring of the mass difference before and after hydration. Before measuring, the samples were dried at 323 K until constant weight was obtained. Dried and weighed membranes were placed in deionized water for 24 h at different temperatures. Subsequently, the samples were taken out from water, wiped with filter paper to remove droplets of non-adsorbed water and weighted immediately. Water uptake is calculated based on 5 independent measurements using the following equation:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \cdot 100\%$$

where $m_{dry}$ and $m_{wet}$ are masses of dry and hydrated membrane, respectively.

## 3. Results and Discussion

The composition of obtained hybrid polymer-inorganic material is an important parameter that determines the membrane properties and ultimately its practical application. To confirm the structure of the synthesized polymers we realized methanol extraction of the obtained films in a Soxhlet apparatus and defined the gel-fraction content in them. The content of gel-fraction in our films was determined to be 98.92–98.98 % (Table 2) indicating that acrylic monomers polymerize till high degree of conversion and practically the entire amount of monomers form copolymer with cross-linked structure insoluble in organic solvent. The absence of stretching vibration of double bonds in FTIR spectra (Fig. 1) of synthesized materials also confirms the completeness of photoinitiated polymerization process.

*Table 2*

**Gel-fraction content in hybrid membranes**

| Sample | Gel-fraction, wt % |
|---|---|
| PS1 | 99.02 |
| PS2 | 98.92 |
| PS3 | 98.98 |
| PS4 | 99.62 |

Since we added a certain amount of sol-gel system to polymerizing composition of monomers before the start of gelling of sol-gel system, we suggest formation of a joint organic-inorganic network due to simultaneous sol-gel reaction and polymerization process. The authors [13] stated that during *in situ* radical polymerization of monomers in a sol-gel reaction the hydrogen bonding interaction and/or physical entrapment of monomers in silica matrix are strong enough to afford homogeneous polymer hybrids. The organic-inorganic hybrids synthesized by us were transparent, indicating their homogeneity.

The synthesized films were characterized by FTIR to investigate their chemical composition (Fig. 1a). The broad bands at around 3400–3100 cm$^{-1}$ are observed due to amino groups without hydrogen bonds and with hydrogen bonds [14, 15]. The characteristic band at 2243 cm$^{-1}$ is ascribed to the stretching vibration of C≡N groups. The most prominent absorption bands are related to NH amide groups at 1655 cm$^{-1}$ characterized by an intensive Amide I band $\nu$(C=O) and Amide II at 1612 cm$^{-1}$, which is typical for polyacrylamide spectrum [12]. A good correlation between theoretically expected and experimentally observed absorption of acrylonitrile and acrylamide characteristic bands in the obtained membranes can be noticed (Fig. 1b). The bands at 1655 and 1612 cm$^{-1}$ are decreasing with the reduction of acrylamide content, whereas the band referred to C≡N group at 2243 cm$^{-1}$ rises with increasing of acrylonitrile content. Furthermore, the infrared spectra shown in Fig. 1a also reveal absorption bands, which prove the presence of inorganic component in all samples: Si–O bonds of siloxane network give an absorption peak at 982 cm$^{-1}$, stretching vibration $\nu$(Si–O), with intensities that remain almost constant for all samples.

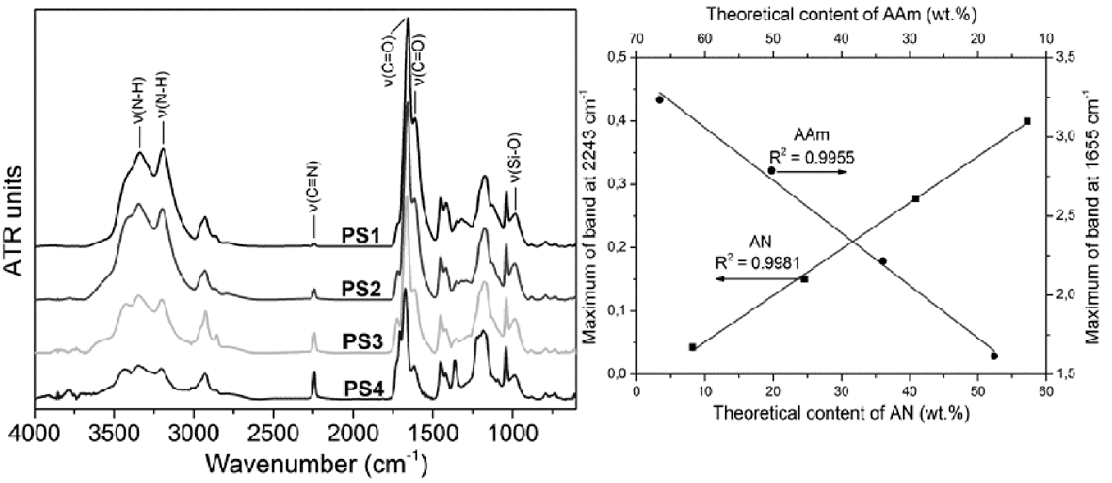
The integral and differential thermograms of hybrid membranes with varied monomer composition are shown in Fig. 2a and 2b, respectively. Three stages of thermal decomposition can be identified for all the membranes. The first weight loss corresponds to the evaporation of bound water, which can be attributed to the presence of sulfonic groups and inorganic component in membrane. Differential curves of the investigated membranes show a band between 473 and 623 K with a peak at 523 K, which is attributed to the decomposition of sulfonic groups [16]. The most pronounced weight loss at the temperatures above 673 K was assigned to the main polymer chain degradation. The effect of polymer matrix composition was observed only at the first stage: the weight loss shifts to the low temperature region with increasing of acrylonitrile content (sample PS4).

SEM images depicting internal morphologies of hybrid membranes with varied AN/AAm ratios are shown in Fig. 3. From SEM overview images, it can be seen that for all samples the whole membrane cross-section is quite uniform. Nevertheless, the ratio of the hydrophobic to hydrophilic monomer content influences the morphology of membranes. Namely, for the samples with lower content of acrylonitrile (PS1 and PS2) holes can be observed (Figs. 3a and 3b). For PS3 sample (Fig. 3c) the number of holes, as well as their size, substantially decrease as compared to PS1 and PS2. Finally, for PS4 sample with the highest AN content no holes were found (Fig. 3d). In contrast, topologically inhomogeneous regions, much larger in size than the holes, are observed in the PS4 sample. From the comparison of SEM images, it is obvious that the number and size of the holes both depend on the amount of acrylonitrile. There are actually two possible reasons of such hole formation: (1) as a result of solvent evaporation during UV-curing, and (2) polymerization-induced phase separation, that is when polymerized chains segregate to the internal interface regions present or formed within polymerized network.

At investigation of our membranes using the microanalysis system INCA Energy 350 the content of silica was found to be ~2 %.

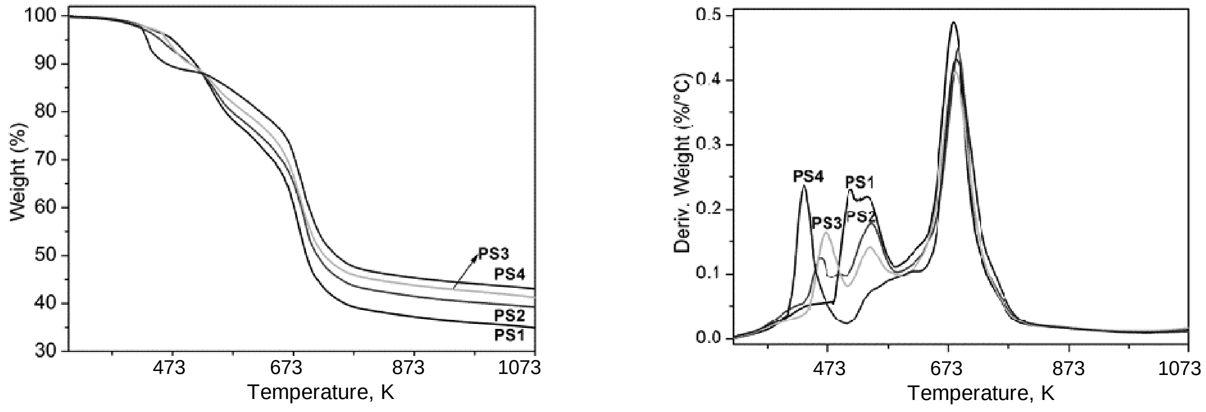
The water uptake (WU) reflects swelling and mechanical stability of a membrane, which are directly related with the performance and suitability of the obtained material. The prepared membranes show relatively high water uptake (up to 1800 wt %) (Fig. 4), that makes them attractive for the application as water superabsorbents [17].

Such high WU values could be attributed to the high sulfonic group content, which has a strong affinity to water. However, the effect of temperature on WU is much smaller as compared to the effect of monomer composition. It was quite interesting to observe that WU of the hybrid membranes containing various acrylonitrile/acrylamide ratios shows non-monotonous dependency. With gradual increase of AN content (up to 40 wt %) WU of hybrid membranes varies slightly, showing weak maxima for PS2 sample (24.5 wt % of AN). However, WU steeply drops down almost three times when AN content increases from ca. 40 to 57 wt %. The obtained results reveal clear correlation between chemical composition of synthesized membranes and their water uptake. Furthermore, the above results suggest that there should be an optimal monomer composition at which preferred properties of the membrane (*e.g.* high water uptake) are maximized. More specifically, the membranes containing up to 40 wt % of AN (monomer feed based) maintain their high water uptake despite substantially increased hydrophobic component content. On the other hand, the presence of holes does not show much influence on WU (compare morphology and WU of PS2, PS3 and PS4).



a) b)

**Fig. 1**. FTIR spectra of hybrid membranes with varied monomer ratios (a) and correlation between the absorption maximum of C≡N band at 2243 cm$^{-1}$ and Amide I band at 1655 cm$^{-1}$ *vs*. monomer feed content (b)



a) b)

**Fig. 2.** Integral (a) and differential (b) thermograms of hybrid membranes with varied monomer ratios

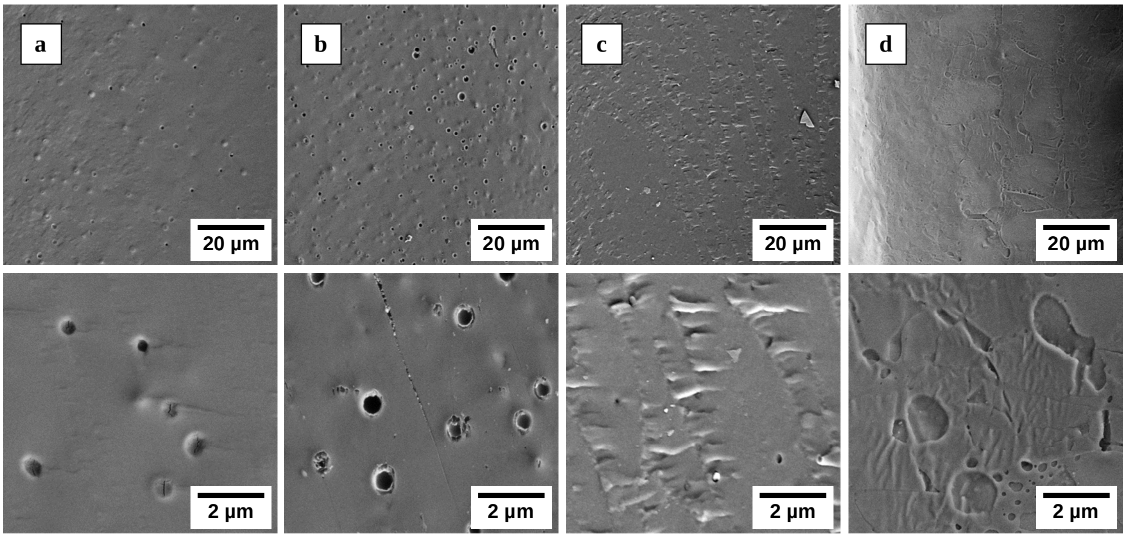


**Fig. 3**. Overview images (top) and high magnification (bottom) SEM images of hybrid membranes with varied monomer compositions: PS1 (a); PS2 (b); PS3 (c) and PS4 (d)

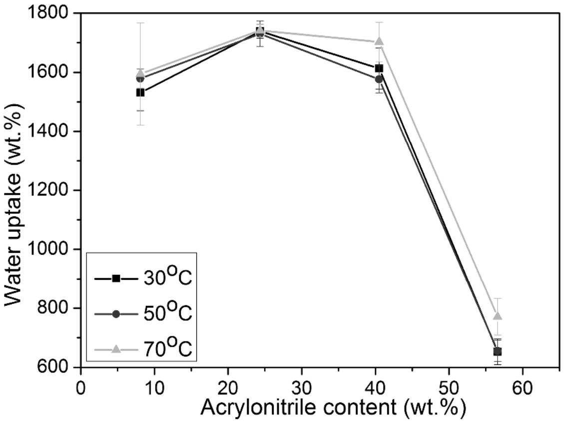


**Fig. 4**. Water uptake of hybrid membranes as function of AN content

## 4. Conclusions

In this work, hybrid polymer-inorganic membranes were synthesized by photo-initiated radical polymerization in combination with *in situ* sol-gel process. The prepared hybrid membranes have potential for the application as hydrogel, ion-exchange membranes or fuel cell electrolyte membranes. The influence of the polymeric matrix composition, namely, the ratio between hydrophobic and hydrophilic components, on the properties of the obtained membranes was investigated. The morphology and thermal stability of the membranes depend on the composition of polymeric matrix. The membranes possess high water uptake capability in relatively large monomer composition range. However, in case of membranes with the highest acrylonitrile content studied (ca. 57 wt % of AN) WU steeply decreased. So far, such behavior is not completely understood. The obtained results suggest that there might be an optimal monomer composition at which membranes maintain high water uptake alone with uniform internal structure (*e.g.* sample PS3). The membrane morphology, in turn, depends on the ratio of hydrophilic and hydrophobic monomers in polymerized mixture. Further investigations which will allow better understanding structure-properties relationship are currently in progress.

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## ВПЛИВ ВМІСТУ ГІДРОФОБНОГО КОМПОНЕНТУ НА ВЛАСТИВОСТІ ГІБРИДНИХ ПОЛІМЕР-НЕОРГАНІЧНИХ МЕМБРАН

***Анотація.*** *УФ-затвердженням суміші акрилатних мономерів з одночасним формуванням неорганічної сітки внаслідок золь-гель перетворення тетраетоксисилану синтезовано гібридні полімер-неорганічні мембрани з різним складом полімерної матриці. Склад полімерної складової варіювався зміною співвідношення гідрофільного і гідрофобного мономерів, у той час як вміст неорганічної складової залишався постійним. Досліджено морфологію, термічну поведінку та водопоглинання синтезованих мембран.*

***Ключові слова:*** *полімер-неорганічна мембрана, УФ-затвердження, золь-гель процес, акрилат, тетраетоксисилан.*