

Hybrid Organic-Inorganic Composites with Different Hydrophobic/Hydrophilic Component Ratio

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Abstract – Hybrid organic-inorganic composites with varied hydrophilic/hydrophobic monomers ratio were synthesized by UV-curing of a mixture of acrylic monomers with simultaneous formation of inorganic network via sol-gel reaction. The composition of obtained composites was investigated by FTIR spectrometry. Thermal stability of the synthesized materials was studied by TGA.

Key words – hybrid organic-inorganic membrane, UV-curing, sol-gel process, acrylate, tetraethoxysilane

I. Introduction

Membrane technology has been widely applied in many fields such as wastewater treatment, seawater desalination, protein purification and gas separator [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]. However, most of the membranes are difficult to meet the requirements of 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.

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. 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 chains will form individual domains. In particular, hydrophobic/hydrophilic macromolecular chains remain their own physical and chemical character, respectively.

One way to achieve such balance is to copolymerize hydrophilic and hydrophobic monomers simultaneously. Direct copolymerization of suitable functional monomers is, in many instances, the optimal route for the design of many functional materials. Membranes functionalized with sulfonic groups have potential application as proton conductive, ion exchange or water purification 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. However, in most cases it is necessary to copolymerize

SPAK with other monomer in order to improve mechanical characteristics of the membrane and control swelling. Among various monomers which can be copolymerized with SPAK acrylonitrile was chosen by us as the suitable candidate. Previously it was shown that copolymerization of hydrophilic monomers with acrylonitrile significantly improves mechanical stability of the resulting membrane and reduces its swelling upon exposure to water or methanol.

Hybrid organic-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, 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 components alone. Recently, the sol-gel reaction was used to prepare the hybrid organic-inorganic materials. The role of inorganic counterpart is to improve thermal stability and water retention. Moreover, sol-gel system might be a compatibilizing agent between two phases in polymer composite when *in situ* polymerization method is used to create hybrid membrane.

In present work, we synthesized series of hybrid organic-inorganic membranes with different content hydrophilic and hydrophobic monomers. Acrylonitrile (AN), acrylamide (AAM) and SPAK were used as monomers, whereas TEOS was used as precursor for the inorganic counterpart. Membranes were synthesized using *in situ* polymerization method that is simultaneous UV-curing of monomers and formation of inorganic network via sol-gel process. The aim of this study was the investigation of the influence of hydrophobic/hydrophilic monomer ratio on the properties and characteristics of the obtained membranes.

II. Experimental

Sol-gel precursor solution was prepared by mixing of TEOS, ethanol, water and phosphoric acid (85%) with respective ratio 1:4:2:1.8 mol/mol. The mixture was continuously stirred at 500 rpm at in 50°C water bath. Then, sol-gel precursor solution (20 wt %) was added to monomer solution till gelation point. Polymer matrix of membrane based on AN, AAM and SPAK was synthesized by photoinitiated free radical copolymerization with 1 % wt. MBA as a cross-linker. All compositions contained 2 % wt. DMPA as a photoinitiator.

ATR-FTIR spectra of membranes were recorded using Hyperion 2000 FTIR (Bruker, Germany) equipped with both MCT-detector and ATR-Objective coupled to FTIR spectrometer Vertex 70 (Bruker, Germany). The wavenumber range was 600-4000 cm⁻¹ with resolution of 4 cm⁻¹. Spectra were normalized with respect to the band of constant component (1183 cm⁻¹, stretching vibration of S-O in potassium 3-sulphopropyl acrylate, internal reference approach).

TGA analysis was done using TA Instruments Q5000 (USA). Samples were heated at the rate of 10 K min⁻¹ from the room temperature to 900°C under nitrogen atmosphere.

III. Results and discussion

The composition of obtained hybrid organic-inorganic material is an important parameter that determines the membrane properties and ultimately its practical application. Synthesized films were characterized by FTIR to investigate their chemical composition (Fig. 1). The broad bands occurring at around 3400-3100 cm^{-1} are observed due to amino groups without hydrogen bonds and with hydrogen bonds. The characteristic band at 2243 cm^{-1} is ascribed to the stretching vibration of $\text{C}\equiv\text{N}$ groups. The most prominent absorption bands are related to NH amide groups at 1655 cm^{-1} characterized by an intensive Amide I band $\nu(\text{C}=\text{O})$ and Amide II at 1612 cm^{-1} , which is typical for polyacrylamide spectrum. It can be noticed a good correlation between theoretically expected and experimentally observed absorption of acrylonitrile and acrylamide characteristic bands in the obtained membranes. The bands at 1655 cm^{-1} and 1612 cm^{-1} are decreasing with the reduction of acrylamide content, whereas the band referred to ciano group rise with increasing of acrylonitrile content. Furthermore, the infrared spectra as shown in Fig. 1, also reveal absorption bands indicate the presence of inorganic components in the samples: Si-O bonds of siloxane network give the absorption peak at 982 cm^{-1} (stretching vibration $\nu(\text{Si-O})$) with an intensities which remain almost constant for all samples.

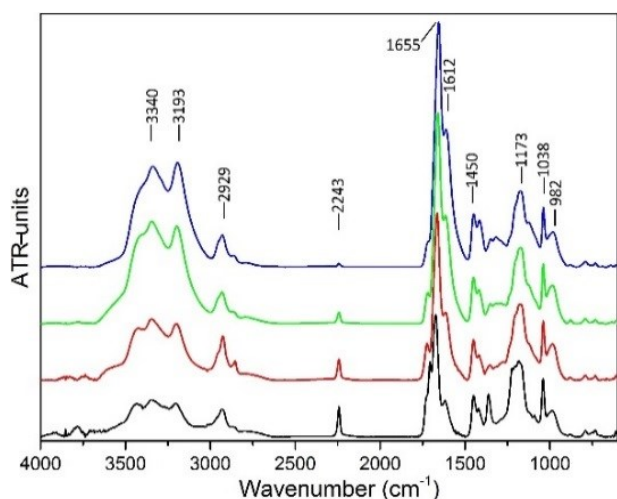


Fig. 1. FTIR spectra of HOIM with varied AN:AAM ratio: (a) 8:67; (b) 25:50; (c) 41:34; (d) 57:18

The integral and differential thermograms of membranes containing varied AN/AAM ratio were recorded. Three stages of the thermal decomposition can be considered for the membrane. The first weight loss was shifted to the low temperature region due to the effect of the membrane composition on thermal stability. In the thermogram for membrane with the lowest content of acrylonitrile two weight losses at the range of 210-250°C exist, close each to other. In contrast, first weight loss shifts to the low temperature region with increasing of acrylonitrile content. The decomposition temperature that occurred at 250°C can be assigned to the decomposition of

sulfogroups. The weight loss at around 400°C was assigned to the main chain polymer degradation.

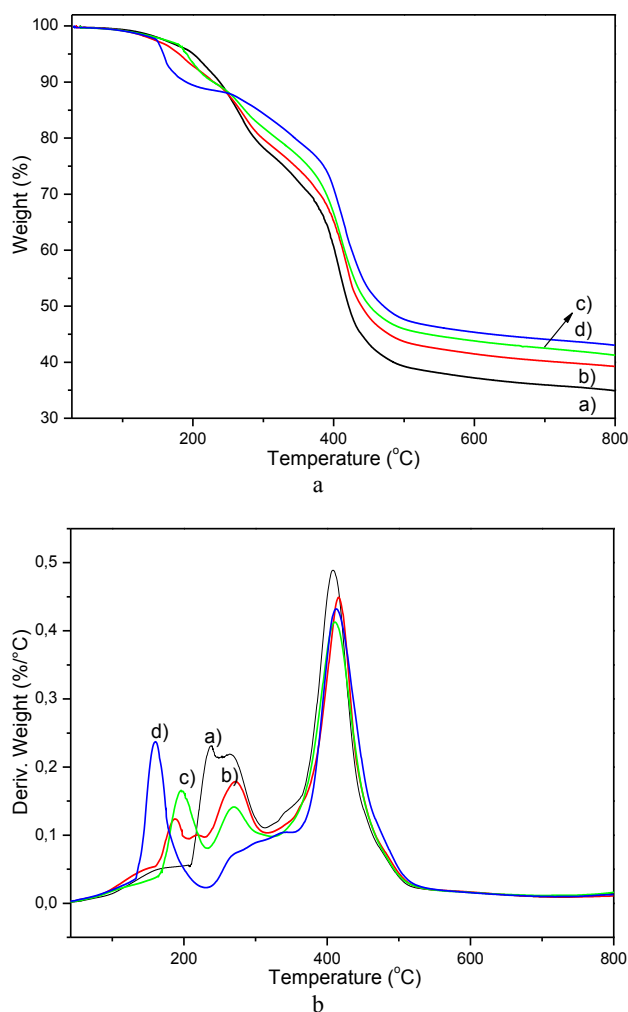


Fig. 2. Integral and differential thermograms of HOIM with varied ratio of AN/AAM (% wt.): (a) 8:67; (b) 25:50; (c) 41:34; (d) 57:18

Conclusion

In this work, hybrid organic-inorganic membranes were synthesized by *in situ* polymerization method. The influence of the polymeric matrix composition, namely, the ratio between hydrophobic and hydrophilic components, on the properties of obtained membranes was investigated. Thermal stability of the membranes depends on the composition of polymeric matrix. Membranes suggested in this paper need further investigation for the application as hydrogel ion-exchange membrane or fuel cell electrolyte membrane.

References

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