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Functionalization of hybrid organosilica based membranes for water desalination – Preparation using Ethyl Silicate 40 and P123

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ABSTRACT

Hybrid organosilica are recency type of membranes derived from Ethyl Silicate 40 (ES40) and pluronic triblock copolymer (P123) precursors. These materials were employed to improve the hydrostability of pure silica matrices becomes stronger especially when applied for water desalination. This work shows for the first time the functionalization of hybrid ES40-P123 materials which prepare for organosilica membranes fabrication. The aim of this work is to investigate the vibration of siloxane (Si-O-Si), silanol (Si-OH) and silica-carbon (Si-C) groups of hybrid organosilica (ES40-P123) xerogels measured by Fourier Transform Infra-Red (FTIR) and fityk software. Silica sols are produced by combining ES40 and P123 materials using sol-gel method through hydrolysis and condensation reactions with acid-base catalysts. P123 was added together with base catalyst in sol mixtures to form hybrid silica P123 structures. This process was held at 50 °C for 3 h of reflux. The final molar ratios of hybrid organosilica (ES40-P123) of the ES40:ethanol:nitric acid:H₂O:ammonia:P123 were calculated to be 1:120:0.0022:16:0.009:0.1, respectively. From the FTIR measurement, the functionalization of organosilica (ES40-P123) xerogels was detected as siloxane (Si-O-Si) groups at the wavelength 1067 and 1220 cm⁻¹. Silanol (Si-OH) groups at 958 cm⁻¹. Then, silica-carbon (Si-C) group was detected at wavelength 801 cm⁻¹. The presence of silica-carbon indicates the organosilica structure become enhanced and more stable toward water.

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1. Introduction

The development of functionalization of silica materials has become an important requirement in recent years. Lately, many studies often get attracted most commonly in silica material for membrane fabrication. The silica membranes give a good performance [1,2], thermal stability [3] and good molecular sieving properties. The process of functionalization of this silica material becomes the basic knowledge to understand the silica materials to be applied for water desalination application. However silica has hydrophilic reacts when in contact with water so that can resulting poor performance on desalination application [4]. Some studies have been reported to improve silica material performance

for water treatment including carbon content [4,5], hybrid organic-inorganic [6] and metal oxide on silica matrices [7].

Recently, Wang, Wang [8] using interlayer-free ES40 derived silica membranes fabricated for seawater desalination by Rapid thermal treatment (RTP). Whereas other researches using Tetra-ethyl orthosilicate (TEOS) as conventional silica precursor membranes to fabricate silica membrane for desalination application. ES40 precursor has a very few studies in literature compared to the extensively studied TEOS precursor especially in the sol-gel process. ES40 as a partially-condensed silica precursor from TEOS can form a strong silica structure which more resistant to thermal stress and expansion. There is a need fundamentally to understand the sol-gel process and functional evolution of the siloxane (Si-O-Si), silanol (Si-OH) and silica-carbon (Si-C) groups from ES40 precursor. The degree of sol-gel evolution was evaluated by the area ratios of silanol versus siloxane and silanol versus silica-carbon groups calculated from FTIR spectra. These studies will form the bases for the preparation of hybrid organosilica (ES40-P123) xerogels for water desalination application.

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Therefore, this work investigates the chemical effects of P123 as carbon content embedded into silica network with ES40 as precursor derived silica membranes via sol gel method for water desalination application. Sol gel method is very popular in the field of membrane technology [9]. Subsequently, an optimised P123 synthesis is chosen to be embedded to the preparation of hybrid organosilica (ES40-P123) membranes. Hybrid organosilica (ES40-P123) xerogels powders were characterised by FTIR and fityk software using Gaussian line shapes with least square fit routine to functionalization the vibration, stretching and bonding modes on silica network. The FTIR determine to the combination of the fundamental of vibrational bands [10]. In addition, fityk software is a tool for providing extensive information on the surface area of materials during vibration and stretching's [11,12]. This work also demonstrates the difference vibration, stretching and bonding modes on silica network between hybrid organosilica (ES40-P123) and pure ES40.

2. Methodology

2.1. Chemical and materials

Hybrid organosilica (ES40-P123) sol was prepared by sol-gel method with acid-base catalyst using ethyl silicate (ES40, Indonesian Chemicals of PT. Grasindo Multi Sentosa) as silica precursor and triblock copolymer Pluronic P123 (PEG, 35 wt%, Sigma-Aldrich) as carbon template. Ethanol (EtOH, 70%) and aquadest as solvent and dilute nitric acid (1M HNO₃, Merck) and ammonia (0.00003M NH₃, Merck) as acid-base catalysts.

2.2. Preparation and characterization of silica xerogels

The synthesis of hybrid organosilica (ES40-P123) thin film procedure by sol-gel method with acid-base catalyst is similar to previous research by Elma, Yacou [13], however in this works using ES40 as silica precursor instead tetraethyl orthosilicate (TEOS). First of all, ES40 was added wisely into ethanol and stirred for 5 min at 0 °C. Nitric acid solution (0.00078M HNO₃, Merck) was dropped wisely into the mixtures during stirring and reflux for an hour at 50 °C as can be seen on Fig. 1. Afterward ammonia solution (0.00003 M) and P123 were added together into solution and drop wisely at the same previous conditions and continued to reflux for 2 h. Whilst pure ES40 sol obtained from organosilica sol without employing of P123. The obtained of organosilica sol were cooled at room temperature and measuring of pH sol. The obtained sol was dried at 70 °C in oven for a day. The dried sol is

called as xerogel of hybrid organosilica (ES40-P123) and grounded it into powder and calcined at 450 °C for an hour by rapid thermal processing (RTP) technique. The final molar ratio of hybrid organosilica (ES40-P123) of the ES40:ethanol:nitric acid:H₂O:ammonia:P123 were calculated to be 1:120:0.0022:16:0.009:0.1, respectively. In other hand, the final molar ratio of pure ES40 sols is ES40:ethanol:nitric acid solution (1M HNO₃, Merck):H₂O:ammonia solution (0.00003M NH₃, Merck) were calculated to be 1:37.5:0.1:35:0.00296, respectively. Xerogel of pure ES40 was calcined at 600 °C. All xerogels were characterized by Fourier Transform Infrared (FTIR) in order to investigate the functional groups of siloxane (Si-O-Si), silanol (Si-OH) and silica-carbon (Si-C) groups at wavelengths ranging from 400 to 4000 cm⁻¹.

3. Results and discussion

3.1. Xerogel characterization

The FTIR spectra was carried out to investigate the existence of functional groups and bonding types of siloxane (Si-O-Si), silanol (Si-OH) and silica-carbon (Si-C) in silica xerogel samples. As shown in Fig. 2. The IR spectra of dried silica xerogels are shown the peak of siloxane (Si-O-Si), silanol (Si-OH) and the bonding groups of silica-carbon (Si-C) groups in the matrices. The IR spectra was vibrational bands at wavelength 600–1400 cm⁻¹.

Peaks shown in the wavelength represent the vibration of functional groups. The asymmetrical vibration (ν_{as}) of siloxane (Si-O-Si) group is represented at 1000–1200 cm⁻¹ [14] as can be seen in this work the presence of siloxane (Si-O-Si) groups on hybrid organosilica (ES40-P123) indicates at wavelength 1067 and 1220 cm⁻¹ then pure ES40 indicates at wavelength 1076 and 1225 cm⁻¹. The peak at 800 cm⁻¹ indicates the symmetrical vibration (ν_s) of siloxane (Si-O-Si) group [15] as can be seen on this work from pure ES40 detected at wavelength at 795 cm⁻¹. Then the existence of silica-carbon (Si-C) group identified as carbon (CH₃) compounds bind silica compounds at wavelengths of 760–960 cm⁻¹ [16]. The copolymer P123 on hybrid organosilica (ES40-P123) has a function as carbon content that changes the silanol (Si-OH) to silica-carbon (Si-C) group. Silanol (Si-OH) was replaced as siloxane (Si-O-Si) or new bonding of silica-carbon (Si-C) groups [17]. As can be seen on Fig. 2. The existence of silica-carbon (Si-C) group detected at wavelength 801 on hybrid organosilica (ES40-P123).

Furthermore, the symmetrical vibration (ν_s) of silanol (Si-OH) group found at wavelength 960 cm⁻¹ and contributes to hydrophi-

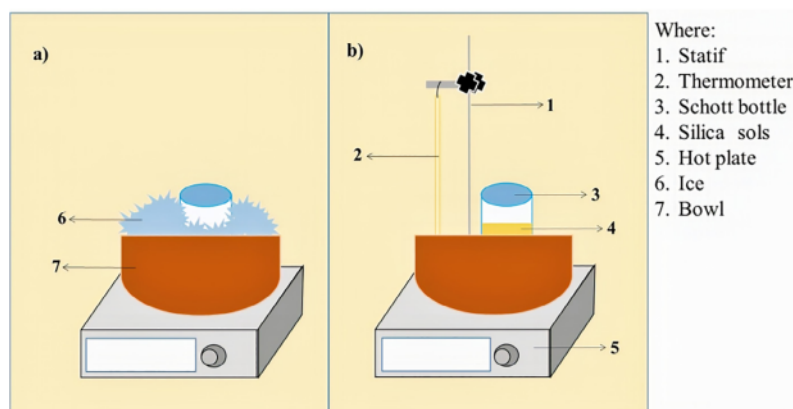


Fig. 1. Set-up for (a) hydrolysis; (b) condensation reaction to form silica structure in the sol-gel process.

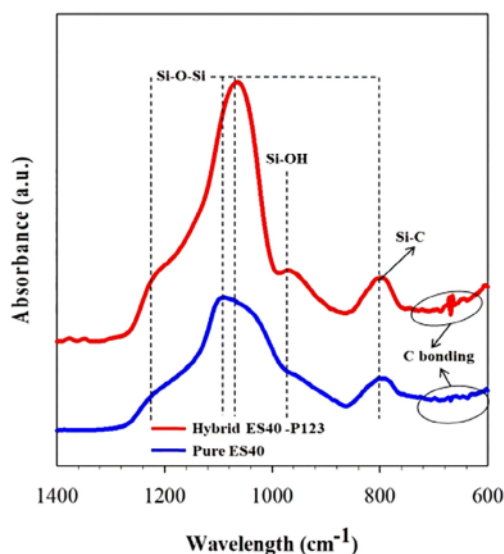


Fig. 2. FTIR Spectra of hybrid organosilica (ES40-P123) calcined at 450 °C and pure ES40 calcined at 600 °C.

lic properties [15]. As can be seen on Fig. 2. The silanol (Si-OH) group for both samples from this work were indicated at wavelength 958 and 952 cm^{-1} between hybrid organosilica (ES40-P123) and pure ES40, respectively.

Furthermore, the peak deconvolution of the absorption bands on organosilica (ES40-P123) and pure ES40 over the wavelength 1280–760 cm^{-1} was performed with fitly software using Gaussian line shapes with least square fit routine [18] and peak areas were measured for the normalized spectra using a local baseline. To perform a quantitative analysis, deconvolution of the peaks was used to identify various vibrations in the overlapping regions. The peak deconvolution position can analysis regarding the area of siloxane, silanol and silica-carbon group for the xerogels are analysed such as presented in Table 1.

As can be seen on Table 1, shows the peak area which allows a comparison of the degree of condensation between hybrid organosilica (ES40-P123) and pure ES40. The copolymer P123 here as carbon content. A carbon contains in P123 is replacing a hydrogen that bonds with silica [17]. There is a strong correlation between carbon content ratio and peak area. Where a high ratio of carbon content corresponds to a low silanol concentration and vice versa. As can be seen on Table 1, that the lowest peak area of silanol is hybrid organosilica (ES40-P123). Through Table 1, was investigated by deconvolution to calculate the peak area ratio of the silanol versus siloxane and silanol versus silica-carbon groups as shown in Fig. 3.

The peak area ratio of silanol versus siloxane and silanol versus silica-carbon between hybrid organosilica (ES40-P123) and pure ES40 show the lowest area ratios are hybrid organosilica (ES40-P123) then the highest ratios are pure ES40. This indicates the high surface area of silanol (Si-OH) was higher than siloxane (Si-O-Si) and vice versa. Otherwise, the lowest ratio indicates the silanol (Si-OH) bond was replaced as siloxane (Si-O-Si) bridges or new

Table 1

The peak area of Siloxane, Silanol and Silica-carbon groups.

Membrane types	Siloxane (Si-O-Si)	Silanol (Si-OH)	Si-C
Hybrid P123	14.3494	0.0146	0.7750
Pure ES40	9.5806	0.6152	0.3718

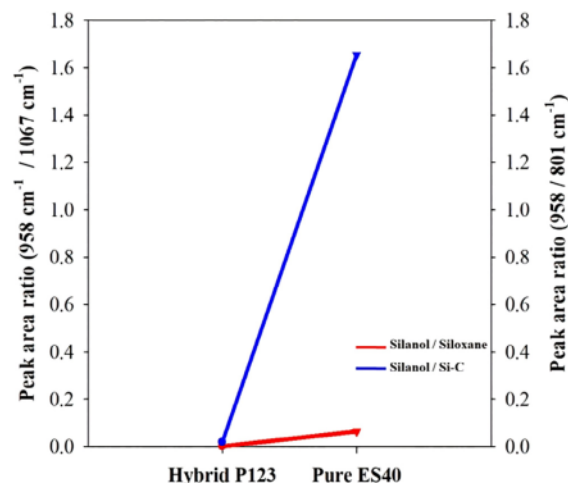


Fig. 3. Illustrates a representative the peak deconvolution of organosilica (ES40-P123) and pure ES40.

bonding of silica-carbon (Si-C) [17]. So, it suggested that siloxane formation is promoted via the condensation reactions by the base catalysed sol-gel method. Therefore, based on these results, the P123 as carbon chain in silica network on hybrid organosilica (ES40-P123) incorporation samples produce more siloxane and silica-carbon groups that should be more hydrophobic and hydro-stable rather than pure ES40. Rangelova, Aleksandrov [19] reported that high bonding of carbon in materials will gives the higher hydrostability. The assignment of the fitted peaks on hybrid organosilica (ES40-P123) and pure ES40 from Fig. 3, are summarized in Table 2.

Meanwhile if this work is compared to the other researches as can be seen on Table 2, the similar results were reported by Elma, Wang [5] that fabricated silica-carbon membrane from TEOS-P123 has a higher area ratio of silanol/siloxane rather than this work of hybrid organosilica (ES40-P123). This could be happened due to the different silica precursor that Elma, Wang [5] research used TEOS. Then another research by Wang, Wang [8] that fabricated silica membrane from pure ES40 also has a higher area ratio of silanol/siloxane rather than this work of pure ES40. This could be explained between area ratios and sol-gel ratios have strong correlation reported by Wang, Wang [20] that the concentration of the silanols is significantly promoted by low nitric acid ratio or high ethanol ratio. This could be happened due to the different sol mixtures composition used in this work.

The research of RTP technique reported by Elma, Setyawan [21] that RTP results in great reducing time fabrication less than 1 day over Conventional Thermal Process (CTP) technique. Whereas CTP is a slow calcination and takes 4 h with 1 $^{\circ}\text{C min}^{-1}$ for dwelling time.

Table 2

Area Ratio of Silanol/Siloxane and Silanol/Silica-carbon.

Membrane typss	Area Ratio		References
	Silanol/Siloxane	Silanol/Si-C	
Hybrid P123	0.0010	0.0188	This work
Pure ES40	0.0642	1.6547	This work
Pure ES40 (630 °C; pH 6)	0.1500	-	[8]
Carbon Template (TEOS - P123 50 wt%)	0.0160	-	[5]

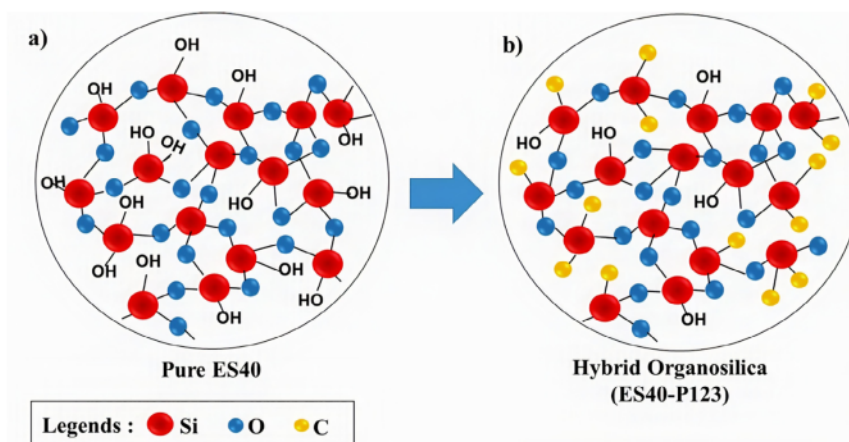


Fig. 4. Silica structures of (a) pure ES40; (b) Hybrid organosilica (ES40-P123).

Hydrostability is a serious problem of silica based membranes for water desalination. To address this problem, a carbon content of P123 is embedded to the silica structure and forms a hybrid organosilica (ES40-P123) structures to modify the surface area of the silica to minimize the interaction of water molecules with the membrane structure. As can be seen in Fig. 4. The schematic representation of various strategies for silica modification.

The presence of carbon content embedded into the silica network as can be seen on Fig. 4(b) can imparted hydrophobicity and prevented the mobility of soluble silica groups under hydrolytic attack. This could improve mechanical properties and makes more strengthen [5]. These results suggest that the embedded carbon in silica matrices has a beneficial role such as could be gained best desalination performance of membrane.

4. Conclusion

This work demonstrates for the first time the preparation of organosilica sols from hybrid organosilica P123 used precursor silica ES40 and P123 by sol-gel method. The dried powder of xerogels were analyzed with FTIR and fitk software using Gaussian line. According to FTIR analysis, the application of copolymer P123 given into silica sols through sol-gel process is a prominent way to produce the combination between silica and carbon crosslinked together in the silica matrices to produce xerogel as a material to fabricate membranes layers applied for water desalination. P123 has a function as carbon content that replaces the silanol (Si-OH) to silica-carbon (Si-C) group. The hydrophobicity properties and pore volume loss of organosilica (ES40-P123) and pure ES40 material depend on area ratio of silanol/siloxane vibrational peaks. The presence of carbon chains in silica network could improve mechanical membrane properties and gained best desalination performance of membrane. Furthermore, this work paves the way for the preparation of sol-gel method using ES40 as precursor derived silica membranes where further can be conferred by embedded with another type of polymer additives as carbon content during membrane fabrication for water desalination application.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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