Volume 2 Number 1 : June 2007

ISSN : 1823-8556

Journal of Sustainability Science and Management

MALAYSIA JOURNAL OF SUSTAINABILITY SCIENCE AND MANAGEMENT
Volume 2 Number 1 June 2007

Contents

STRUCTURE AND BIREFRINGENCE PROPERTIES OF SiO_2 - THIOPHENES XEROGELS SYNTHESIZED BY SOL-GEL-TEMPLATE

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ABSTRACT

Keywords: *Sol-gel-template; Mesoporous; SiO_2-thiophene hybrids; Lamellar Structure; Birefringence*

The ceramic tubular substrates of SiO_2-thiophenes as a ceramic membrane were prepared successfully by the combining method of sol-gel-template process. The organic precursor of 2,5-bis(trimethoxysilyl)terthiophene was used as a template agent and tetraethoxysilane(TEOS) was used as organic or inorganic silicon source. The gel formations of alkoxides are taken by condensation and polymerizations of TEOS with the catalyst ammonium fluoride, after mixing with the precursor. Characterizations were taken by NMR solid, SEM and XR-powder diffraction.

The results showed that surface morphologies of its membranes are defect-free, and the bond-linking structure has been formed between silicate and template agent. The (SiO_2) membrane prepared from TEOS has amorphous phase. The studies reveal that the silicone is mainly in tetrahedral coordination and combining with terthiophene units as a nanostructure to form lamellar structure. The optical birefringence properties of SiO_2-thiophenes hybrid aerogels in the visible range strongly depend on amount of organic unit's modifier. The higher transparency is observed for aerogels having higher content of alkoxysilane (TEOS), and than for the higher birefringence, normally observed for aerogels containing higher quantity of thiophenes units.

INTRODUCTION

Preparation of ceramics via sol-gel processing from alkoxysilane containing motif organic precursor is very widely used for development of new materials with certain characteristic of optical applications. The alkoxysilane functions were partially hydrolyzed and condensed as the matrix formation [1].

The alkoxysilane are usually used are tetramethoxysilane $Si(OMe)_4$, more usually know ast TMOS and tetraethoxysilane, $Si(OEt)_4$, known as TEOS. Both compounds have become a notorious chemical precursor in two important and widely used applications: (a) the preparation of inorganic materials by sol-gel methods [1], and (b) the formation of SiO_2, films deposited by chemical vapor deposition [2].

The preparation ceramics via sol-gel process are studied by the base concepts of solid NMR spectra, in the solid siliceous materials analyzed with ^{29}Si-CP MAS NMR, that the most likely structures of siliceous gels materials as the matrices -(Si-O_4)-Si- were sequenced by T (tertiary), and for the porous aerogels are sequenced by Q (quaternary). The pure aerogel product has NMR spectra dominant as Q^4, absolutely pure as aerogels or technical terminology is called as ceramics [1].

This research has studied about effect of organic motif on microstructure and birefringence phenomena's, in the matrices of ceramics formed via sol-gel processing. TEOS has been chose in this research observation as a matrixes or template source due to less reactive than TMOS. The motif organic terthiophenes are bisilylated to use as precursor[5, 6, 7].

METHODOLOGY

Chemical are used: TMOS and TEOS from Aldrich, 1% NH_4F in H_2O as catalyst and syntheses product's of hybrid precursor 2,5-bis(trimethoxysilyl)terthiophene (= BTS3T) [8], dimethylformamide (DMF) and tetrahydrofurane (THF). Materials and equipment: teflon, non-silicone glue and polarization microscope.

The first synthetic methods of sol-gels processing are used to observe with SEM and XRD. In the reaction tube in the oil basin at 60 ºC, add the precursor 2,5-bis(trimethoxysilyl)terthiophene and TEOS in present of catalyst 1% NH_4F/H_2O by the variation mole ratio as sample : (a) 1 : 4, (b) 1 : 6 and (c) 1: 8. Than observed time by time their gels formation (jellification time). After that mixture formed sol-gels, than ageing for 24 hours at 100 ºC. Gels formed divided in two parts: one is non washing as sample (A) and another one is washing with diethylether as sample (B), and both of these parts sample (A) and (B) are continued to sintering separately at 150 ºC for 4 hours. The two products are grained separately to analyses of SEM and powder X-Ray observation.

The second synthetic methods based on a molecular chemistry approach to observe of the birefringence phenomenon. In the teflon cell's with thickness pores 15 x 10^{-6} µm injected mixtures of precursor 2,5-bis(trimethoxysilyl)terthiophene and TEOS in present of catalyst 1% NH_4F/H_2O by the variation mole ratio: (a) 1 : 4, (b) 1 : 6 and (c) 1: 8, than observe for each 5 hours by polarisation microscope.

RESULT AND DISCUSSION

Results of the first experiment are preparation of aerogel (ceramics), characterization product are shown in **Figure 1 (a)** and **(b)**. Spectra's of ^{29}Si-CP MAS NMR shown that the most likely structures of the matrices -(Si-O_4)-Si- were dominant as Q^3 than Q^4 (aerogels), but still leaved of the formation T^2 and T^3. The first product prepared by BTS3T/TEOS (1 : 4) is not absolutely pure as aerogels or ceramics. The second product BTS3T/TEOS (1 : 6) with matrices of -(Si-O_4)-Si- form were dominant as Q^2, Q^3 than Q^4, where T^2 and T^3 disappeared have formed absolutely as pure aerogels.

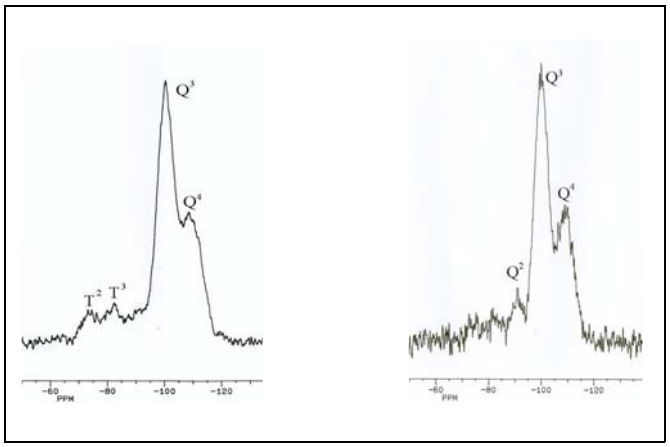

Figure 1. (a) Spectra ^{29}Si CP MAS NMR of BTS3T/TEOS (1 : 4); (b) Spectra ^{29}Si CP MAS NMR of BTS3T/TEOS (1 : 6)

Figure 2., has shown the powder X-Ray diffractogram with certain pattern of intensity as the absorbance of energy on the characteristic maters. The parabolic curve determine that there formation of the repetion sequence of matrices with the certain layer distance on tubular structure of SiO_2. This phenomena concluded that TEOS totally formed of matrices as aerogels backbone, whereas the precursors BTS3T formed as terthiophene-briged silsesquioxane net-work; $[O_{1.5}Si\text{-}(C_4H_2S)_n\text{-}SiO_{1.5}]_n$. That's are understood that TEOS are more favorable substrate in polymerization reactions due to the ability to eliminate ethylene and ethanol as neutral products via cyclic mechanisms, so that reacted more dominant as matrices.

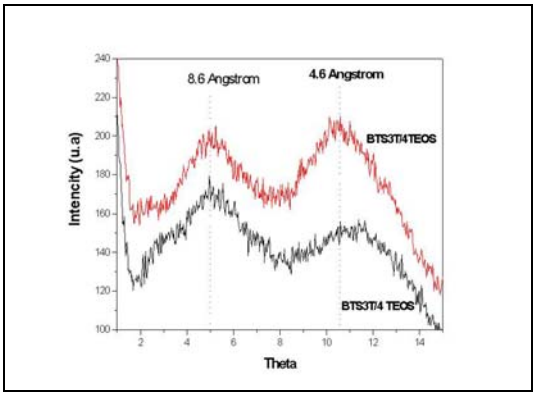

Figure 2. X-Ray Diffractogram of BTS3T/TEOS (1 : 4) and (1:6)

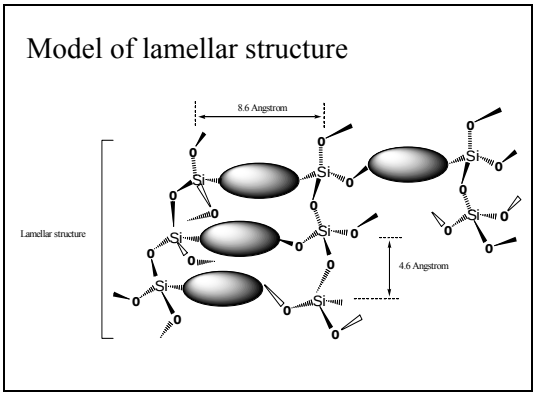

Figure 3. Modification structure BTS3T/TEOS (1 : 4) and (1:6) as the lamellar structure

Figure 3., modification structure of the products, according combination analyses of the ^{29}Si-CP MAS NMR and X-RD, it's concluded that terthiophene-briged silsesquioxane formed in the product shown two picks characteristics. The pick 4.6 angstroms as a distance between two organic precursors (terthiophene as a template) and the pick of 8.6

angstroms as distance between two matrices layer of O-Si-O. These aerogel products were prepared via sol-gel with more quantity of alkoxysilane, shown the same picks in the same position. These phenomena's are concluded that the ordered microstructures in these solids organizations most probably can modified as the lamellar structure [6, 7].

Results of the second experiment; the microstructure studied of solids organization and birefringence are characterized by SEM and polarization microscopy.

Figure 4, shown that products with quantity variation of TEOS have aggregates particles as molecular building with certain sphere contain of silica and thiophenes unites. In the SEM and TEM observation shown there share of cloud particles as the primary particles of about diameter Φ = 10μm. That particles would formed the secondary particles with diameter Φ = 40 – 60μm as the agglomeration.

Figure 5 (a) and (b) shown birefringence phenomena as the effect of terthiophene on anisotropic organisations molecular structure. There effect really fact on the behaviour microscopic, that they are weaker in higher quantity of SiO_2 matrices.

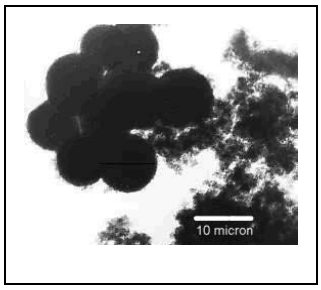

Figure 4. Morphology of BTS3T/TEOS (1 : 4) by SEM

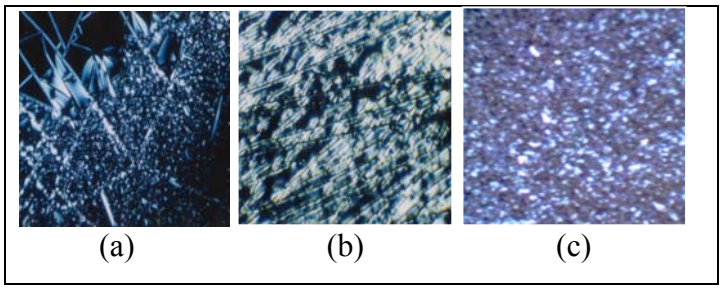

Figure 5. Micrograph polarization BTS3T/TEOS by ratio of (a) 1:4, (b) 1:6 and (c) 1:8

Table 1, shown agglomeration ratio element contain, that composition ratio of principle element in the BTS3T/TEOS product's have spheres rich in silicon. The higher quantity of SiO_2 matrices, will fully protect sulfur existentce in terthiophenes unites. That matrices has amorphous phase with pore size of 4.2 to 6.0 nm [6,7].

Table 1. Yields of microanalyses composition ratio of principle element in the sol-gel formed by BTS3T/TEOS

Washing sol-gels by (ratio mixtures)	**Calculation ratio of**		**Experiment data's**	
	Si/S	**Si/C**	**Si/S**	**Si/C**
BTS3T/TEOS (1:4)	3.33	0.83	3.57	1.00
BTS3T/TEOS (1:6)	6.00	1.5	6.21	1.80
BTS3T/TEOS (1:8)	11.33	2.83	11.72	3.40

Table 2, shown birefringence data detected on products prepared with different mole ratio of terthiophene and alkoxysilane. Birefringence in the ratio of BTS3T/TEOS (1:8) have detection limit of 1.06 x 10^{-3}. On the result reported before [6, 7]; that pure oligothiophene (mole ratio of 1:0) shown a maximum isotropic birefringence on 9 x 10^{-3}. So that, in this product, isotropic values is significantly differences by 1/8 (9 x 10^{-3}) or decrease every 1.125 x 10^{-3} per mole SiO_2 formed. According to SiO_2 matrices formed, can concluded that the higher quantity alkoxysilane, are the weaker of birefringence.

Table 2. Birefringence value of the gel prepared by BTS3T/TEOS

Ratio of SiO_2 sel prepared by	Value of birefringence (Δn)
BTS3T/TEOS (1:4)	2.15×10^{-3}
BTS3T/TEOS (1:6)	1.50×10^{-3}
BTS3T/TEOS (1:8)	1.06×10^{-3}

CONCLUSION

Materials ceramics products based on SiO_2 gels and terthiophenes units have been synthesized via sol-gels-template processing. The spheres as SiO_2 matrices formed have average diameter 10μm are rich in silicon, that matrices fully protected existentce of sulfur in terthiophenes unites. The less alkoxysilane, the thiophenes unites will reduced.

The structure silsesquioxane terthiophene-briged, $[O_{1.5}Si\text{-}(C_4H_2S)_n\text{-}SiO_{1.5}]_n$ formed have a layer distance of 4.6 and 8.6 angstroms. The microstructure of SiO_2 in presence of oligothiophenes gives an effect on the characteristic pattern as lamellar structure.

The effect of terthiophenes unites on SiO_2 gels formed on the birefringence are the higher quantity of terthiophenes units, more stronger of their birefringence. The birefringence phenomena's will decrease with increase quantity of alkoxysilane. The values differences are decreased every 1.125×10^{-3} per mole SiO_2, whereas the optical transparency of SiO_2 gels formed are increase.

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