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EFFECT TERTHIOPHENES UNITS ON THE MICROSTRUCTURE AND BIREFRINGENCE OF SiO_2 GELS PREPARED VIA SOL-GELS PROCESSING

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ABSTRACT

Key Word : *terthiophene-briged silsesquioxane, tergothiophene, lamellar, and birefringence*

Materials ceramics products based on SiO_2 gels have been produced via sol-gels processing in present of 1% NH_4F/H_2O as catalyst. Alkoxysilane from tetraethoxysilane (TEOS) are chose as a matrices or template sources, than the product's of syntheses precursor: 2,5-bis(trimethoxysilyl)terthiophene (= BTS3T) used as a motif organic compound. That product formed matrices as silicate backbone of terthiophene-briged silsesquioxane net-work; $[O_{1.5}Si\text{-}(C_4H_2S)_n\text{-}SiO_{1.5}]_n$. The structure silsesquioxane terthiophene-briged formed have layer distance of 4.6and 8.6 angstroms. So, that terthiophenes units in their structure give an effect on the characteristic pattern as an ordered micro lamellar structure. Electron microscopy analyses in matrices -Si-O-Si- there spheres formed by diameter about 10 μm which are rich in silicon.

The effect of terthiophenes unites on SiO_2 gels formed shown that birefringence phenomenas are strong in presence of higher quantity oligothiophenes units, and will decrease with increase quantity of alkoxysilane, with anisotropic values differences decrease every 1.125×10^{-3} per mole SiO_2, whereas the optical transparency of SiO_2 gels formed are increase.

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 as 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 application TEOS is more familiar used to study and observation due to less reactive than TMOS and recent experiments have explored used of TEOS to plasma enhanced chemical vapor deposition processes [3, 4].

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. Bisilylated terthiophenes are hybrid organic-inorganic precursor, the synthesed are silylated with methoxysilane groups (Si-OMe) from methoxychlorosilane to become a molecule which have relative rigid to arrange their structure as nanostructure in rich of electrons and have better optical properties in present of siliciumoxyde (Si-O-). So that, the materials ceramics formed will have the certain optical properties with the know structure [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 described as following: Formation of gels using catalyst 1% NH_4F/H_2O at temperature 60 ºC, so that polymerization was carried out at controlled temperature by irradiating the sample under natural UV or visible light. The jellification time are note for sample (a) gelled in less than 20 s, and the hydrogel was yellow light strong color, sample (b) gelled in 34 s with the hydrogel yellow more transparent and sample (c) gelled in more than 40 s with the hydrogel transparent.

After ageing at 150 ºC for 4 hours Sample sample (A) and (B) were coagulated immediately than both resulting in yellow-white coagulant. For higher quantity of TEOS, sample B gelled more slowly that sample A, and sample B not gelled until loss of solvents were evaporated after more than 20 h and became transparent gel within several

minutes after further addition of excess of 1% NH_4F/H_2O. That are concluded that the higher of liquid contents made the systems gel formation are slower when the base concentration are kept constant [6,7].

Figure 1., shown the analyses with ^{29}Si-CP MAS NMR 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 meaning that the product not absolutely pure as aerogels or ceramics.

Figure 2., has shown the diffractogram of X-Ray that there certain pattern of distance in the different intensity as the energy absorbed by the characteristic maters in the gel BTS3T/TEOS (1:4) and (1:6). The parabolic curves 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 SiO_2 matrices.

According to the powder X-Ray analyses, the distance among the layer SiO_2 matrices are 4.6 angstrom, than the layered distance between terthiophene-briged silsesquioxane formed in the gels are 8.6 angstroms. For the ceramics that was prepared with more quantity of alkoxysilane, the peaks characteristics are exist in the same position, as such these ordered microstructures in these solids organizations can be concluded as the lamellar structure [6, 7].

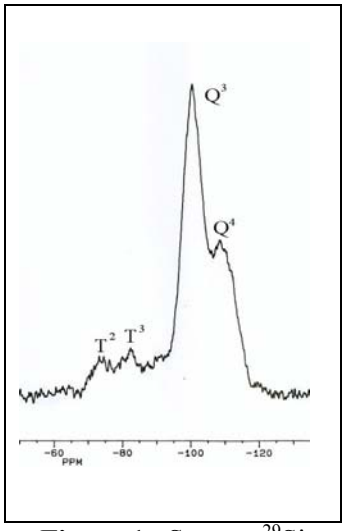

Figure 1. Spectra ^{29}Si CP MAS NMR of BTS3T/TEOS (1 : 4)

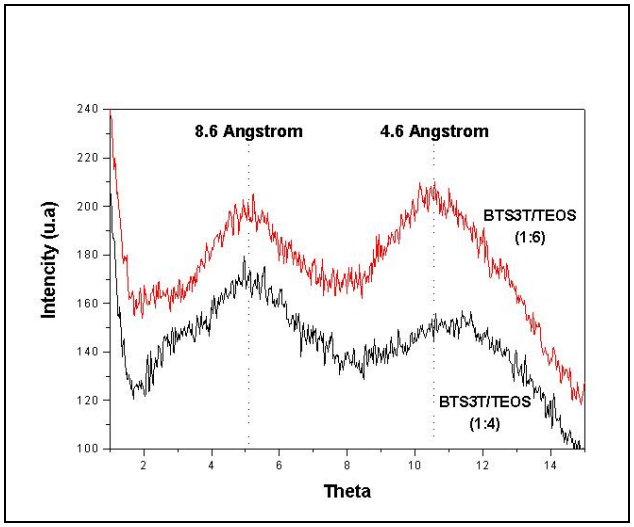

Figure 2. X-Ray Diffractogram of BTS3T/TEOS (1 : 4) and (1:6)

Results of the second experiment; The microstructure solids organization properties are characterized by scanning electron microscope shown in **Figure 3**. Almost of all products with whatever quantity variation of TEOS shown aggregates particles as molecular building with the certain sphere contain of the silica and thiophenes unites.

Figure 3. Morphology of BTS3T/TEOS (1 : 4) by SEM

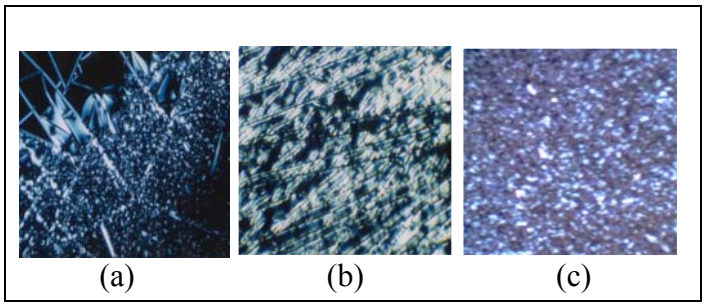

Figure 4. Micrograph polarization BTS3T/TEOS by ratio of (a) 1:4, (b) 1:6 and (c) 1:8

Figure 3. shown the observation in electron microscopies (SEM and TEM) that there share of the cloud particles as the primary particles of about diameter Φ = 10 μm. That particles would formed the secondary particles with diameter Φ = 40 – 60 μm as the agglomeration. **Table 1.** shown agglomeration element contain, that composition ratio of principle element in the sol-gel formed by BTS3T/TEOS ceramics product's based on SiO_2 gels have spheres rich in silicon. The meaning is the higher quantity of SiO_2 matrices formed, will fully protect sulfur existentce in terthiophenes unites. That matrices SiO_2 formed by TEOS 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 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

Figure 4(a) and 4(b) shown birefringence phenomena as the effect of terthiophene on anisotropic organisations molecular structure. There effect really fact on the behaviour microscopic and their birefringence, that they are weaker in higher quantity of SiO_2 matrices.

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

Ratio of SiO_2 gel 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}

According to data in **table 2**, birefringence phenomena's detected on this ceramics prepared with mole ratio of 1: 8 of terthiophene and alkoxysilane have detection limit of 1.06 x 10^{-3}. On the result reported before [6, 7]; that pure oligothiophene (mole ratio of 1:0) shows 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 these SiO_2 ceramics formed then concluded that for the higher quantity of alkoxysilanes added, are the weaker of their birefringence.

CONCLUSION

Materials ceramics products based on SiO_2 gels and terthiophenes units have been synthesized via sol-gels processing. Spheres as matrices SiO_2 formed in the product by average diameter 10μm are rich in silicon, that matrices fully protected existentce of sulfur in terthiophenes units. The phenomenon concluded that the quantity of motif organic thiophenes units will reduced in SiO_2 gels formed with less of alkoxysilane.

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. According to microstructure analyses shown that solids organisations on SiO_2 gels in presence of oligothiophenes give an effect characteristic pattern as micro lamellar structure.

The effect of terthiophenes units on SiO_2 gels formed shown that birefringence phenomenas are strong in presence of higher quantity terthiophenes units, and will decrease with increase quantity of alkoxysilane, with anisotropic values differences decrease every 1.125 x 10^{-3} per mole SiO_2, whereas the optical transparency of SiO_2 gels formed are increase.

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