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Araştırma Makalesi / Research Article

Synthesis and Characterization of Silica and Carbon Aerogels from Hemp Fiber via freeze-drying Process

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Keywords
Aerogel; Carbon aerogel; Freeze-drying; Hemp fiber; Sol-gel method

Abstract

In this study, it was aimed to synthesize and characterize cellulose based silica carbon aerogel by sol-gel method. Pooled and hand-peeled hemp fibers were used as the source of cellulose at the time of October-2018 harvest in Vezir Köprü, Samsun province. Hemp fiber containing crude cellulose was mechanically made into cellulose pulp. Then, Silica aerogel (SA) sample was synthesized by Sol-gel method and subsequent freeze-drying process. Finally, the synthesized SA sample was kept in a tube oven at a heating rate of 5 ^{o}C/min under a nitrogen flow of 120 ml/min for 2 hours at 500 ^{o}C to obtain cellulose-based carbon aerogel (SCA). Synthesized samples; Scanning Electron Microscopy (SEM), Energy dispersive spectrometer (EDS), Surface analysis measurement (BET), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction method (XRD) and electrical conductivity analyzes were performed. As a result of electrical conductivity analysis, the electrical resistances of the silica aerojels was found to be very high. It was interpreted that the synthesized samples could be used as an insulator.

Freeze-drying İşlemi ile Kenevir Lifinden Silika ve Karbon Aerojellerin Sentezi ve Karakterizasyonu

Anahtar kelimeler
Aerojel; Karbon aerojel; Dondurarak kurutma; Kenevir lifi; Sol-gel yöntemi

Öz

Bu çalışmada selüloz esaslı silika karbon aerojelin sol-jel yöntemi ile sentezlenmesi ve karakterize edilmesi amaçlanmıştır. Samsun ili Vezir Köprü'de Ekim-2018 hasadı sırasında toplanmış ve elle soyulmuş kenevir lifleri selüloz kaynağı olarak kullanılmıştır. Ham selüloz içeren kenevir lifi, mekanik olarak selüloz hamuru haline getirildi. Daha sonra Silika aerojel (SA) numunesi Sol-gel yöntemi ve ardından dondurularak kurutma işlemi ile sentezlendi. Son olarak, sentezlenen SA numunesi, selüloz esaslı karbon aerojel (SCA) elde etmek için 500 ° C'de 2 saat boyunca 120 ml / dakika azot akışı altında 5 ^{o}C / dakika ısıtma hızında bir tüp fırınında tutuldu. Sentezlenmiş örnekler; Taramalı Elektron Mikroskopisi (SEM), Enerji dağılım spektrometresi (EDS), Yüzey analizi ölçümü (BET), Fourier dönüşümü kızılötesi spektroskopisi (F-TIR), X ışını kırınım yöntemi (XRD) ve elektriksel iletkenlik analizleri yapıldı. Elektriksel iletkenlik analizi sonucunda silika aerojellerin elektrik dirençleri çok yüksek bulunmuştur. Sentezlenen numunelerin bir izolatör olarak kullanılabileceği yorumlandı.

1. Introduction

Aerogels are porous and low density solids and because of the excess air in the pores of the material (88% to 99.8% porosity), it gives aerogels to be light weight properties like air due to excess air in the pores of the material (Hajizadeh *et al*. 2015).

Silica aerogel alone has less use due to its poor mechanical strength. Several methods have been used to improve the mechanical properties of silica aerogels. Shafi et al. 2019 investigated the effects of the added silica gel on the thermal conductivity and mechanical strength. Thus, they found that the composite not only had stronger mechanical

strength but also gave ultra-low thermal conductivity (Shafi *et al*. 2019).

Cellulose-based carbon aerogels (SCA) have many uses and are environmentally friendly materials due to their high surface area and pore structure controllability. SCA stands out for its renewable and sustainable production, low thermal and electrical conductivity, and high mechanical properties. Due to its thermal conductivity, it is used in building construction and insulation, solar panels, automobiles and space vehicles. The fact that cellulose in this material is extremely abundant and sustainable shows its applicability for large-scale industrial applications (Pircher *et al*. 2015). In addition, the development of super hydrophobic materials has been made by treating the synthesized cellulose nanofiber aerogels with titanium dioxide nanoparticles and silanes to be used as the separation medium for oil adsorbents or oil / water mixtures (Ciftci *et al*. 2017; Cervin *et al*. 2012).

Wang et al. fabricated spherical cellulose aerogels via supercritical CO_2 drying technology. Also, they determined the physical properties of the materials (i.e., shrink-age, specific surface area, thermal degradation, and micro-struc-ture), such as a weak shrinkage of 4.03%, a specific surface area of up to 353 m^2/g , and an average pore size of 8.86 nm (Wang *et al*. 2016)

Zhang et al. (2019) showed that hydrophobic porous carbon-200 aerogel (SHPC-200 aerogel) is a cost-effective raw material and can be easily produced in industry on a large scale. In particular, the authors stated that there is an aerogel that can be applied to less contaminated oil spill and wastewater pollution (Zhang *et al*. 2019).

Nguyen et al.(2013) investigated the use of aerogels made of paper waste cellulose fibers as absorbent materials to remove crude oil spills. In their work, they tested cellulose aerogels synthesized from paper waste cellulose fibers to remove different crude oils and found that they exhibit high absorption capacity (Nguyen *et al*. 2013).

Neugebaue *et al*. (2014) synthesized compressed granular aerogels in a sandwich panel with three-dimensional lattice core designed for insulation of walls due to low thermal conductivity (Neugebauer *et al*. 2014).

In this paper, the results of electrical conductivity measurements performed on the silica and cellulose-based carbon aerogels are reported.

2. Material and Method

Hemp fibers consisting of raw cellulose with 1-2% lignin content, pooled and peeled by hand, were used as cellulose raw material during the harvest period of Vezir Köprü district of Samsun province in October-2018.

2.1. Cellulose pulp production by mechanical method

10 grams of hemp fiber were added and soaked with water at a ratio of 1: 100 and boiled in a pressure cooker for 3 hours. The softened fibers were then forged for half an hour. This procedure was repeated three times.

2.2. Synthesis of cellulose based silica aerogel by sol-gel method

Synthesis of silica aerogel by Sol-Gel method using hemp fiber cellulose pulp was performed as follows. First, 0.2 g of the raw material was added to the mixture of 320 ml ethanol and 80 ml deionized water (DI). While the resulting solution was mixed homogeneously, 12 ml of NH_3H_2O (Ammonium hydroxide) was slowly added to the solution. The resulting mixture was stirred on magnetic stirrer for 1 day and then transferred to a glass flask and then stirred at room temperature for 5 hours. Then, 1.2 ml TEOS (tetraethyl orthosilicate) was added dropwise to the mixture and stirred continuously at 400 rpm for 18 hours. After the resulting mixture was washed several times with DI water and ethanol, the mixture was homogenized with 50 mL of anhydrous ethanol. The sample was converted to silica aerogel by freeze-drying for 120 hours at a vacuum pressure of 0.027 mbar and a temperature of -52.6 ^oC (Yuan *et al*. 2018).

2.3. Carbon aerogel synthesis

The silica aerogel synthesized was heated to 500 ° C under a nitrogen flow of 120 ml / min at a heating rate of 5 ° C per minute in the MSE Furnace and held at 500 ° C for 1 hour. Silica carbon aerogel (SCA) was obtained after pyrolysis was completed (Yuan *et al*. 2018).

3. Results and Discussion

3.1 Characterizations of the aerojels

Characterizations were performed on cellulose-based silica aerogel and cellulose-based silica carbon aerogel. The bulk density of the nanostructure was classically calculated. The potentiostatic impedance measurements (EIS) were performed within the scope of synthesized SA and SCA characterization studies.

FTIR spectrum was collected by Perkin Elmer Spectrum Two FTIR spectrometer with KBr technique in the range from 400 to 4000 cm^{-1}. The obtained FTIR spectra are given in Fig. 1.

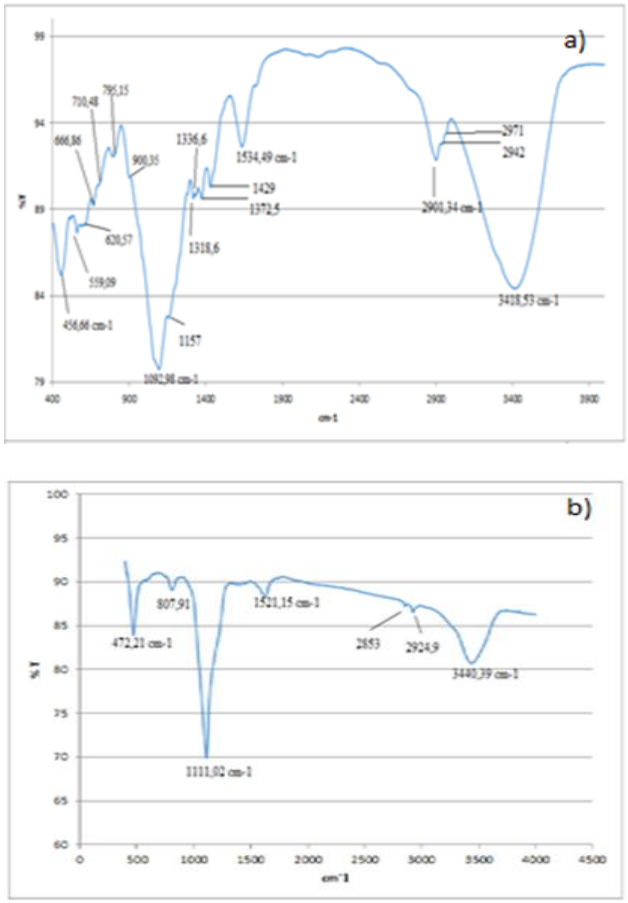

Figure 1. FTIR spectra of aerogels
a) SA **b)** SCA

The structural changes in the samples prepared for each different condition from the spectra were determined by the peaks given by the functional groups.

Silica aerogels have been shown to exhibit a spectrum similar to literature. Figure 1 shows the FTIR spectrum of the aerogel obtained. When this spectrum is examined, there is the O-H functional group at the center of 3418 cm^{-1}, CH_3 at the center of 2901 cm^{-1}, C = C at the center of 1634 cm^{-1} and the C-H tension vibration at the center of 1372 cm^{-1}, respectively. Si-O voltage vibrations asymmetric band was seen at 1093 cm^{-1}. This indicates the presence of SiO_2. The O-Si symmetric band is 804 cm^{-1}, the Si-O-Si mesh band is 471 cm^{-1} and the -OH absorption band is 3440 cm^{-1}/1630 cm^{-1}. The presence of the crystal structure also shows that the fiber retains its crystal structure with the peak in the absorption band at 1429 cm^{-1} (Yuan *et al*. 2018; Zhang *et al*. 2005).

Compared to the spectrum of cellulose-based silica carbon aerogel, after the carbonization process of silica aerogel, the intensity of the O-H functional group at 3440 cm^{-1} and the C-H functional group at 2901 cm^{-1} is seen to be significantly weakened.

Crystal and amorphous structure of SA and SCA samples were analyzed by Panalytical MPYRA brand XRD and recorded in range of diffraction angle 2Θ from 0° to 70° (Fig. 2). When looking at Figure 2a, It shows that a broad peak at 2θ = 12 °- 30 ° in the XRD patterns of the cellulose-based silica aerogel corresponds to the amorphous peak of SiO_2 (Yuan et al., 2018). Also, it can be seen that the corresponding peak of SiO_2 can be covered by the two peaks at 2θ = 15 ° and 25 °, corresponding to the (110) and (200) planes of the crystal structure of cellulose (Zhang et al., 2019).

When Figure 2b is examined for cellulose-based silica carbon aerogel, it is seen that the peak at 15 ° has disappeared and the peak at 25 ° has become weaker. The wide peak (between 15° and 30°) of carbon aerogel obtained after pyrolysis shows the disappearance of the crystal structure and the

presence of amorphous structure. As a results, it can be seen that the cellulose-based silica carbon aerogel still retained their amorphous structure, and no crystalline structure could be detected (Yuan et al., 2018). These results demonstrated that the successful preparation of SA and SCA aerogels via using the Hemp fibers as raw materials by the freeze-drying/ pyrolysis process.

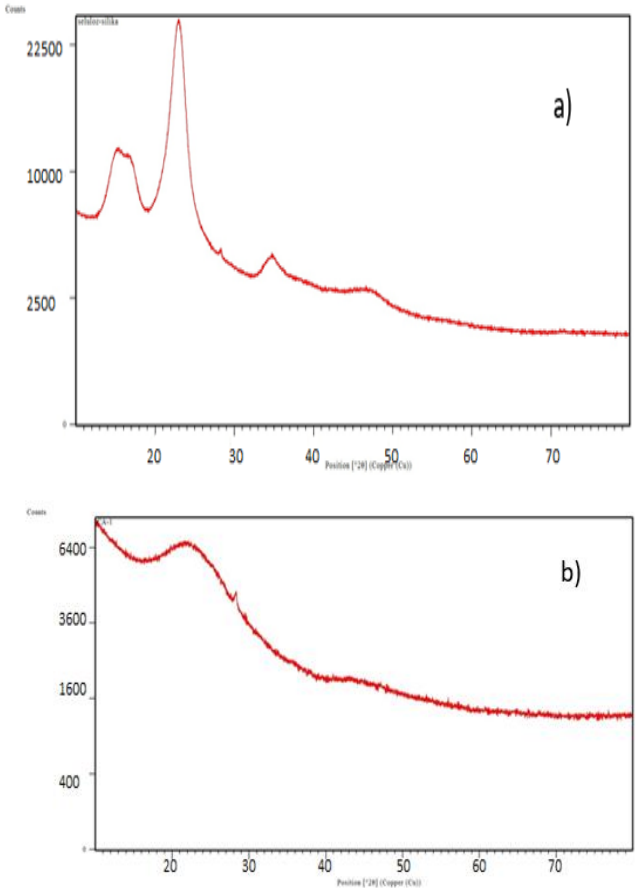

Figure 2. XRD spectra of aerogels **a)** SA **b)** SCA

SEM was used to analyze the surface morphology of nano-cellulose aerogels. Images were taken at 100 µm using a JEOL brand JSM 5600 scanning electron microscope (JSM-5600, JEOL, Japan). The SEM results are presented in Fig. 3. As shown in Fig. 3b, after prolysis, it was found that the SCA retained the structure and contained more pores and as a result increased total pore volume (0.244 ml/g).

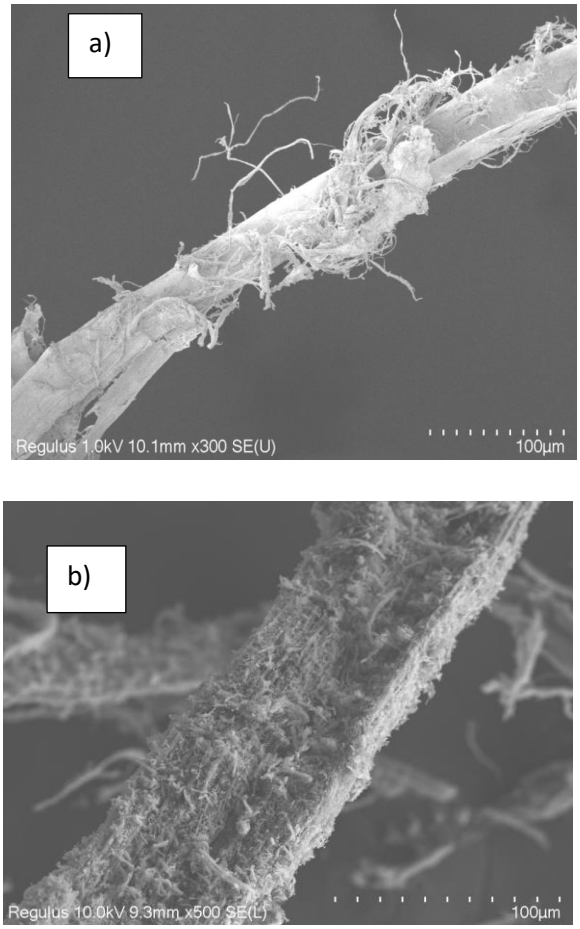

Figure 3. SEM images of aerogels **a)** SA **b)** SCA

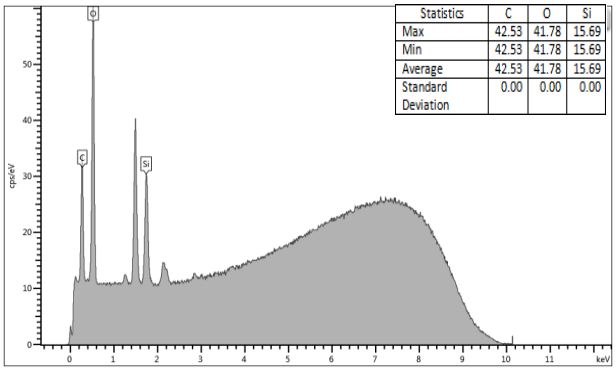

Figure 4. EDS analyse aerojel of Silica

As a result of EDS analysis of SA sample (Fig. 4) it was found that Si (15.69%) was added to the structure and the amount of C (42.53%) is in the result of the presence of cellulose based raw material (hemp fiber). With the addition of 1.2 ml TEOS, it is seen that the structure is compatible with approximately 15.16% Si in the calculation.

Density determination by weight:

The volume of the synthesized material was calculated as a result of the data. The density of the cellulose-based silica aerogel was calculated using the amount of mass. As a result the density of the synthesized SA material was determined to be 0.007 g/cm^3 (close to the range given in the literatüre) (Fu et al., 2016).

N_2 sorption method:

Multi-point BET surface area of SA and SCA samples was determined using adsorption device (Quantachrome, Autosorb-1C) at 77 K by nitrogen adsorption-desorption measurements. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) formula. The samples of SA and SCA were degassed under vacuum at 100 °C and 200 °C respectively for 12 h prior to analysis. According to BET analysis, the specific surface area and total pore volume of the SA and SCA samples was determined 12 m^2/g ve 0.0279 ml/g; 102.85 m^2/g ve 0.244 ml/g, respectively (Zhang et al., 2019; He et al., 2017).

Electrical measurements:

The potentiostatic impedance measurements (EIS) were carried out by applying electical frequency from 1 to 1x10^6 Hz and operating voltage of 10 V at room temperature. The results of electrical resistance analysis for SA and SCA applied in Gamry ZRA Reference 3000 were given Fig. 5. The dependence of electrical resistance on applied frequency for two aerogels at 25 °C shows that the resistance increased greatly with decreasing frequency between 1 MHz and 1 kHz, and the resistance rise became less with frequency drop from 1 kHz to 1 Hz. Aerogels appear to have low resistance in this range (Huang, L., 2012**).**

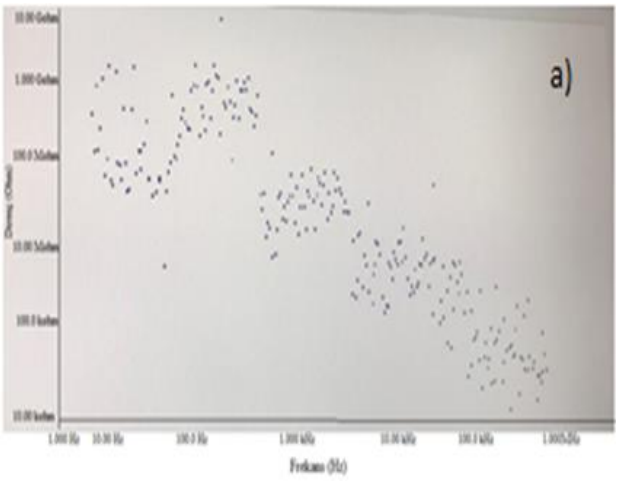

Figure 5. Electrical resistances of aerogels as functions of frequency, measured at 25 °C **a)** SA **b)** SCA

4. Conclusion

In this study, cellulose based silica aerogel (SA) was synthesized by sol-gel method by using pooled and hand-peeled hemp fiber containing 98% crude cellulose as starting material. The resulting silica aerogel was converted to carbon aerogel (SCA) by pyrolysis. The total surface area of the synthesized SA was found to be 12 m^2/g. After pyrolysis, it was shown that the surface area of SCA increased to 102.85 m^2/g. The morphology of the aerogel was observed under SEM and silica aerogel converted to carbon aerogel (SCA) by pyrolysis had more porosity compared to cellulose aerogel prepared by freeze-drying. In addition, as a result of electrical conductivity analysis, the electrical resistance of both aerogels was found to be too high (approximately 10 Gohm). Huang (2012) showed that silica aerogel has the lowest thermal conductivity value with 0.0144 W/mK and

accordingly it has the highest thermal resistance (Huang, L., 2012**).** As a result, it makes silica eorogels a good choice for energy saving and insulation in the building industry. It is seen that the aerogels in this study may be appealing. Thus, it was interpreted that these aerogels could be used as an insulator.

Compliance with ethical standards

Conflict of interest The corresponding author declares that there is no conflict of interest.

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