Synthesis and Characterization of Poly(vinyl alcohol)/ Water Glass (SiO₂) Nano-Hybrids via Sol-Gel Process

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ABSTRACT: A new class of materials based on inorganic and organic species combined at a nanoscale level has received large attention recently. In this work the idea of producing hybrid materials with controllable properties is applied to obtain foams to be used as catalyst supporting. Hybrids were synthesized by reacting poly(vinyl alcohol) in acidic solution with water glass. The inorganic phase was also modified by incorporating a hexamethyldisiloxane as precursor. The hybrid aerogel powder was analyzed by scanning electron microscopy, TG-DTA, Nitrogen adsorption–desorption, X-ray diffraction and fourier transform infrared spectroscopy (FTIR) spectroscopy. The powder obtained had a higher porosity varying from 65 to 90% and the nanopore diameter ranged from 17 to 20 nm. The surface area and nanopore volume decreased as polymer content increased in the hybrids. The sharp decline in the weight observed at around 500°C accompanied an exothermic peak of the DTA curve. The sharp peak was observed around 211°C represents the DTA curve of Poly vinyl alcohol constituent in nano hybrids. The peak at 1638 cm^{-1} in the FTIR indicated the formation of Si—O—PVA—O—Si bridge in aerogel powder. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3533–3538, 2010

Key words: PVA; water glass; nano-hybrids; micro structure and textural properties

INTRODUCTION

Nano hybrid materials have been widely used since 1990s[1] mainly in the aerospace and electronic industries due to their reliable higher performance stability, chemical resistance, dielectric properties, and good mechanical strength. Many studies have also been carried out on hybrid materials with various conventional organic polymers, including vinyl polymers to obtain a new class of vinyl containing hybrid materials.[2] The preparation of organic/inorganic hybrid materials has attracted research interest because they are potential candidates for catalysts[3,4] and gas separative membranes.[5] In recent years, various investigations on PVA-silica hybrids have been carried out to examine changes in their properties.[6] Inorganic materials such as silica exhibits excellent thermal stability and higher hardness. The incorporation of well dispersed (preferably on the nanometer scale) silica particles into polymer matrix was proven as an extremely effective way to improve the thermal and mechanical properties of polymers.[7]

Recent investigations suggest that there are several ways to obtain PVA-silica hybrids.[8] Among them, the superior method i.e., formation of covalent bond between organic and inorganic components, produces materials with superior properties.[9,10] The said method is all time available. Based on the previously furnished idea, our entire studies are focused on the sol–gel reaction of a PVA and silica solution using coprecursor method. This work describes the preparation and evaluation of the results pertaining to physical, thermal, crystallinity, microstructure, and textural properties of the PVA/Silica nano hybrid materials. The PVA/Silica nano hybrid materials were analyzed by X-ray diffractometer, thermogravimetric and differential thermal analysis (TG–DTA) techniques. The micro structural and textural properties were studied by field emission scanning electron microscopy (FE-SEM) and N₂ adsorption-desorption method respectively.

EXPERIMENTAL

Materials

The chemicals, used for the synthesis of silica/poly(vinyl alcohol) hybrid materials were, sodium

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silicate (SS) (water glass 29 wt %) purchased from II Shin Chemical, South Korea, Hexamethyldisiloxane (HMDS) obtained from Acros Organics, ciatel, nitric acid, n-hexane, and poly(vinyl alcohol) ($M_w \sim 1500$) were received from Junsei Chemicals, Japan. All chemicals were of reagent grade and were used without further purification.

Synthesis of silica aerogel powder

The SS solution was diluted first with the deionized water so as to obtain 5.68 wt % of silica as the starting material. The silylated hydrogels were then prepared by a coprecursor method wherein the nitric acid and HMDS were added to the SS (5.68 wt %) under constant stirring. The sol undergoes gelation in 3–5 min, at room temperature (27°C). The silylated hydrogels prepared by the coprecursor method were immersed in n-hexane for one-step solvent exchange and sodium ion removal which could be accomplished in 3 h. During this process, the water present in the hydrogels was given out as a consequence of surface modification by organic groups (—$(CH_3)_3$) present in HMDS and simultaneous intrusion of n-hexane into the gel resulted in the solvent exchange.

The displaced pore water was then removed from the beakers and the silylated organo-gels were dried at ambient pressure in a furnace in one step and kept at 190°C for 90 min, to obtain the aerogel powder. A simple and rapid method for drying wet gels like squeezing the gel material in between filter papers which are then kept in oven at 80° C for 30 min was also developed. The ambient pressure drying (APD) process, in which squeezing step involved is known as squeeze drying.

Preparation of PVA/water glass nano hybrids

Poly(vinyl alcohol) portions of 2, 4, 6, and 8 g were added and dissolved in 100 mL of distilled water at 60°C. The hot solution was cooled and a known amount of water glass was added to the solution.[11] The solution was stirred for 2 h at room temperature. The silylated hydrogels were then prepared by a coprecursor method wherein the nitric acid and HMDS were added to the SS (5.68 wt %) under constant stirring. The sol undergoes gelation in 3–5 min, at room temperature (27°C). The silylated hydrogels prepared by the coprecursor method were immersed in n-hexane for one-step solvent exchange. The reaction mixture was heated at 40°C for one week with an aluminium foil cover.[12] The silylated hybrid organo-gels were dried at ambient pressure in a furnace in one step
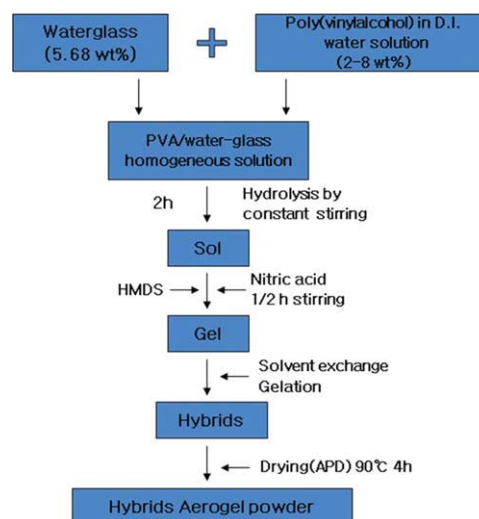
Figure 1 Schematic representation of the preparation of poly(vinyl alcohol)/water glass (SiO$_2$) nano hybrids. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and kept at 90°C for 4 h to obtain the hybrid aerogel powder (Fig. 1).

Characterization of aerogel powder

The N$_2$ adsorption measurements were made for the aerogel powder using a surface area analyzer (Quantachrome Autosorb-1) and the Brunauer, Emmett and Teller (BET) surface area and the pore volumes were calculated. The pore size distributions were estimated by the Barrett-Joyner-Halenda (BJH) method. The microstructure of the aerogel powder was probed by a field emission scanning electron microscopy (FE-SEM, JSM 6700 F microscope, JEOL). The tapping density of the silica powder was calculated from its mass to volume ratio. For this purpose, the silica powder was filled in a cylindrical column of known volume and the measurements were performed on the silica powder produced without evacuating them.

The measurements were obtained in triplicates of 5 for each sample and the average value was taken as the tapping density of the silica powder. To study the hydrophobic properties and the surface chemical modification of the aerogels the fourier transform infrared spectroscopy (FTIR) (Perkin–Elmer, Spectrum GX model) was used. The weight loss behavior of the hydrophobic silica aerogel powder and its hybrids were studied by TG-DTA (Perkin–Elmer TGA 7 thermal analyzer-TG–DTA) which was carried out in N$_2$ atmosphere in the temperature range of 50–900°C.[13] The crystallinity of the resultant hybrid aerogel powder was studied using the X-ray diffractometer (X pert MPD Philips X-ray Diffractometer).

TABLE I
**Physical and Textural Properties of Water-Glass Based Silica Aerogel Powder
as a Function of PVA Content**

Sample ID	Tapping density (g/cm^3)	BET surface area (m^2/g)	S_{micro} (m^2/g)	V_c (cm^3/g)	V_{micro} (cm^3/g)	Pore diameter (nm)	Porosity (%)
AP$_0$	0.131	749.9	314.2	1.029	1.20	22.3	94.1
HAP$_2$	0.554	795.8	363.3	0.871	1.28	20.6	74.6
HAP$_4$	0.456	794.1	372.4	0.747	1.08	18.5	79.1
HAP$_6$	0.558	795.2	380.3	1.02	1.04	19.6	74.4
HAP$_8$	0.739	794.3	287.9	0.706	0.94	17.7	66.2

RESULTS AND DISCUSSION

Physical properties

The poly(vinyl alcohol) content in the sol strongly influences the tapping densities and porosity of the resulting aerogel powder obtained via APD with squeezing technique. The effect of the poly(vinyl alcohol) content on the physical properties of the aerogel powder was investigated varying the PVA content from 0 to 8 wt % by dissolving into deionized water. The experimental results on the tapping density and porosity of the hybrid aerogel powder (WG/PVA-based) synthesized by the coprecursor method are given in Table I. For comparison, the results of the pure aerogel powder are also presented in the same table. The significant change has been observed in the tapping density of the hybrid aerogel powder and the values were in the range of 0.13–0.73 g/cm^3. However, no change in the shape and appearance has been found of the resultant aerogel powder.

The tapping density of the aerogel powder essentially increased from 0.131 to 0.739 g/cm^3 with an increase the PVA content in the sol from 0 to 8 wt %. This is because of the fact that the PVA content in the sol significantly affects the spatial arrangement of the silica chains in the resulting gel network which ultimately decides the density of the resulting aerogels. The sols having less silica and PVA content, upon gelation, lead to the development of a gel network in which the silica chains are quite separated from each other forming bigger pores.[14] On the other hand, the sols with high silica and PVA content lead to the formation of a dense hybrid network with relatively smaller pores. Further, the porosity of pure silica aerogel powder is higher [94.1%] than the hybrid aerogel powder. From Table I, it is shown that the properties of the HAP$_4$ (water glass/4% PVA) sample are superior to those of other samples.

FTIR analysis

The FTIR spectrum of the pure silica aerogel powder and silica/PVA hybrid powder is shown in Figure 2.

The high homogeneity was maintained in all samples. In the spectrum, the absorption bands corresponding to the inorganic silica phase are observed at 1256 and 1075 cm^{-1} which is assigned to the —Si (CH$_3$) stretching and Si—O—Si bending vibration, respectively. The peak at 845 cm^{-1} that corresponds to Si—C network is identified. The same bands are observed in the hybrids (Fig. 2) although the intensity of the Si—O—Si bands was lower in the hybrids. The characteristic peaks of PVA component are clearly observed at 3452, 3445 cm^{-1} for Si—OH and at 2957, 2969 cm^{-1} for C—H stretching[15] in the hybrid powder. The intensity of the C—H stretching vibration peak increased with an increase of the amount of PVA content in the sol. The peak at around 1738 cm^{-1}, which is associated with the stretching of C=O group. Obviously, all the peaks attributed to the hydrolysis and condensation of water glass is weakened after PVA was added in, and the peak at 1638 cm^{-1} may indicate the formation of Si—O—PVA—O—Si bridge. Because a number of silonal groups have been condensed with the hydroxyls on PVA chain to form Si—O—C linkage, the vibrating intensity of Si—O—Si, Si—C, and —Si (CH$_3$) bonds was weakened in the hybrid aerogel powder. Considering all the peaks of the spectrum it is obvious that a PVA/Silica hybrid has been formed.
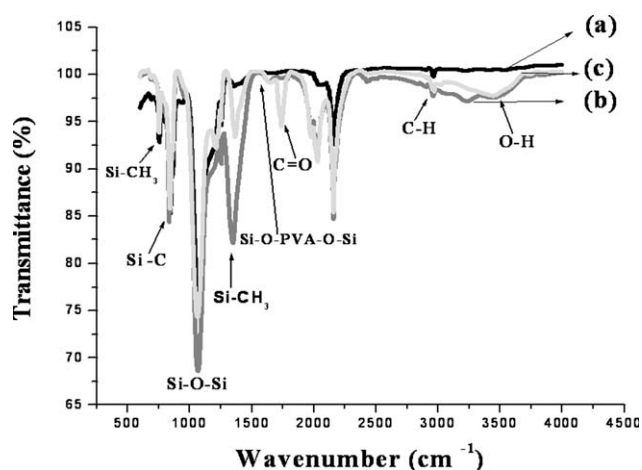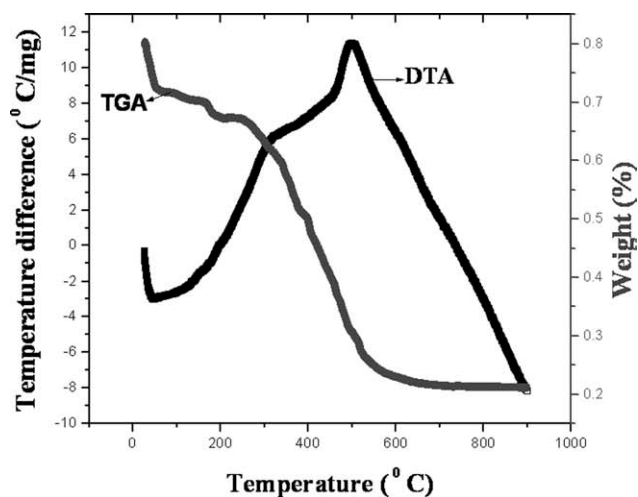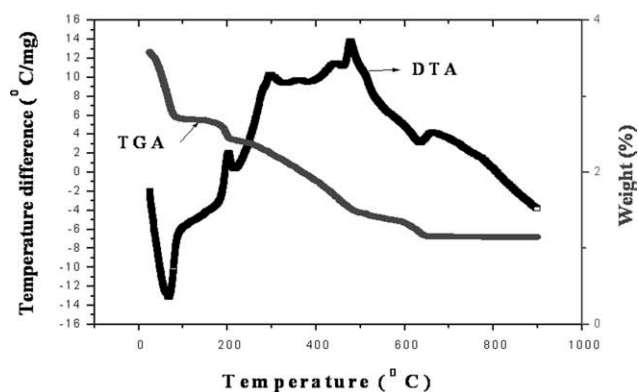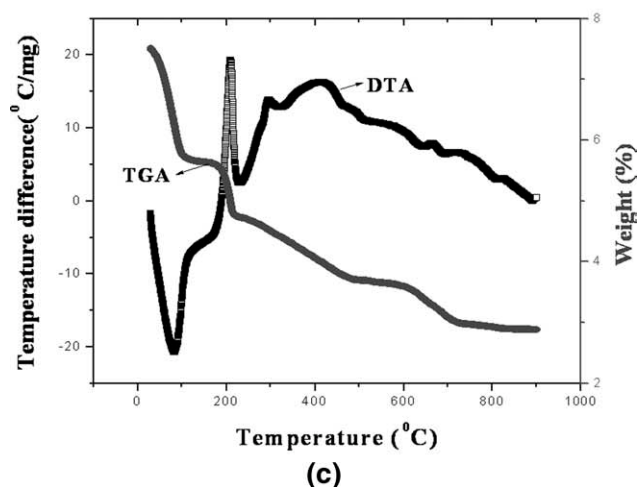

Figure 2 FTIR spectrum of aerogel powder (a) AP (0% PVA) (Pure); (b) HAP (2% PVA); and (c) HAP (8% PVA).
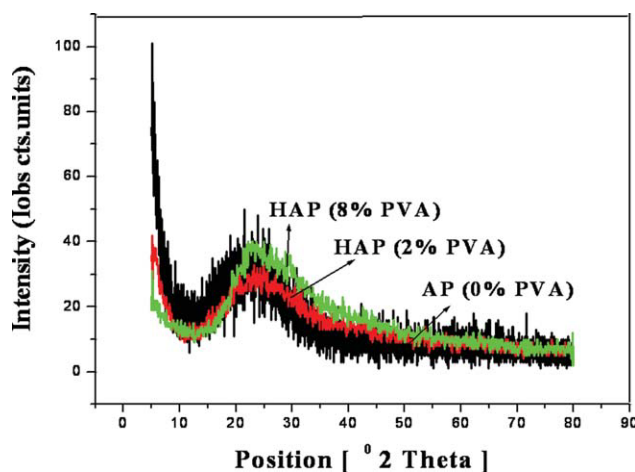
(a)

(b)

(c)

Figure 3 TG-DTA curves obtained in an N2 atmosphere for the (a) AP (0% PVA); (b) HAP (2% PVA); and (c) HAP (8% PVA).

Thermal analysis (TG AND DTA)

The thermal stability behavior of the hydrophobic hybrid aerogels has been investigated precisely by means of thermogravimetric (TG) and differential

Figure 4 X-ray diffraction patterns of pure aerogel powder and hybrid aerogel powder. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thermal (DTA) analysis in the temperature range of 50–900°C. Figure 3(a–c) depicts the TG–DTA curves obtained in nitrogen atmosphere for the water glass based hybrid aerogel powder synthesized at the ambient pressure. The sharp decline in the weight observed around 500°C [Fig. 3(a,b)] accompanied an exothermic peak of the DTA curve which indicates the decomposition temperature of that sample. Similarly, HAP_4 and HAP_6 (water glass/4% and 6% PVA) samples show DTA peaks at around 450°C. In Figure 3(c) the sharp peak around 211°C on DTA thermograms of PVA could be due to the presence of OH groups in hybrid aerogel powder. The significant weight loss observed in the temperature range 400–550°C can be attributed to the thermal decomposition of the organic component i.e., —CH_3 groups present in the aerogel powder [Fig. 3(a)]. This result supports the oxidation of the —CH_3 groups from the surface of the hydrophobic aerogel powder.

In the TG-DTA studies of the hybrid aerogel powder, the peak at 211°C related to weight decrease and exothermic peak reveals that the aerogels are hydrophobic for the temperature increase of upto

TABLE II
X-Ray Diffraction Properties of Water-Glass Based Silica Aerogel Powder as a Function of PVA Content

Name of the sample	Peak position 2θ (degree)	X-ray diffraction property
AP_0 (pure aerogel powder)	20–28	Amorphous nature
HAP_2 (water glass/2% PVA)	20–30	Amorphous nature
HAP_4 (water glass/4% PVA)	23–31	Amorphous nature
HAP_6 (water glass/6% PVA)	23–35	Amorphous nature
HAP_8 (water glass/8% PVA)	24–35	Amorphous nature
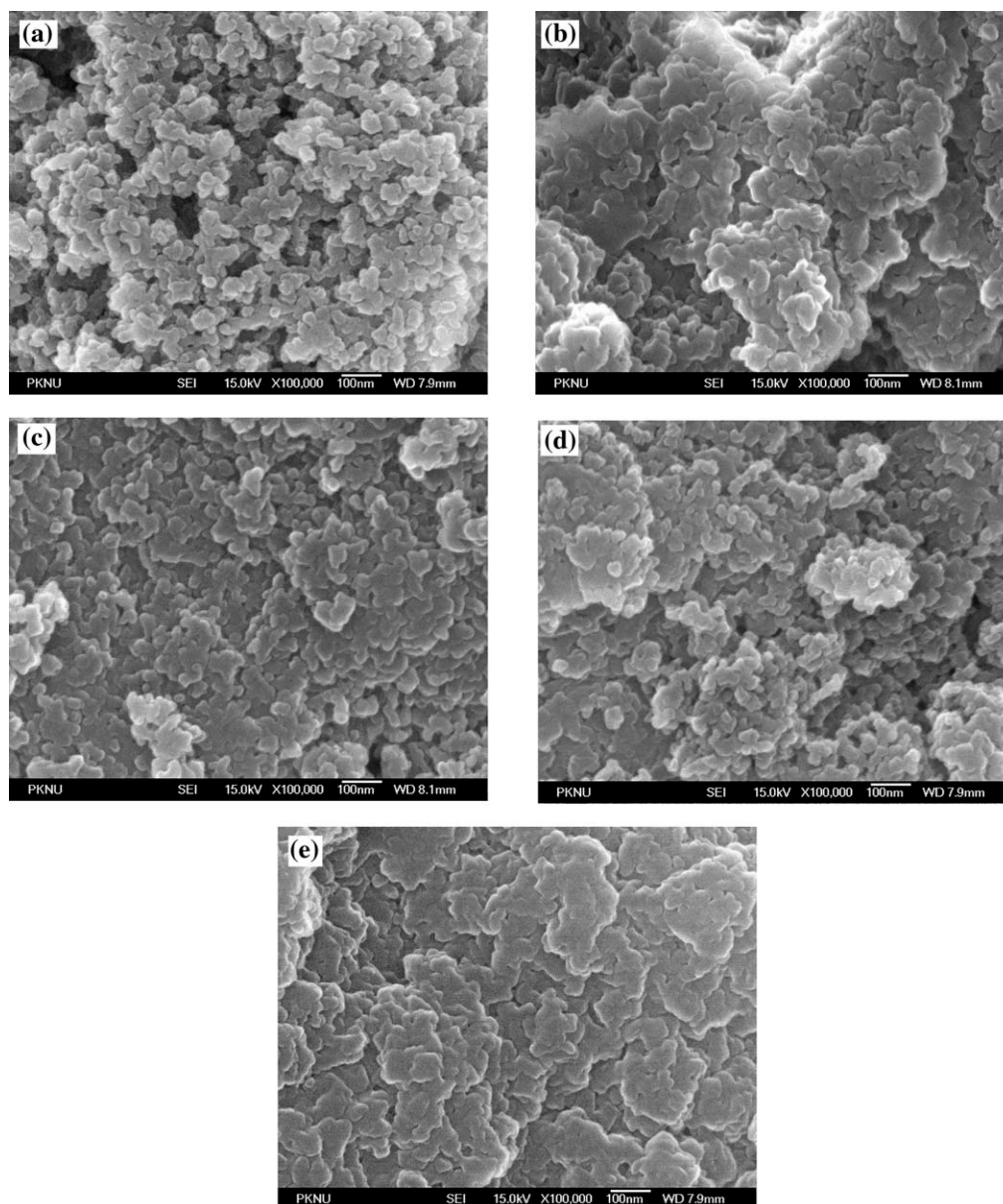
Figure 5 FE-SEM pictures of Silica/PVA nano-hybrids (a) AP (0% PVA); (b) HAP (2% PVA); (c) HAP (4% PVA); (d) HAP (6% PVA); and (e) HAP (8% PVA).

211°C [Fig. 3(c)]. It was observed that there is a sharp exothermic peak corresponding to oxidation of the surface vinyl groups[16,17] in DTA and weight decrease in TGA. The transition from hydrophobic to hydrophilic behavior of the hybrid aerogel powder was also observed at 211°C, when it was heated in a furnace upto a temperature of 211°C and is evaluated by testing it time to time with water. The aerogel powder is heated above the 211°C temperature, readily absorbs water which shows the hydrophilic behavior. The Figure 3(a–c) shows the effect of PVA content on the thermal stability of the nano hybrid aerogel powder. The figures clearly show that increase of PVA content in the powder (6, 8 and 10% PVA) decrease the thermal stability of the

powder. The lower PVA content in the powder (2 and 4%) influence lesser effect while higher PVA content (6 and 8%) has greater effect on thermal stability of the powder. The HAP$_2$ and HAP$_4$ (water glass/2% and 4% PVA) samples show high thermal stability while HAP$_6$ and HAP$_8$ samples have the lower thermal stability.

XRD analysis

The XRD patterns of pure silica aerogel powder and silica/PVA hybrid powder are shown in Figure 4 and the peak positions are presented in Table II. XRD analysis was carried out at the equator over a 2θ range from 10 to 80° at a scan

speed of 4°/min. The XRD patterns shown in Figure 4 of pure silica aerogel powder (AP 0% PVA) displays a broad hump peak when the contact angle was around 2θ ranging between 15 and 35°, originating from amorphous phase of water glass-HMDS, and do not show the crystallization. For the water glass/PVA hybrids such as water glass/2% PVA and water glass/8% PVA (Fig. 4), the diffraction patterns show only a broadly amorphous peaks ($2\theta = 13$–35°) derived from homogeneously amorphous SiO_2-PVA hybrids. This result indicates that the complete and homogeneous mixing of water glass (SiO_2)/HMDS and PVA, and inorganic phase caused by balanced hydrogen bonding interaction in hybrid systems result in the disappearance of the crystallinity of SiO_2/HMDS-PVA hybrids. This also indicates that SiO_2 and PVA do not form sufficiently large clusters for XRD during hydrolysis via APD process. The diffraction peak at $2\theta = 19.5$° indicated the crystallinity of pure PVA[18] that was absent in the SiO_2/HMDS-PVA hybrids.

Microstructure and textural properties

The microstructures of the silica aerogel powder were probed by means of FE-SEM. Figure 5 represents the SEM pictures of Silica/PVA hybrid aerogel powder (a) AP (0% PVA); (b) HAP (2% PVA); (c) HAP (4% PVA); (d) HAP (6% PVA); (e) HAP (8% PVA). The microstructure of the ambient pressure dried water-glass based aerogels showed a three-dimensional nano-porous structure consisting of aggregation of primary particles, nearly 22 nm in size [Fig. 5(a)]. The microstructure of the hybrid aerogel powder differs from the typical microstructure of the pure silica aerogel powder, which generally consists of the rectangle shaped silica clusters forming a three-dimensional network.[19] All the PVA modified silica powder (HAP_2–HAP_8) exhibited relatively denser network with lesser pores than that of AP_0 (pure aerogel Powder). The aerogel powder with high PVA content (8 wt %) showed relatively denser silica network with higher surface area than low PVA content in it. These results are in good agreement with the average pore diameters (Table I), cumulative (V_c) and micro pore volumes (V_{micro}) obtained for these aerogel powder. This is due to the fact that the water-rich gel shrinks more during the APD because of the high surface tension of water resulting in a denser silica network.[20] Whereas, the aerogel powder AP_0 exhibited highly porous silica network due to the less water content. As seen in the Figure 5 (b–e), the PVA covered the inorganic network as a layer.

CONCLUSIONS

PVA/water glass based hybrid aerogel powder was successfully obtained using the coprecursor method by sol-gel process. The obtained hybrid aerogel powder has medium porosities varying from 66 to 74% and the average pore diameters ranged from 17 to 20 nm. The tapping density of the aerogel powder was increased from 0.131 to 0.739 g/cm^3 with an increase in the PVA content in the sol. The model micropore diameters decreased with an increase in PVA content in the inorganic phase. The surface area and mesopore volume decreased with polymer content in the hybrids. The peak at 1638 cm^{-1} indicated the formation of Si─O─PVA─O─Si bridge. Considering all the peaks of the FTIR spectrum it is obvious that a PVA/Silica hybrid was formed. In the TG-DTA curves, the sharp peak at 211°C represented the DTA curve of poly vinyl alcohol constituent in nano hybrids. The higher PVA contents in hybrid powder decreased the thermal stability of the powder. The water glass/2% PVA and water glass/8% PVA, diffraction patterns showed only a broadly amorphous peaks ($2° = 13$–35°) derived from homogeneously amorphous SiO_2-PVA hybrids. All the PVA modified silica powder (HAP_2–HAP_8) exhibited relatively denser network with lesser pores than that of AP_0 (pure aerogel powder).

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