Macromolecules **2007,** *40,* 4823−4828

Amphiphilic Poly(vinyl alcohol) Hybrids and Electrospun Nanofibers Incorporating Polyhedral Oligosilsesquioxane

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Received January 9, 2007; Revised Manuscript Received May 7, 2007

ABSTRACT: Polyhedral oligosilsesquioxane (POSS)-containing amphiphilic poly(vinyl alcohol) (PVA) hybrids (PVA−POSS hybrids) were synthesized by urethane linkage between the hydroxyl groups of PVA and the monoisocyanate group of POSS macromers. The hydrophobicity of the amphiphilic PVA−POSS hybrids was varied by changing the incorporated amounts of the hydrophobic POSS macromers, resulting in control over water resistance. The synthesized amphiphilic PVA−POSS hybrids were characterized by ^{1}H NMR, FT-IR, DSC, and TGA and revealed modified thermal stability and solubility depending on the incorporated amounts of POSS macromers. That is, modification in both solid form and solution is observed, which is attributed to the bulkiness and hydrophobicity of POSS moieties. As a result, the amphiphilic PVA−POSS hybrids with the molar ratio of POSS macromer to −OH mole of PVA ranging from 1.0 to 15.0 could be obtained. Amphiphilic PVA−POSS hybrids showed microstructural features characteristic structure of two separate crystalline components, that is, the dual system of PVA and POSS crystalline phases. In addition, the electrospun nanofibers of PVA−POSS hybrids suggest a new method to enhance/control the water resistance of PVA nanofibers without cross-linking.

Introduction

Poly(vinyl alcohol) (PVA) is a highly hydrophilic, nontoxic, and biocompatible semicrystalline polymer with excellent properties such as the strength, water solubility, gas permeability, and thermal characteristics. These properties of PVA have led to their utilities in a variety of industry areas, including chemical engineering, pharmaceutics, textiles, medical devices, and food additives.[1−5] In order to be useful in areas of medical and pharmaceutical applications, the stability of PVA should be controlled, such as by cross-linking either chemically or physically. For instance, PVA membranes have been chemically cross-linked with difunctional glutaraldehyde (GA) in the presence of sulfuric acid, acetic acid, or methanol.[6] Other methods of chemical cross-linking of PVA, which include the use of electron beam or gamma irradiation, have been investigated.[7] Heat treatment or annealing of membranes at elevated temperature can form crystallites, which serve as physical cross-links. In addition, it has reported that the properties of environmentally sensitive PVA membranes can be controlled by external conditions such as pH and temperature, and hence they have applications in controlled drug delivery, protein separations, etc.[8,9] The temperature-sensitive membranes were prepared by graft copolymerization of *N*-isopropylacrylamide (NIPAM) onto PVA.[10,11]

In this paper, we report on the new class of amphiphilic PVA hybrids incorporating polyhedral oligosilsesquioxanes (POSS) nanoparticles (PVA−POSS hybrids) and explore the stability and electrospinnability of the amphiphilic PVA−POSS hybrids with different amounts of POSS contents. POSS-containing materials are a new class of nanostructured hybrid materials, which are the hybridization of an organic polymer and inorganic material on a nanosize scale, as an interesting building block for the construction of organic−inorganic hybrid structures,[12−18] and have the higher thermomechanical properties and better thermooxidative stability in both thermoplastics and thermosets. Like Mather's PEG−POSS telechelic system,[19−21] the synthesized PVA−POSS hybrids are amphiphilic; that is, they possess lyophilic (oil-loving) POSS moieties chemically bonded to hydrophilic (water-loving) PVA backbone. Thus, in solutions, amphiphiles self-assemble into aggregates such as spheroidal and wormlike micelles, vesicles, and bilayers. Amphiphiles are not only of great interest scientifically but also of immense practical value as detergents, emulsifiers, encapsulants, lubricants, and so on. So far, most of the researches have been focused on the thermomechanical studies of the POSS-containing polymers, but not less attracted on the solution properties and nanoassemblies using nanoprocessing techniques, such as electrostatic spinning, etc. As far as we know, there is no prior report on enhanced water resistance and electrospinning studies of such amphiphilic PVA−POSS hybrid materials incorporating polyhedral oligosilsesquioxane (POSS) macromers.

The objective was first to synthesize and characterize a series of amphiphilic PVA−POSS hybrids incorporating POSS macromers as pendent groups. The solubility and thermomechanical properties of various PVA−POSS hybrids with different amounts of POSS content are investigated, and electrostatic spinning of PVA−POSS hybrids is explored. A detailed further study of association behaviors of the amphiphilic PVA−POSS hybrids and cell cultures of the electrospun PVA−POSS hybrid nanofibers are in progress.

Experimental Section

Materials. Poly(vinyl alcohol) (PVA) with a molecular weight (MW) = 65 000 g/mol and degree of hydrolysis (DH) = 85.5−88.5% were obtained from Dong Yang Chem. Co., Korea. Isocy-

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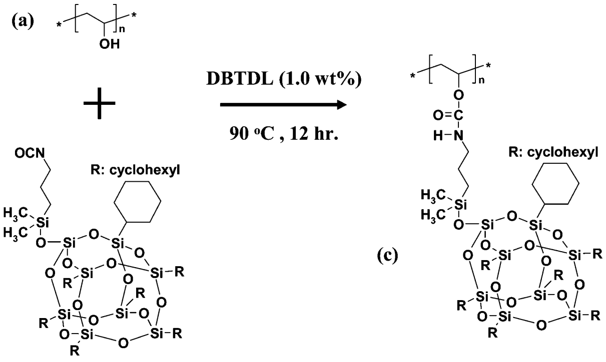
10.1021/ma070056e CCC: $37.00

Scheme 1. Reaction Scheme of Amphiphilic PVA−POSS Hybrids[a]



[a] (a) Poly(vinyl alcohol) (PVA), (b) isocyanatopropyldimethylsilylcyclohexyl-polyhedral oligosilsesquioxane (POSS macromer), and (c) amphiphilic PVA−POSS hybrids.

anatopropyldimethylsilylcyclohexyl-polyhedral oligosilsesquioxane (POSS macromer) was provided by Air Force Research Lab, AFRL/PRSM, and its chemical structure was confirmed by ^{1}H NMR spectroscopy. Dibutyl tin dilaurate (DBTDL; Aldrich, 95% purity) as a catalyst for urethane formation was used as received. Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were dried over CaH_2 and then distilled under nitrogen prior to use. All chemicals were of analytical purity or higher quality and were used without further purification.

Synthesis. Solutions of PVA and POSS macromer were prepared separately in dried DMSO and THF. A mixture of dried PVA (1.0 g, 19.6 mmol equivalent to −OH group) and DMSO (19.0 g) was charged in a four-necked flask, equipped with a stirrer, a nitrogen inlet, an outlet, and a thermometer and then further stirred at 60 °C until the mixture is completely dissolved. Subsequently, POSS macromer solutions ($r = 1.0-15.0$, molar ratio $r =$ moles of POSS macromer/OH moles of PVA), containing 1.0 wt % of catalyst (DBTDL) based on the weight of the reactant, were added slowly via syringe within 20 min into a flask containing a preweighted amount of PVA. The reaction mixture was vigorously stirred at 90 °C under a nitrogen atmosphere for about 12 h. Then the reaction mixture was precipitated in an excess amount of THF and washed with fresh THF several times to remove the unreacted POSS macromer and catalyst, and then the precipitated PVA−POSS hybrids were filtered. The isolated products were subsequently washed with deionized water carefully to remove unreacted pure PVA, as a precautionary measure. The resulting products were dried under vacuum and P_2O_5 at 80 °C for at least 2 days to remove residual solvent. An illustration of the synthetic procedure for amphiphilic PVA−POSS hybrids formation is shown in Scheme 1.

Characterization. To establish their chemical structures, ^{1}H NMR spectra were recorded with a 400 MHz FT/NMR spectrometer (JEOL, JNM-EX400) in DMSO-d_6 using tetramethylsilane (TMS) as an internal standard. To further identify the chemical structures of the product polymers, FT-IR analysis was done using a Varian FTS 1000 spectrometer. The powders were ground into a dry KBr disk. The spectra were analyzed using Varian Resolutions Pro version 4.0.5 from Varian.

The thermal property of PVA−POSS hybrids was determined with DSC (Perkin-Elmer Diamond DSC) in a nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 220 °C. All of samples were dried under vacuum overnight before measurement. The thermal stability of the synthesized amphiphilic PVA−POSS hybrids was carried out with a Pyris TGA (Perkin-Elmer) by heating from 50 to 800 °C under a continuous nitrogen purge of 20 mL/min. The heating rate was 20 °C/min.

The wide-angle X-ray intensity curves of the PVA−POSS hybrids were measured with graphite-monochromatized Cu Kα radiation generated at 30 kV and 150 mA in a Rigaku D/MAX 2500 diffractometer at a scanning speed of $2\theta = 4°$/min.

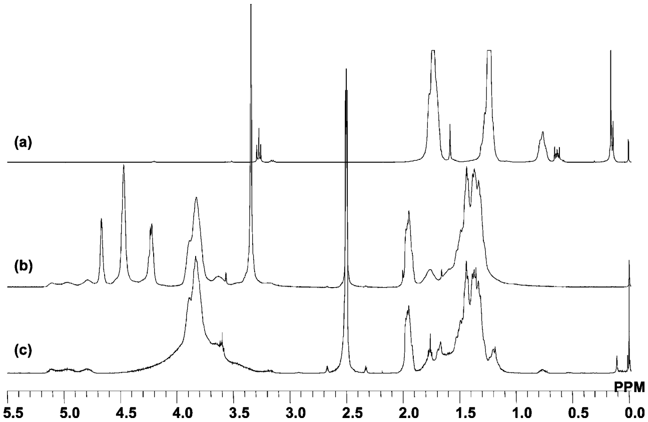


Figure 1. ^{1}H NMR spectra of (a) POSS macromer, (b) pure PVA, and (c) amphiphilic PVA−POSS hybrids ($r = 4.5$).

Preparation of Electrospun PVA−POSS Hybrid Fibers. A high-voltage power supply (CPS-60 K02V1, Chungpa EMT Co., Republic of Korea), capable of generating voltages up to 60 kV, is used as a source of electric field. The amphiphilic PVA−POSS hybrid solutions of 9.0 wt % dissolved in mixture (3/2, w/w) of DMSO and methanol was supplied through a plastic syringe attached to a capillary tip. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution, and a negative electrode (cathode) was attached to a metallic collector at 50 °C. The voltage was fixed at 15 kV. The distance between the capillary tip and the collector was fixed to be 15 cm, and the plastic syringe was placed at an angle of 10° from the horizontal direction.

Results and Discussion

Synthesis of Amphiphilic PVA−POSS Hybrid Materials. The amphiphilic PVA−POSS hybrids were synthesized by forming the urethane bond between a monoisocyanate group of POSS macromer and a hydroxyl group of PVA. The solubility in water significantly depended on POSS content incorporated into PVA backbone. It was found that the amphiphilic PVA−POSS hybrids ($r = 7.4$ and $r = 12.1$) with molar ratio of POSS more than 7 did not dissolve in water, but rather swell, whereas the amphiphilic PVA−POSS hybrids ($r = 1.3$ and $r = 4.5$) with molar ratio of POSS less than 4 dissolve in water maybe by forming the micelles in solution.[20] The results indicate the successful incorporation of the hydrophobic POSS macromers onto PVA polymer backbone giving rise to dramatically altered solubility. As a result, the hydrophobicity of the synthesized PVA−POSS hybrids could be varied by controlling the added amounts of POSS macromers. Like the previously reported papers,[19−21] we therefore expect that hydrophobic/hydrophilic balance may have an important role in both the liquid-state aggregation and solid-state structural/morphological behaviors.

The synthesized amphiphilic PVA−POSS hybrids were characterized by ^{1}H NMR and FT-IR spectroscopy. Figure 1 presents a comparison of the ^{1}H NMR spectra of the POSS macromer, PVA−POSS hybrids, and pure PVA:POSS macromer (Figure 1a), ($CDCl_3$) δ 3.27 ppm ($-\mathrm{C}H_2-\mathrm{NCO}$), δ 1.73 ppm (cyclohexyl ring, $-\mathrm{C}H_2-$), δ 1.22 ppm (cyclohexyl ring, $-\mathrm{C}H_2-\mathrm{CH}-$ and $-\mathrm{C}H_2-\mathrm{CH_2}-\mathrm{NCO}$), δ 0.76 ppm (cyclohexyl ring, $-\mathrm{CH_2}-\mathrm{C(CH_2)}H-$), δ 0.63 ppm ($-\mathrm{O}-\mathrm{Si(CH_3)_2}-\mathrm{C}H_2-$), δ 0.16 ppm ($-\mathrm{O}-\mathrm{Si(C}H_3)_2-\mathrm{CH_2}-$); pure PVA (Figure 1b), (DMSO-d_6), δ 1.33−1.75 ppm (PVA backbone, $-\mathrm{C}H_2-$), δ 3.56−3.82 ppm (PVA backbone, $-\mathrm{C}H-$), δ 1.94 ppm (acetate group of PVA, $-\mathrm{C}H_3$), δ 4.22/4.47/4.66 ppm (hydroxyl group of PVA, $-\mathrm{O}H$).

Figure 1c shows ^{1}H NMR spectra of the amphiphilic PVA−POSS hybrids. As seen in Figure 1c, all the peaks, which have

Table 1. Thermal Properties of the Amphiphilic PVA−POSS Hybrids

samples	r^a	T_g (°C)	T_m (°C)	T_d (°C)	ash (%)^b
PVA		72	183	332	3.4
PVA−POSS hybrids	1.3	79	176	331	3.9
PVA−POSS hybrids	4.5	74	172	327	5.7
PVA−POSS hybrids	7.4	75	156	324	8.9
PVA−POSS hybrids	12.1	73	158	324	17.3

[a] r indicates the molar ratio of POSS macromer to −OH mole of PVA. [b] The residual char mass percentage was taken as the mass percentage remaining at $T = 700$ °C.

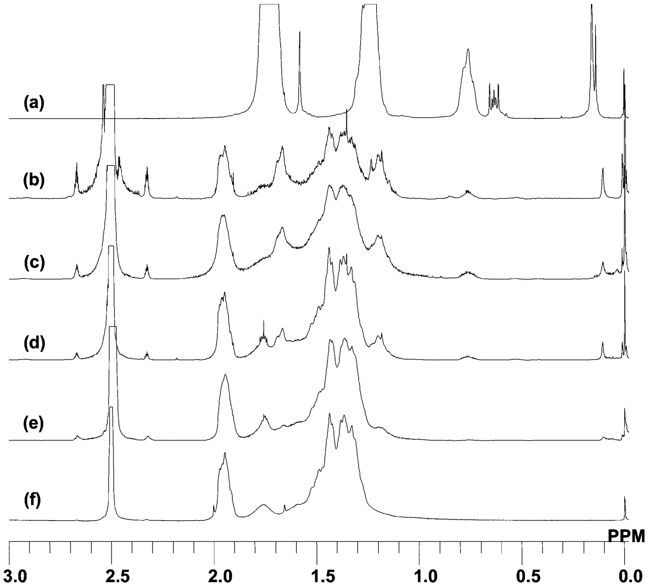


Figure 2. ^{1}H NMR spectra of (a) POSS macromer, the amphiphilic PVA−POSS hybrids with different molar ratio r of POSS macromer to −OH mole of PVA ((b) $r = 12.1$, (c) $r = 7.4$, (d) $r = 4.5$, (e) $r = 1.3$), and (f) pure PVA.

appeared in both PVA and POSS macromer, have also appeared in the PVA−POSS hybrids with a very little change in the chemical shift values. In general, commercial PVA is obtained by the hydrolysis of poly(vinyl acetate) and consequently is in fact poly(vinyl alcohol-*co*-vinyl acetate) containing about 12−15% acetate groups, as confirmed by ^{1}H NMR spectroscopy. The distinctive feature of PVA−POSS hybrids is the new observation at $\delta \sim 1.67$ ppm, which corresponds to the cyclohexyl ring, $-CH_2-$, and allows the estimation of the level of incorporation of POSS macromers in the amphiphilic PVA−POSS hybrids quantitatively by the monitoring of the resonances for the cyclohexyl groups of POSS macromers.[19,22] They were obtained by comparing the ratio of the PVA $-CH_3$ (acetate group of PVA, δ 1.94 ppm) integration value, normalized to that for a single proton, to the average integration value for the POSS $-O-Si(CH_3)_2-CH_2-$ (δ 0.16 ppm) integral. As a result, the weight percentages of POSS macromers in the amphiphilic PVA−POSS hybrids were found to be 1.3, 4.5, 7.4, and 12.1 wt %. The compositions of the amphiphilic PVA−POSS hybrids calculated by ^{1}H NMR are summarized in Table 1.

Moreover, it was observed that the characteristic peaks of POSS macromers at δ 1.67, 1.20, 0.76, 0.53, and 0.11 ppm, which correspond to cyclohexyl ring $-CH_2-$ (cyclohexyl ring, $-CH_2-CH-$ and $-CH_2-CH_2-NCO$), cyclohexyl ring $-CH_2-C(CH_2)H-$, $-O-Si(CH_3)_2-CH_2-$, and $-O-Si(CH_3)_2-CH_2-$, become evident as the POSS content increases (Figure 2).

Figure 3 represents the FT-IR spectra of POSS macromer (Figure 3a), PVA−POSS hybrids (Figure 3b−d), and pure PVA (Figure 3e). For the case of the amphiphilic PVA−POSS hybrids, we found the new absorption band at 1530 cm^{-1} attributed to the N−H bending vibration in urethane linkage and characteristic strong absorption bands at 1447 and 895 cm^{-1} attributed to the $-CH_2-$ bending vibration in strained cyclohexyl ring and the rocking vibration of cyclohexyl ring structure, respectively, together proving the successful urethane bond formation between the hydroxyl groups of PVA and the isocyanate group of POSS macromers. It was also observed that the absorption intensity at 1447 cm^{-1} attributed to the $-CH_2-$ bending vibration in strained cyclohexyl ring increases with the increase of POSS content. On the other hand, unfortunately, the N−H stretching vibrations of the urethane group cannot be distinguished since they overlap with the −OH stretching vibrations of hydrogen-bonded hydroxyl groups of PVA. In addition, the sharp band at about 1735 cm^{-1} corresponds to the $-C{=}O$ stretching of the acetate group of PVA and the urethane amide groups of PVA−POSS hybrids. The PVA−POSS hybrids spectra also show absorption bands in the 1000−1300 cm^{-1} range, the strong C−O and Si−O stretching vibrations, and in the 1200−1400 cm^{-1} range, $Si-CH_3$ and $Si-CH_2$ bending vibrations. In addition, as the POSS content increased, the intensity of the absorption bands at 1530 and 895 cm^{-1} attributed to the N−H bending and cyclohexyl ring rocking vibrations also increased.

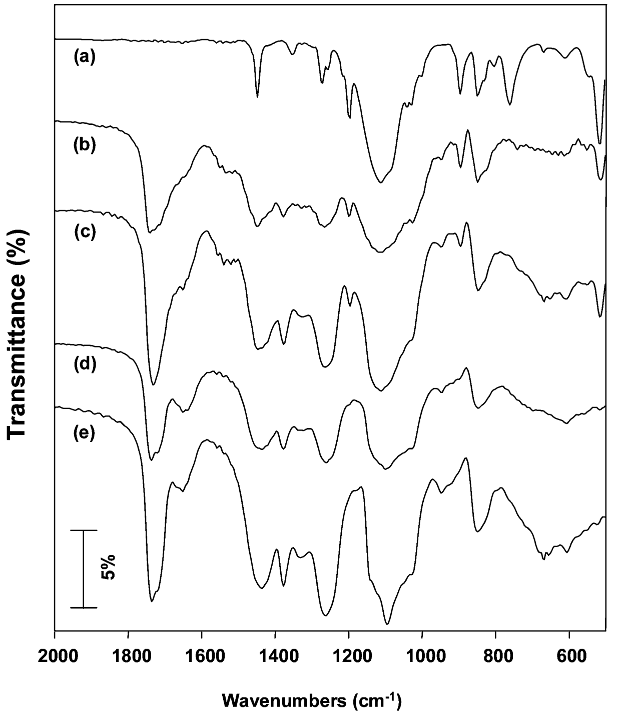


Figure 3. FT-IR spectra of (a) POSS macromer, the amphiphilic PVA−POSS hybrids with different molar ratio r of POSS macromer to −OH mole of PVA ((b) $r = 12.1$, (c) $r = 7.4$, (d) $r = 1.3$), and (e) pure PVA.

Thermal and Structural Properties of PVA−POSS Hybrid Materials. Because of higher thermal stability of POSS macromers,[22−24] the thermal stability of the synthesized amphiphilic PVA−POSS hybrids is expected to be improved over unmodified PVA. Figure 4 represents the TGA results of the amphiphilic PVA−POSS hybrids.

As seen in Figure 4, the pure PVA shows one continuous sharp decomposition event, while the amphiphilic PVA−POSS hybrids exhibit clearly two-step thermal decomposition behaviors, suggesting the altered thermal decomposition due to the incorporation of POSS macromers.[19] In addition, the thermal stability of PVA−POSS hybrids at higher temperature above

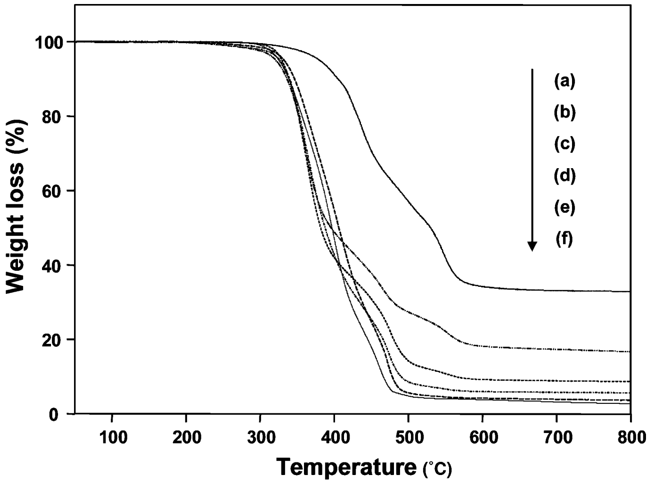


Figure 4. Thermogravimetric analysis of (a) POSS macromers and the amphiphilic PVA−POSS hybrids with different molar ratio *r* of POSS macromer to −OH mole of PVA ((b) $r = 12.1$, (c) $r = 7.4$, (d) $r = 4.5$, (e) $r = 1.3$), and (f) pure PVA. A heating rate of 20 °C was placed to samples in a nitrogen environment.

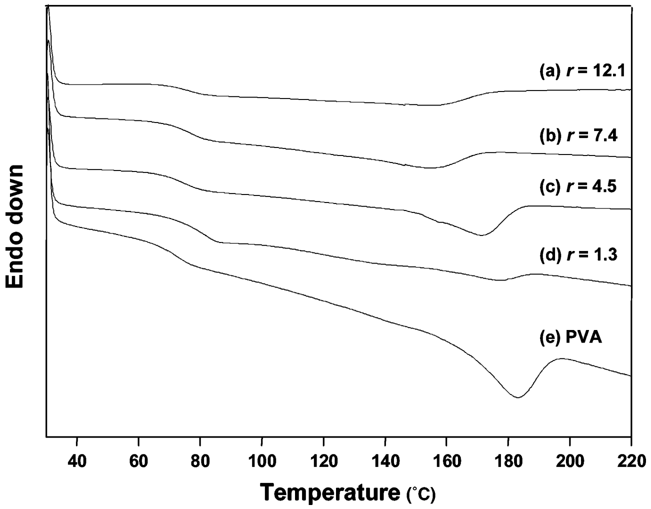


Figure 5. DSC thermograms (second scans) of the amphiphilic PVA−POSS hybrids with different molar ratio *r* of POSS macromer to −OH mole of PVA ((a) $r = 12.1$, (b) $r = 7.4$, (c) $r = 4.5$, (d) $r = 1.3$) and pure PVA (e).

400 °C was remarkably enhanced. Figure 5 represents the DSC thermograms (second scans) of the pure PVA and the PVA−POSS hybrids with various POSS contents.

In the case of pure PVA, as seen in Figure 5, T_g and T_m were clearly observed and found to be 72 and 183 °C, respectively. On the other hand, the T_m of the amphiphilic PVA−POSS hybrids are slightly lower than that of pure PVA, while the values of melting point do not show any trend with respect of POSS contents. The slight decrease in T_m with an increase of POSS content indicates that incorporation of POSS macromer as a pendent group onto PVA backbone hinders the crystallization process and results in crystallites with lower thermal stability. Moreover, it is also found that the amphiphilic PVA−POSS hybrid with higher POSS content ($r = 12.1$) do not show sharp endothermic peaks, suggesting that an increased disturbance of bulky and rigid POSS blocks results in less intermolecular or intramolecular interaction between PVA segments during crystallization. In addition, T_g values of the soft PVA segments in the amphiphilic PVA−POSS hybrids were slightly increased with an increase of POSS content, although the magnitude of this shift is difficult to quantify.

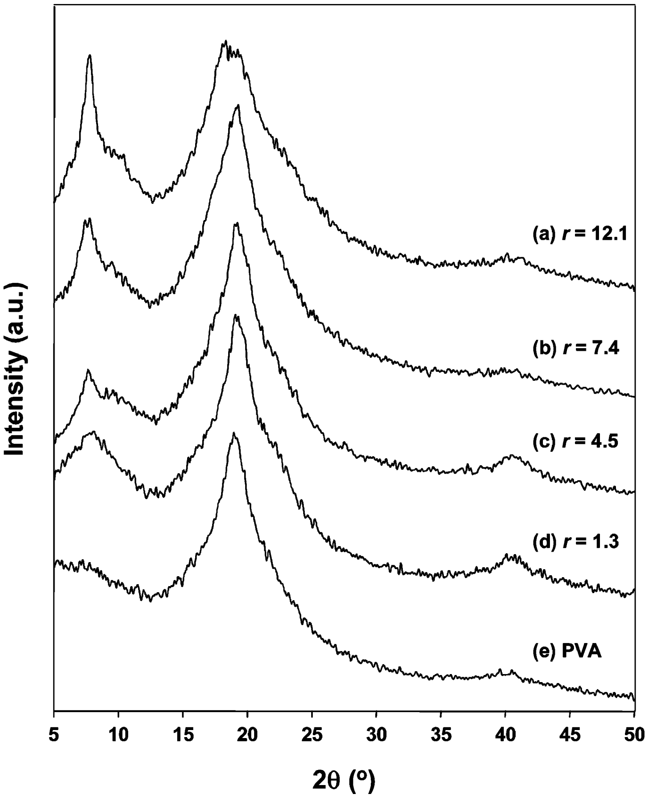


Figure 6. Wide-angle X-ray diffraction (WAXD) patterns of the amphiphilic PVA−POSS hybrids with different molar ratio *r* of POSS macromer to −OH mole of PVA ((a) $r = 12.1$, (b) $r = 7.4$, (c) $r = 4.5$, (d) $r = 1.3$) and pure PVA (e).

Figure 6 shows the WAXD patterns of pure PVA and amphiphilic PVA−POSS hybrids at room temperature.

In general, pure PVA exhibits an evident peak at 19.5° and 24.5°, corresponding to the (101) and (200) reflections.[25] In the PVA−POSS hybrids, the same reflections, and thus the same crystalline microstructure, were observed. These peaks are less ordered as POSS content increases probably due to the steric hindrance during the PVA crystallization, while characteristic strong reflections at 2θ values of 7.84° (1.13 nm), 10.38° (0.85 nm), and 18.32° (0.48 nm), corresponding to a crystalline POSS phase, are preserved in the PVA−POSS hybrids. These results agree well with the previously reported papers,[21] resulting in a dual crystalline system wherein both POSS and PVA can crystallize. Accordingly, as POSS content in the PVA−POSS hybrids increases, the additional peaks become predominant while the strong PVA reflections were gradually weakened and broadened. Considering that the (101) diffraction of the PVA crystal was due to the intermolecular interference between the PVA chains in the direction of the intermolecular hydrogen bonding, the decrease in the intensity of the (101) diffraction corresponded to the decrease in the number of the regular PVA chains packing together. That is, the decrease in the (101) diffraction intensity with the increasing POSS content suggests that the size of the PVA crystallite in the PVA−POSS hybrids became smaller because of the difficulty of the crystallization. This result is well in accordance with the DSC results discussed earlier.

Electrospun Nanofiber and Stability of PVA−POSS Hybrids. Even though PVA has good mechanical properties in the dry state, its applications are limited by its high solubility in water. Specifically, improving the water resistance of the nonwoven fabrics composed of electrospun PVA fibers having a large specific surface area and a small pore size is the most

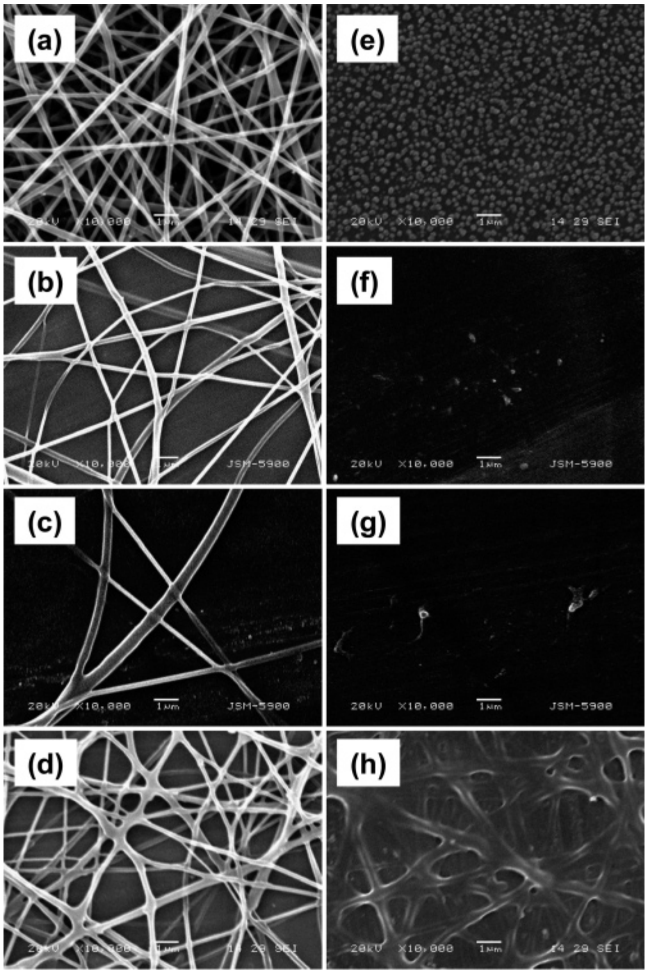


Figure 7. Scanning electron microscopy (SEM) images of the pure PVA and amphiphilic PVA−POSS nanofibrous mats before ((a) PVA, (b) PVA−POSS ($r = 1.3$), (c) PVA−POSS ($r = 2.1$), (d) PVA−POSS ($r = 4.5$)) and after ((e) PVA, (f) PVA−POSS ($r = 1.3$), (g) PVA−POSS ($r = 2.1$), (h) PVA−POSS ($r = 4.5$)) contact with water.

important toward the biomedical applications. For instance, PVA fiber aggregates have been cross-linked by using cross-linking agents for improved water resistance.[26,27] Here, we attempt to introduce new electrospun PVA nanofibers with the enhanced/controlled water resistance without the covalent cross-linking. Along these lines, the synthesized amphiphilic PVA−POSS hybrids are very attractive candidates because new PVA−POSS hybrids show the controlled water stability depending on POSS contents. Interestingly, we could successfully electrospin the PVA−POSS hybrid solutions dissolved in DMSO while we fail to electrospin pure PVA solution dissolved in DMSO, but not in water. Figure 7 shows scanning electron microscopy (SEM) images of pure PVA and PVA−POSS hybrids nanofibrous mats ($r = 1.3$, 2.1, and 4.5).

It was observed that the electrospun fibers are deposited as a randomly oriented states, forming a highly porous structure, which is held together by connecting sites such as crossing and bonding between the fibers.[28−33] The morphologies of both pure PVA and PVA−POSS hybrids nanofibers are regular, and a narrow distribution of diameters is observed, with an average diameter of 250 nm.

To test the stability of the amphiphilic PVA−POSS hybrid nanofibers in water, a water droplet is placed on both pure PVA and PVA−POSS hybrid e-spun fiber mats. Afterward, the pure PVA electrospun fibrous mats and PVA−POSS electrospun fibrous mats ($r = 1.3$ and 2.1) immediately absorbed the water and then are dissolved in water while PVA−POSS electrospun fibrous mats ($r = 4.5$) maintain their fibrous shapes, but rather swell. This fact clearly demonstrates that the water resistance of the amphiphilic PVA−POSS hybrid nanofibers ($r = 4.5$) in comparison with pure PVA nanofibers is dramatically enhanced due to the incorporated POSS macromers with a hydrophobic nature. It is therefore expected that such PVA−POSS hybrid nanofibrous mats with a controlled water resistance may be promising candidates as a scaffold for cell culture and will be reported in other reports.

Conclusions

The synthesis, water resistance, and electrospinning studies of amphiphilic PVA−POSS hybrid materials incorporating polyhedral oligosilsesquioxane (POSS) macromers were carried out. We found that the incorporation of the hydrophobic POSS hybrid nanoparticles onto hydrophilic PVA backbone resulted in an altered solubility and enhanced water resistance with an increasing POSS content. The amphiphilic PVA−POSS hybrids with the molar ratio of POSS macromer to −OH mole of PVA ranging from 1.0 to 15.0 could be obtained. It was found that the amphiphilic PVA−POSS hybrids ($r = 7.4$ and $r = 12.1$) with molar ratio of POSS more than 7 did not dissolve in water, but rather swell, whereas the amphiphilic PVA−POSS hybrids ($r = 1.3$ and $r = 4.5$) with molar ratio of POSS less than 4 dissolve in water, indicating the successful incorporation of the hydrophobic POSS macromers onto PVA polymer backbone giving rise to dramatically altered solubility. As a result, the hydrophobicity of the synthesized PVA−POSS hybrids could be varied by controlling the added amounts of POSS macromers. Amphiphilic PVA−POSS hybrids showed microstructural features characteristic structure of two separate crystalline components, that is, the dual system of PVA and POSS crystalline phases. In addition, the electrospun nanofibers of PVA−POSS hybrids suggest a new method to enhance/control the water resistance of PVA nanofibers without cross-linking.

Acknowledgment. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (the Center for Healthcare Technology Development, Chonbuk National University, Jeonju 561-756, Republic of Korea). B.S.K. is grateful for kind supply of POSS macromers by Prof. P. Mather (Dept. of Macromolecular Sci. & Eng., Case Western Reserve University).

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MA070056E