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Electrospun novel super-absorbent based on polysaccharide–polyvinyl alcohol–montmorillonite clay nanocomposites

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ABSTRACT

A novel super-absorbent material was fabricated by electrospinning the natural polysaccharide pullulan (PULL) with polyvinyl alcohol (PVA) and montmorillonite (MMT) clay to form nonwoven webs, which were then heat treated. Transmission electron microscopy (TEM) micrographs, X-ray diffraction (XRD) patterns, and Fourier transform infrared (FTIR) analysis of the novel super-absorbent nanofibers suggest the coexistence of PULL, PVA, and MMT through the exfoliation of MMT layers in the super-absorbent nanofiber composite. The heat-treated PULL/PVA/MMT webs loaded with 5 wt% MMT electrospun nanofibers exhibited a water absorbency of 143.42 g g^{-1} in distilled water and a water absorbency of 39.75 g g^{-1} in a 0.9 wt% NaCl solution. Under extremely dry conditions, the PULL/PVA/MMT webs exhibited the ability to retain 43% distilled water and 38% saline water after being exposed to the atmosphere for one week. The heat treatment improved the crystallinity of the electrospun PULL/PVA/MMT super-absorbent webs and thus made the webs highly stable in aqueous environments. Overall, the addition of MMT resulted in improved thermal stability and mechanical properties and increased the water absorbency of the PULL/PVA/MMT composite.

1. Introduction

Super-absorbent polymers (SAPs) are functional polymeric materials that have the ability to absorb and retain significant amounts of water. These materials can retain such a significant amount of water that the weight of the super-absorbent plus retained water can reach several hundred times the weight of the material, even under some externally applied pressure. SAPs have application potential in many fields, including: agriculture, hygiene products, waste-water treatment, drug-delivery, and coal dewatering (Chu, 2006; Ende, 1995; Kamat & Malkani, 2003; Sadeghi & Hosseinzadeh, 2008; Yi & Zhang, 2008).

A large number of materials have been used to prepare SAPs. The most common types of materials are based on acrylic acid and acryl amide compounds, both of which have poor biodegradability. Approximately 90% of SAPs are used in disposable products, most of which are eventually disposed of in landfills or are incinerated (Kiatkamjornwong, 2002). This considerable accumulation of such a robust absorbent materials in the environment leads itself to a significant environmental concern related to soil, water, and air pollutions (Zhang, J., 2007; Zhang, Y., 2007; Zhang, 2006). Moreover, the applications of SAPs have been limited due to their low absorption rates for concentrated electrolyte solutions, their lower water-retention capacities, and their high production costs (Wang & Liu, 2004). To address these issues, considerable attention has been focused on naturally available resources, such as polysaccharides and inorganic clay minerals (Li, 2007; Ray & Bousmina, 2005).These compounds have greater commercial and environmental values, along with the advantages of having low production costs, higher renewability, and better biodegradability when SAPs are derived from polysaccharides (Pourjavadi & Mahdavinia, 2006; Yoshimura, 2005).

Electrospinning is a very simple and effective approach for producing nanofibers, and this approach has attracted significant interest among academic and industrial scientists (Brenner, 2012). In the electrospinning process, a polymer solution is subjected to an electric field. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension of the solution, a charged jet of the solution is ejected from the tip of a capillary tube. Because the jet is charged, its trajectory can

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be controlled by another electric field. As the jet travels through air, the solvent evaporates, leaving a charged polymer fiber that lies randomly on a metal collecting screen. Nanofibers prepared using this technique have been employed in various applications, including filtration, protective clothing, absorbent processes, and food preservation (Han, 2006; Islam, 2012; Qin & Wang, 2006; Su, 2012).

Pullulan is an extracellular microbial polysaccharide produced by different strains of *Aureobasidium* (Lazaridou, 2003). Aside from the advantages afforded by natural polysaccharides, pullulan has attracted increasing interest in the biomaterial sciences because of its superior level of water solubility, water-absorbing capability, and its ability to form strong resilient films and fibers because of its chemical structure (Deshpande, 1992; Iwamoto, 1991; Singh, 2008a,b). Films and fibers composed of pullulan are colorless, tasteless, odorless, transparent, and flexible and have excellent mechanical properties (Kristo, 2007; Yuen, 1974). These properties make pullulan a candidate compound for producing nanofibers that possess an excellent absorbent capacity.

Polyvinyl alcohol (PVA) is a semi-crystalline hydrophilic polymer with good chemical and thermal stability. PVA is a highly biocompatible and non-toxic polymer that can easily be processed and that possesses high water solubility. PVA can form physical gels in various types of solvents, which leads to the use of PVA in a wide range of applications in the medical, cosmetic, food, pharmaceutical, and packaging industries (Duan, 2007; Hong, 2006; Lee, 2009; Ren, 2006; Ristolainen, 2006; Shao, 2003; Zhang, J., 2007; Zhang, Y., 2007). Due to its improved flexibility and toughness, PVA can be used to improve the physical properties of a system through mixing with other materials that have poor physical properties. PVA with functional groups is useful in practical investigations of functional polymers because of its easy preparation as a bulk material, as films, and as fibers.

Montmorillonite (MMT) clay is a useful inorganic material, due to its ability to induce remarkable improvements in the mechanical, thermal, flame-retardant, barrier, and wettability properties of polymeric composites when small amounts (1–10%) of MMT fillers are added (Park, 2012).In general, the structures of polymer/clay nanocomposites are classified according to the levels of intercalation and exfoliation of polymer chains into the clay galleries (Alexander & Dubois, 2000; Mondal, 2013). Various parameters, including the clay nature, organic modifier, polymer matrix, and preparation method, have effects on the levels of intercalation and exfoliation. Therefore, depending on the nature and properties of the clay and polymer, as well as on the methodology for preparing the nanocomposite, different composite structures can be obtained.

Composite nanomaterials have the ability to produce a synergetic combination of properties that cannot be obtained from their individual components (Hayder, 2011). The overall goal of this study was to develop super-absorbent composite materials using PULL, PVA, and naturally occurring MMT clay via a cost-effective and efficient electrospinning technique. This technique is much more facile than the currently used polymerization method, in which difficulties arise from the autoacceleration and separation of solvents that are possibly environmentally unfriendly. In this study, PULL/PVA/MMT composite nanofiber webs are prepared using the electrospinning process for the first time for use as a SAP. To the best of the authors' knowledge, the super-absorbent material prepared from the eco-friendly polymer blend (PULL/PVA) with MMT provides higher water absorbency than any commercially available biodegradable super absorbents. Both PULL and PVA are biocompatible polymers. Hence, the blended material composed of these two types of polymers would be biocompatible (Tang, 2011). The filler component of the super absorbent is MMT clay, which is a natural product that does not exhibit any adverse environmental effects.

2. Experimental

2.1. Materials

PVA with a number-average degree of polymerization of 1700 (M_w = 89,000–98,000, fully hydrolyzed, degree of saponification = 99.9%) was obtained from the DC Chemical Co., Seoul, Korea. Food-grade preparation (PF-20 grade) pullulan (PULL) (greater than 90% purity, M_w = 200,000 Da) was procured from Hayashibara Biochemical Laboratories Inc. (Okayama, Japan). Montmorillonite (MMT) (1–3 nm in width, 100–200 nm in length, and 1 nm in thickness of each MMT layer) was purchased from Kunimine Industries Co. Ltd., Japan. Double-distilled water (DDW) was used as the solvent for preparing all solutions.

2.2. Preparation of solutions for electrospinning

MMT powder was dispersed in double-distilled water using magnetic stirring at 300 rpm for 1 h at room temperature. At 1 h, PVA was added to the solution, which was then heated at 80 °C and magnetically stirred at 300 rpm for 2 h; then, the solution was cooled to room temperature. PULL powder was separately dissolved in double-distilled water using magnetic stirring for 2 h at room temperature. PULL/PVA/MMT blend solutions were prepared by mixing PVA/MMT and PULL solutions to a total solid concentration of 14 wt% with a 60/40 (PULL/PVA) mass ratio and various MMT contents (1, 3, 5, and 10 wt% MMT). Pure PULL, PVA, and PULL/PVA blend aqueous solutions of 14 wt% each one were prepared separately for electrospinning. PULL/PVA blend with 60/40 blend ratio at 14 wt% total polymer concentration is enable to provide the best electrospun nanofiber (Islam, 2012). 5 wt% MMT content disperses well in the polymer matrix to give the best development of new property of the composite (Ji, 2009).

2.3. Electrospinning

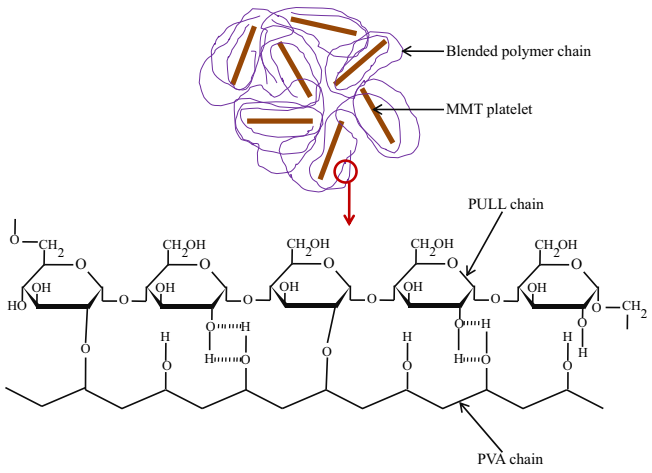
During electrospinning, high-voltage electricity (model CPS-60K02 VIT, Chungpa EMT Co., Ltd., Seoul, Korea) was applied to the PULL/PVA/MMT solution in a syringe (10 mL) via an alligator clip attached to the syringe needle. The applied voltage was adjusted to 15 kV. The solution was delivered to the blunt needle tip via a syringe pump to control the solution flow rate. Fibers were collected on electrically grounded aluminum foil placed at a 15 cm vertical distance below the needle tip. The same procedure was followed to prepare the PULL, PVA, and PULL/PVA blend nanofiber webs.

2.4. Heat treatment

The synthesis of the electrospun PULL/PVA/MMT nanofiber webs was completed with a heat treatment. The prepared nanofiber webs were placed in the empty space between the plates of a hot press for 4 min; however, the electrospun PULL/PVA/MMT nanofiber webs were not in direct contact with the hot plates. The plates were set at 150 °C and were separated by 1 cm. The heat-treated PULL/PVA/MMT composite is shown in the Scheme 1. The heat treatments for all of the other samples (pristine and blended) were conducted using the same method described above.

2.5. Measurement of water absorbency

To determine the water absorption capacity, 0.50 g samples of the material were immersed in either distilled water or in a saline solution (0.9% NaCl) for 12 min at room temperature to swell. The swollen sample was removed from the solution, and excess water was removed using a 100-mesh gauze. The weight of the swollen



Scheme 1. A schematic representation of the heat-treated PULL/PVA/MMT composite with an exfoliated clay layer.

sample was measured. The water absorbency (Q, g g^{-1}) was calculated using the following equation (Zuohao, 2011):

$$Q = (M_2 - M_1)/M_1$$

where, M_1 and M_2 are the weights of the dry and swollen samples (g), respectively.

2.6. Water retention measurement

The water retention of the nanofiber webs was expressed using the weight remaining (WR) of the nanofiber mats. Briefly, 3 g of dried nanofiber mat was immersed in water until the swelling reached equilibrium, at which point a constant weight was obtained. After surface water was removed using filter paper, the samples were placed in a desiccator at 30 °C. At different time intervals (24 h), samples were removed, weighed, and then placed back into the desiccator. The WR percentage was calculated as follows, where W_o and W_t correspond to the weights of the swollen nanofiber mats before and after the period in the desiccator, respectively (Lu, 2010):

$$\mathrm{WR}(\%) = W_t \times 100/W_o.$$

2.7. Characterization

The morphologies of the electrospun nanofibers were analyzed using a field emission scanning electron microscope (FE-SEM) (model JSM-6380, JEOL, Germany). Coexistence of the constituents of the composite materials was investigated using transmission electron microscopy (TEM) (HITACHI, model H-7600, Japan) with an accelerating voltage of 100 kV, X-ray diffraction (X'Pert APD, Philips, United Kingdom) patterns, and Fourier transform infrared (FTIR) analysis (Bruker IFS 120HR, Germany). The thermal stabilities of the nanofibers were studied using a TGA analyzer (model Q-50; TA Instruments, USA). Tensile strength tests were performed using a Zwick (Germany) Z005 material testing machine. Heat treatment of the nanofiber mats was conducted using equipment from Namyang Machinery MFG, Korea.

3. Results and discussion

3.1. Morphology of electrospun nanofibers

Morphology of electrospun nanofibers can be affected by electrospinning instrument parameters including the electric voltage, tip-to-collector distance, and by the solution parameters, such as the polymer concentration, feed mass ratio, and surface tension (Huang, 2004). Changing the polymer solution distinctly altered the fiber morphology, as shown in Fig. 1. A Fixed applied voltage of 15 kV and a tip-to-collector distance of 15 cm were used to prepare electrospun nanofiber mats from 14% PULL (Fig. 1a), PVA (Fig. 1b), and PULL/PVA (60/40) blend (Fig. 1c). It was found that the PULL/PVA (60/40) blend with a 14% total polymer concentration was ideal for obtaining more uniform nanofibers (Fig. 1c), which can be seen from its SEM image.

Fig. 1(d–f) displays the morphologies of heat-treated PULL, PVA, and PULL/PVA blend nanofibers, respectively. After heat treatment, the PULL/PVA blend nanofibers became thinner and more uniform (Fig. 1f) than the pure PULL or PVA fibers (Fig. 1d and e) because of the favorable solution viscosity for electrspinning of the blend system. Fig. 2a presents the FE-SEM image of electrospun nanofibers composed of PULL, PVA, and MMT (5%). Some beads were observed in the PULL/PVA/MMT blend due to the incorporation of MMT in the PULL/PVA blend. Fig. 2(b–e) shows the heat-treated PULL/PVA blend nanofibers with various MMT contents (1%, 3%, 5%, and 10%, respectively). Significant morphological changes, such as bead formation, were observed when MMT clay was introduced in the polymer blend. Through careful examination of the FE-SEM images in Fig. 2(b–e), it was evident that both the number and size of beads increase as the amount of added MMT increases. It is likely that the formation of beads is strongly influenced by the viscoelasticity of the solution; beads and beaded fibers are less likely to be formed in more viscous solutions (Fong, 1999). By increasing the MMT concentration, larger and more highly beaded nanofibers were formed, suggesting that less favorable beaded nanofibers could be obtained only at low MMT concentrations due to the higher viscosity of the solution (Park, 2009). By comparing the Figs. 1 and 2, uniform fibers are obtained from PULL/PVA blend (Fig. 1c), however, beads are forming with increasing fiber diameter due to the addition of 5% MMT (Fig. 2a). Diameter of the composite fiber are decreasing after heat treatment because of the successful crosslinking of polymers in the fibers (Fig. 2(b–e)) (Shen, 2014).

TEM observation of the heat-treated PULL/PVA/MMT composite nanofiber revealed that the MMT clay was well distributed in the nanofiber matrix (Fig. 2f). It is evident that each silicate platelet forms a dark line in the nanofiber. The size of the dark line is approximately 1–3 nm in width and 100–200 nm in length, indicating extremely good dispersion and exfoliation of MMT layers within the nanofiber matrix and their orientation along the fiber axis. This result clearly indicates the feasibility of electrospinning the 2-D platelet structures and the potential for achieving proper alignment of these clays along the fiber axis, which is critical for the fabrication of nanocomposite fibers (Fong, 2002).

3.2. XRD analysis

Fig. 3A presents the XRD patterns of the PULL, PVA, PULL/PVA blend (non-heat-treated and heat-treated), and PULL/PVA/MMT composite (non-heat-treated and heat-treated) nanofiber webs. A broad peak was observed near 19.4°, corresponding to a d-spacing of 4.52 Å for pure PULL (Fig. 3A(a)) (Biliaderis, 1999). Pure PVA shows a significant crystalline peak at approximately 19.3°, which is due to the occurrence of strong inter- and intramolecular hydrogen bonding (Fig. 3A(b)) (Park, 2010). With the addition of PULL to PVA at a 60/40 mass ratio in the PULL/PVA blend nanofibers, the intensity of the diffraction peak at approximately 19.4° of pristine PULL decreases three-fold (Fig. 3A(c)). The change in the intensity of the diffraction peak from pristine PULL could likely be attributed to the hydrogen-bonding interaction between PULL and PVA macromolecules in the PULL/PVA blend.

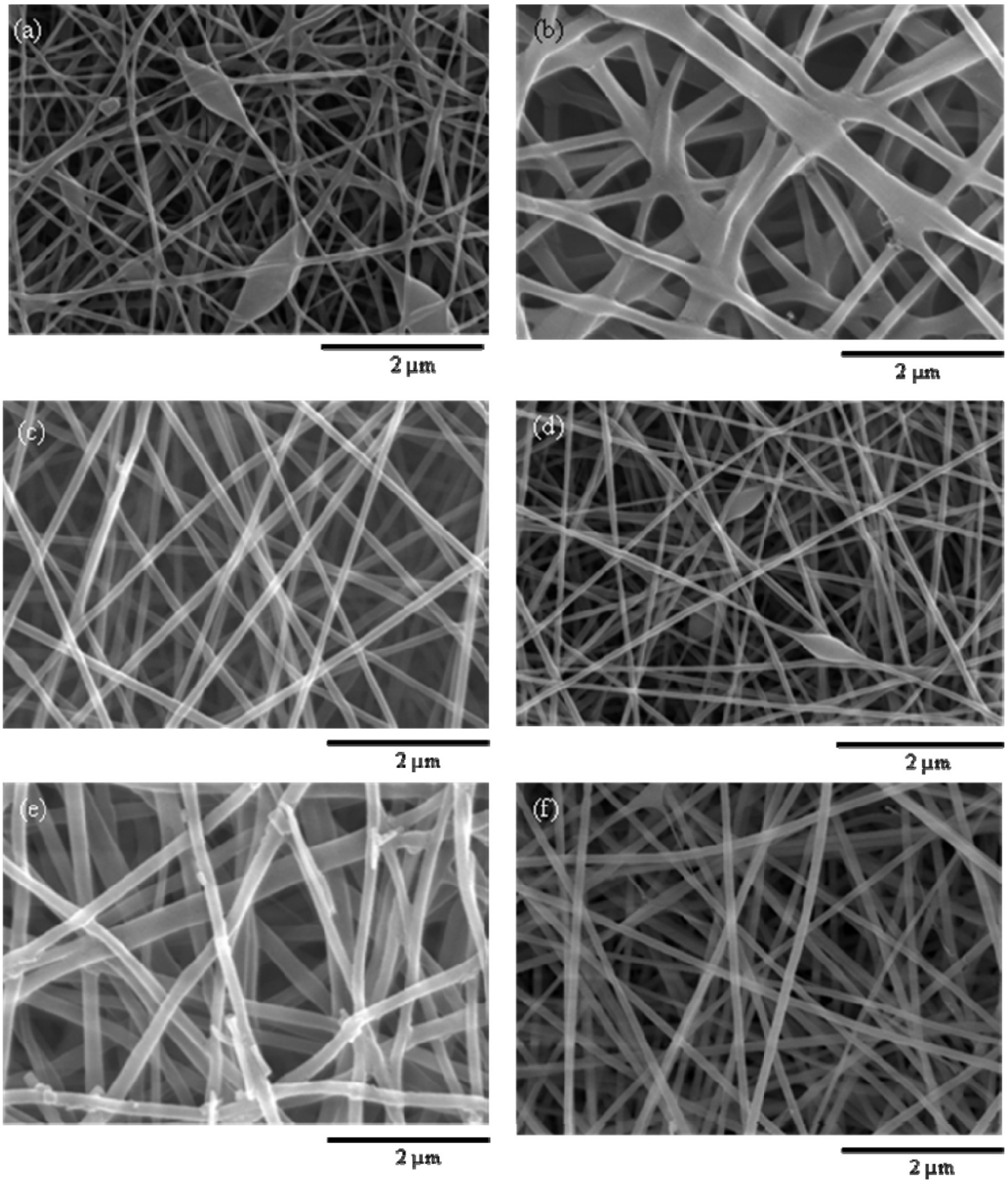


Fig. 1. FE-SEM images of electrospun nanofibers of (a) PULL, (b) PVA, (c) PULL/PVA blend, (d) heat-treated PULL, (e) heat-treated PVA, and (f) heat-treated PULL/PVA blend [total polymer concentration = 14%, Blend ratio (PULL/PVA) = 60/40, applied voltage = 15 kV, and TCD = 15 cm].

Hydrogen bonds between PULL and PVA were formed through the hydroxyl groups of these two polymers. However, the peak intensity of the heat-treated PULL/PVA blend nanofibers exhibited a greater increase than that of the non-heat-treated PULL/PVA blend nanofibers (Fig. 3A(d)). These results clearly illustrate that the crystallinity of the PULL/PVA blend is increased after heat treatment due to the crosslinking between the —OH groups of PULL and PVA. It is ovserved that in a nanoclay/polymer composite, unexfoliated or intercalated MMT often has a peak in the 3–9°(2θ) range. For exfoliated nanocomposites, in contrast, single silicate layers (1 nm thick) are homogeneously dispersed in the polymer matrix and no distinct diffraction peak in the 3–9° (2θ) range is detected (Barber, 2005; Zhu, 2007). For PULL/PVA/MMT nanofibers with 5% MMT content, there was no diffraction peak in the 3–9° (2θ) range (Fig. 3A(e)). This result suggests that MMT clays are well dispersed in the PULL/PVA blend nanofibers and are predominantly exfoliated. The intensity of the peak at approximately 19.4° for the heat-treated PULL/PVA/MMT blend nanofibers (Fig. 3A(f)) is greater than that of the non-heat-treated PULL/PVA/MMT blend nenofibers, indicating higher crystallinity in the heat-treated composite nanofiber webs. This higher crystallinity potentially arises from the crosslinking between PULL and PVA, which occurs through the loss of one molecule of water from the hydroxyl groups of PULL and PVA.

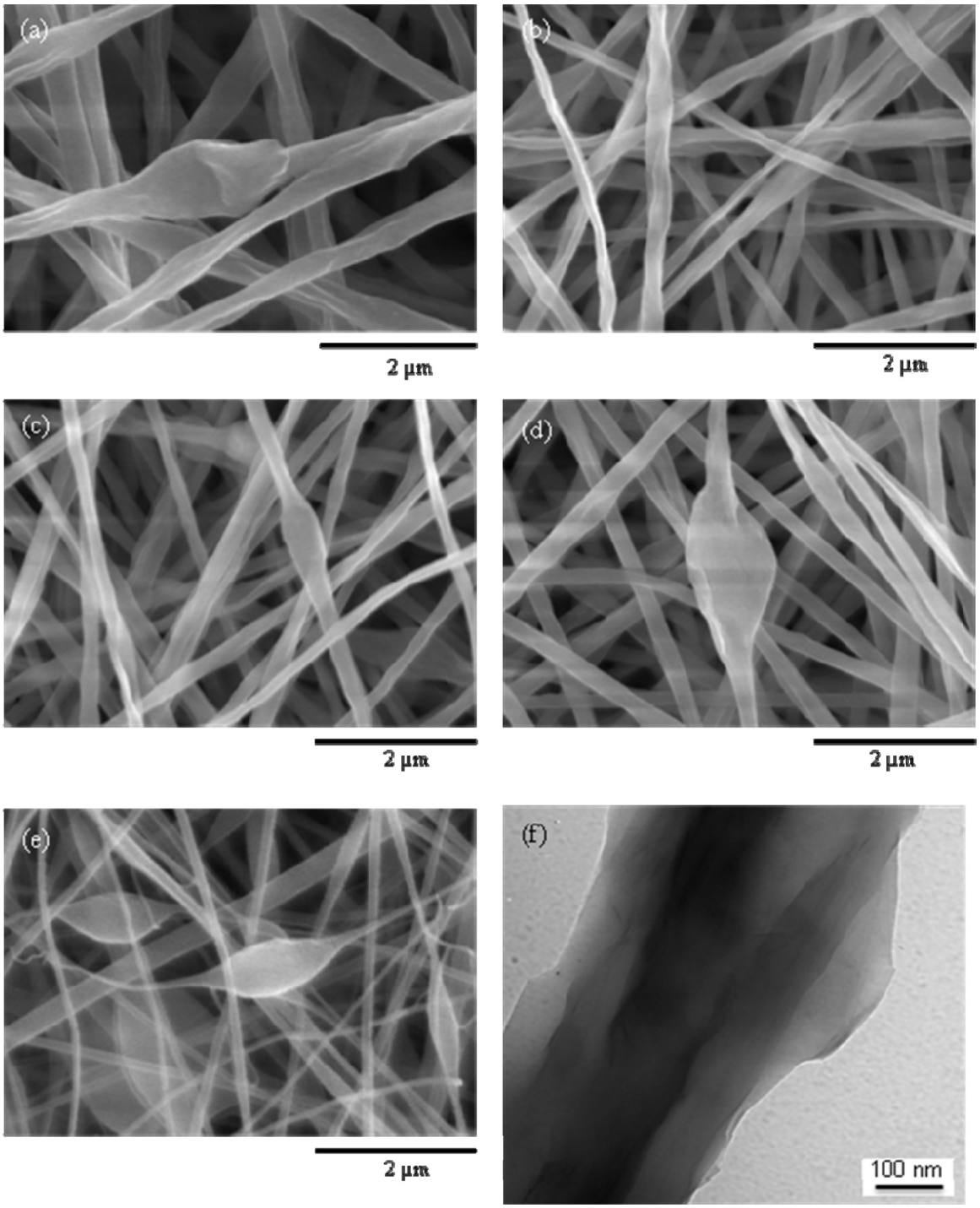


Fig. 2. FE-SEM images of (a) PULL/PVA/MMT nanofibers with a 5% MMT content and heat-treated PULL/PVA blend nanofibers with MMT contents of (b) 1%, (c) 3%, (d) 5%, and (e) 10% and (f) TEM image of heat-treated PULL/PVA/MMT nanofibers with a 5% MMT content [total polymer concentration = 14%, Blend ratio (PULL/PVA) = 60/40, applied voltage = 15 kV, and TCD = 15 cm].

3.3. FTIR data

FTIR spectra provides information about the structure of the blend nanofiber mats in this study. In Fig. 3B, spectra of electrospun pristine PULL, PULL/PVA (no-heat-treated and heat-treated) and PULL/PVA/MMT (no-heat-treated and heat-treated) blend nanofiber webs at 500–4000 cm^{-1} range are shown. Pristine PULL nanofibers exhibit characteristics bands for their functional groups, as shown in Fig. 3B(a). The spectra show strong peaks at 850 cm^{-1}, which are attributable to the α-glucopiranoside units. The peaks at frequencies of 755 cm^{-1} and 932 cm^{-1} are attributed to the presence of α-(1,4) glucosidic and α-(1,6) glucosidic bonds, respectively (Seo, 2004). The bands observed at 2850–3000 cm^{-1} correspond to the stretching vibrations of CH and CH_2 groups and bands attributed to CH/CH_2 deformation vibrations are present at 1300–1500 cm^{-1} range. Furthermore, a very intense, broad hydroxyl band occurs at 3000–3600 cm^{-1}, and accompanying C—O stretching exists at 1000–1260 cm^{-1}. With the addition of PVA, some of the absorption peaks of PULL become lower in intensity, and peaks at 1096 and 1447 cm^{-1} are observed (Fig. 3B(b)). This result suggests that

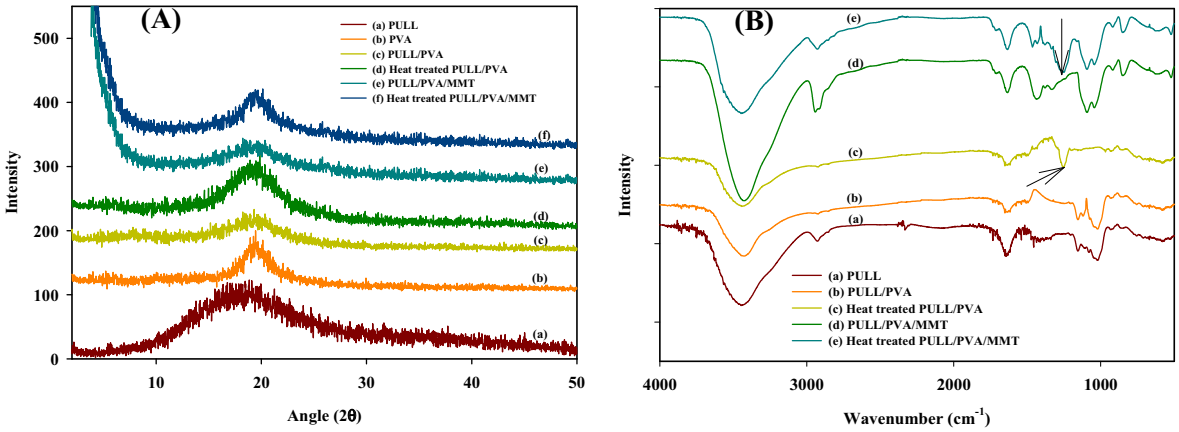


Fig. 3. (A) XRD patterns of electrospun nanofibers of (a) PULL, (b) PVA, (c) PULL/PVA blend, (d) PULL/PVA/MMT, and (e) heat-treated PULL/PVA/MMT and (B) FTIR spectra of electrospun nanofibers of (a) PULL, (b) PVA, (c) PULL/PVA blend, (d) PULL/PVA/MMT, and (e) heat-treated PULL/PVA/MMT [total polymer concentration = 14%, Blend ratio (PULL/PVA) = 60/40, MMT concentration = 5%, applied voltage = 15 kV, and TCD = 15 cm].

hydrogen bonds between the hydroxyl groups in PULL and PVA could possibly play a role in the shifting of the peaks. Thus, the FTIR spectra supports the interactions between PULL and PVA (Karim, 2011), suggested by the XRD data. The heat-treated PULL/PVA blend nanofiber mats exhibit a characteristic peak at 1250 cm^{-1}, indicating the formation of C—O bonds through the loss of one molecule of water from the two hydroxyl groups of PULL and PVA (Fig. 3B(c)). The peaks observed at 1035 (Si—O stretching), 916 (Al—O stretching), 842 (Al—O stretching), and 519 (Si—O bending) cm^{-1} confirm the presence of MMT in the PULL/PVA/MMT composite (Fig. 3B(d)) (Yurudu, 2006). Similarly, the heat-treated PULL/PVA/MMT nanofiber webs exhibit a peak at 1250 cm^{-1}, indicating the formation of a new type of bond due to the heat treatment (Fig. 3B (e)). Overall, the FTIR spectra demonstrate the possible interactions between the PULL/PVA blend and MMT clay (before and after heat treatment), which is also supported by the XRD data.

3.4. Thermal gravimetric analysis

The thermal stabilities of the heat-treated electrospun PULL/PVA blend nanofiber mats were investigated using TGA in a nitrogen (N_2) atmosphere. Fig. 4A presents the TGA thermograms at different decomposition temperatures of pure PULL, pure PVA, and the PULL/PVA blend with a mass ratio of 60/40 of PULL to PVA at different decomposition temperatures. Three weight loss peaks are clearly observed in the TGA curve for pure PULL (Fig. 4A(a)). The first peak at 25–95 °C is due to moisture vaporization, decomposition, and some volatility characteristics of the polymers; the second peak at 230–270 °C is due to the thermal degradation of PULL; and the third peak at 300–400 °C is due to the formation of byproducts of PULL during the TGA thermal degradation process. The pristine PVA nanofiber mats exhibit higher thermal stability than PULL upto a temperature of 380 °C (Fig. 4A(b)). However, in the higher temperature range (from 381 °C to 600 °C), the PULL and PULL/PVA blend show greater thermal stability than PVA. The higher thermal stability at the mid-point degradation temperature of PULL could clearly be obtained with the addition of PVA to the PVA/PULL blend nanofiber mats (Fig. 4A(c)). The PULL/PVA/MMT nanofiber mats with 14% polymer and a 60/40 mass ratio of PULL to PVA with various MMT contents possess different decomposition temperatures (Fig. 4B). The thermal stability is clearly increased with increasing MMT content in the range of 1–10% by weight. This result may be attributed to the higher chain compactness of the polymer blend due to the interaction between the PULL/PVA blend and clay.

3.5. Tensile strength

Some of the fascination with the behavior of polymers comes from the large changes in the physical properties and the wide range of mechanical behaviors (Stepto, 1998). The tensile strength of the heat-treated PULL/PVA blend nanofibers increased with increasing weight percentage of PVA, as shown in Fig. 5a. Fig. 5b shows the tensile strength of heat-treated PULL/PVA/MMT nanofiber mats containing different contents of MMT. The tensile strength of the PULL/PVA blend nanofibers increased with increasing MMT content, indicating that MMT clay has a reinforcing effect on the PULL/PVA blend fibers. A sharp increase in tensile strength was observed with the addition of 5% by weight MMT, likely due to the combinatory effect of molecular chain orientation and the well-exfoliated MMT layer structure inside the nanofiber; therefore, the tensile strength of the electrospun nanofibers increased as the clay concentration increased. However, any further increase in clay concentration over 5% resulted in only a slight increase in tensile strength. This may be due to the aggregation of MMT particles in the polymer matrix at higher concentrations (over 5%) (Chang, 2003).

3.6. Water absorbency

The heat-treated PULL/PVA blend nanofiber mats absorbed 88.85 g g^{-1} and 26.43 g g^{-1} in distilled and in saline water, respectively, due the presence of a greater number of hydrophilic–OH groups (Fig. 6). Moreover, the crosslinking of polymer blends after heat treatment may also contribute to the increased water absorbancy of the composite material (Kibiri, 2003). The water absorbency of the nanofiber webs increased with increasing MMT content (Fig. 6a and b). A 5% MMT content resulted in a significant increase in water absorbency in both distilled (143.42 g g^{-1}) and saline water (39.75 g g^{-1}). These values are even higher than those of the super-absorbent based on wheat straw (absorbencies of 133.76 g g^{-1} in distilled water and 33.83 g g^{-1} in saline water) (Zuohao, 2011). This result is likely due to the inclusion of MMT in the polymer blend matrix (Fig. 6a and b). The nature of water absorbency of MMT in the polymer matrix is therefore likely due to the wettability and hydrophilicity of the MMT and polymer blend (Park, 2012).

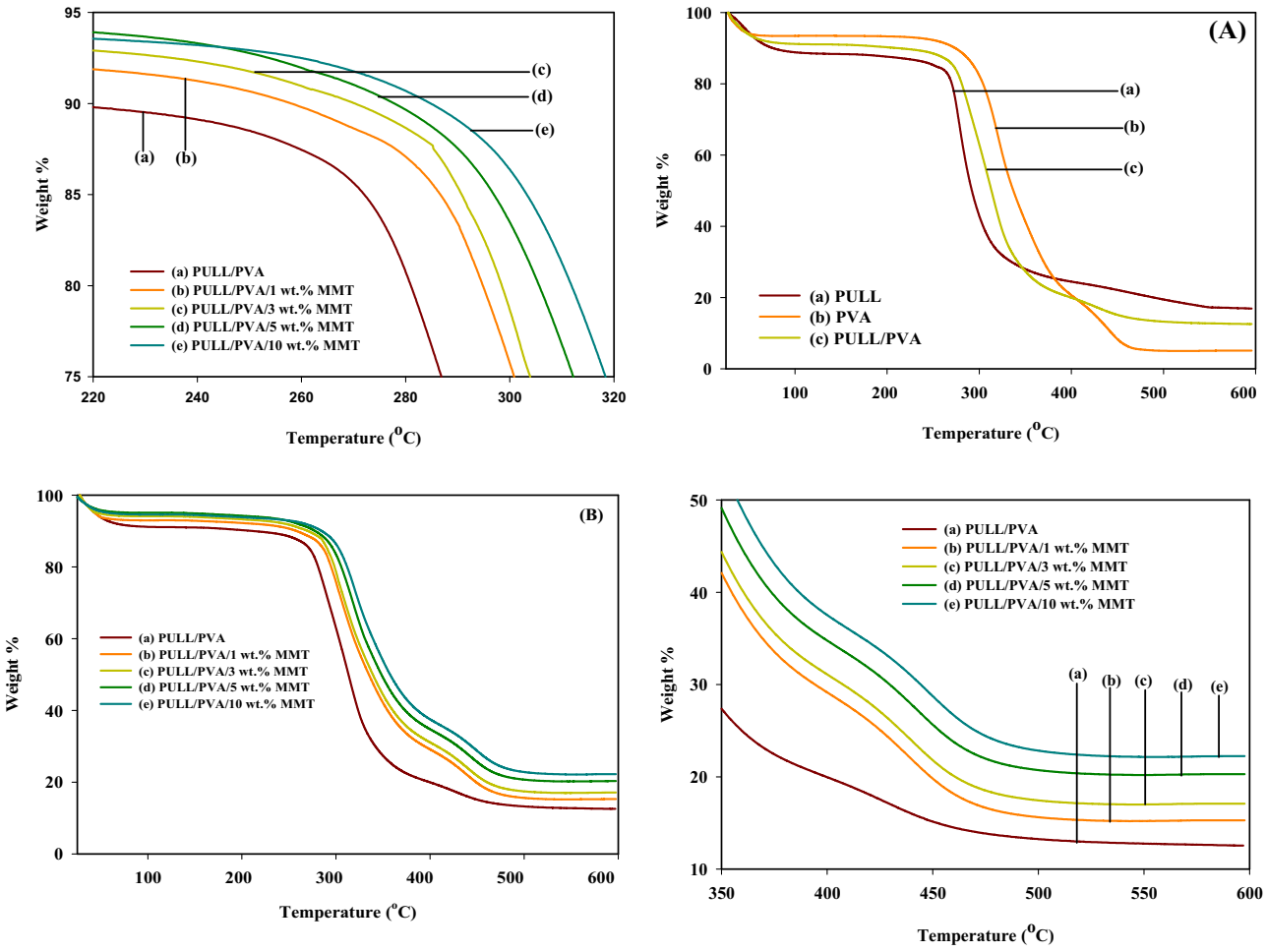


Fig. 4. (A) TGA data of heat-treated electrospun nanofibers of (a) PULL, (b) PVA, and (c) PULL/PVA blend and (B) TGA data of heat-treated PULL/PVA blend electrospun nanofibers with different MMT contents of (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 10% [total polymer concentration = 14%, blend ratio (PULL/PVA) = 60/40, applied voltage = 15 kV, and TCD =15 cm].

3.7. Mechanism of water absorption

The water absorption mechanism for the electrospun PULL/PVA/MMT composite super-absorbent is outlined in Scheme 2. MMT platelets of the composite nanofibers contain polar hydroxyl groups. The two other components of the composite also have polar hydroxyl groups in the polymer chains. The cross-links between the polymer chains are formed as ether groups through the reaction between the hydroxyl groups of PVA and PULL. Hence, the nanofiber composed of PULL, PVA, and MMT clay would be hydrophilic in nature. A hydrophilic fiber provides the capacity to absorb liquid via fiber imbibitions, thereby resulting in fiber swelling. It also attracts and holds liquid external to the fiber and structure voids. In fact, water molecules are drawn into the network structure of the polymers in the fibers across a diffusion gradient. The polymer chains want to straighten

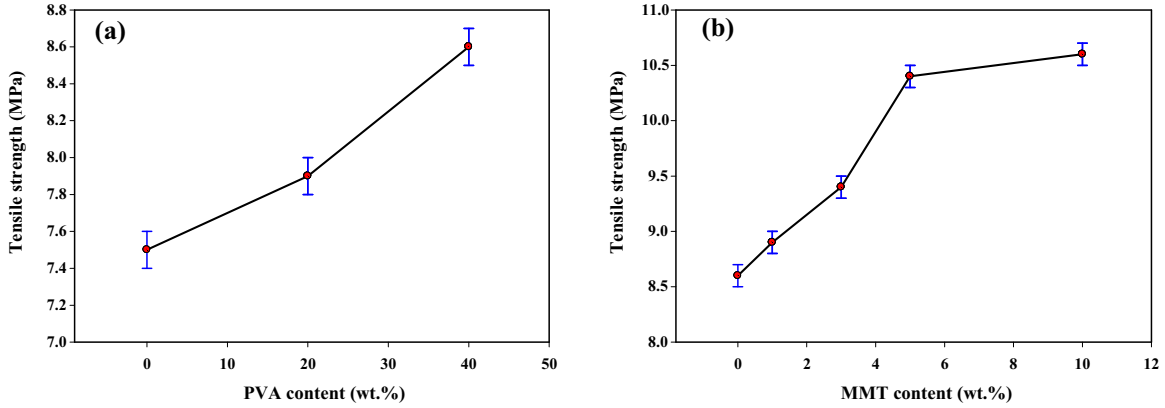


Fig. 5. Tensile strengths of (a) heat-treated electrospun PULL/PVA blend nanofibers as a function of the PVA content and of (b) heat-treated electrospun PULL/PVA/MMT nanofibers with a 40% PVA content as a function of the MMT content [total polymer concentration = 14%, applied voltage = 15 kV, and TCD = 15 cm].

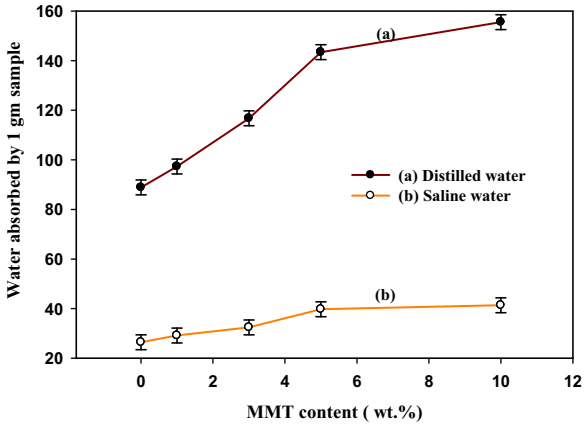


Fig. 6. Effects of MMT contents on the water absorption capacities for heat-treated electrospun PULL/PVA/MMT nanofibers for (a) distilled water and (b) saline water [total polymer concentration = 14%, blend ratio (PULL/PVA) = 60/40, applied voltage = 15 kV, and TCD = 15 cm].

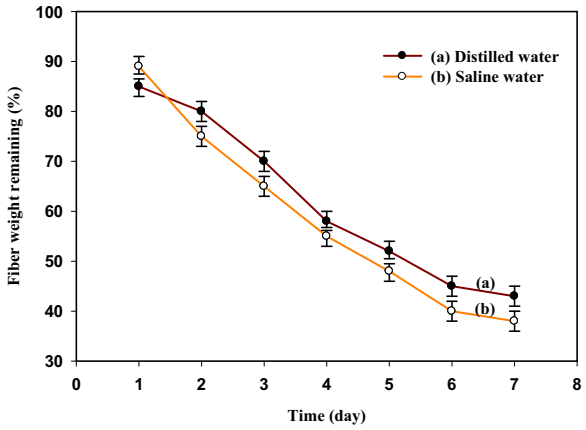
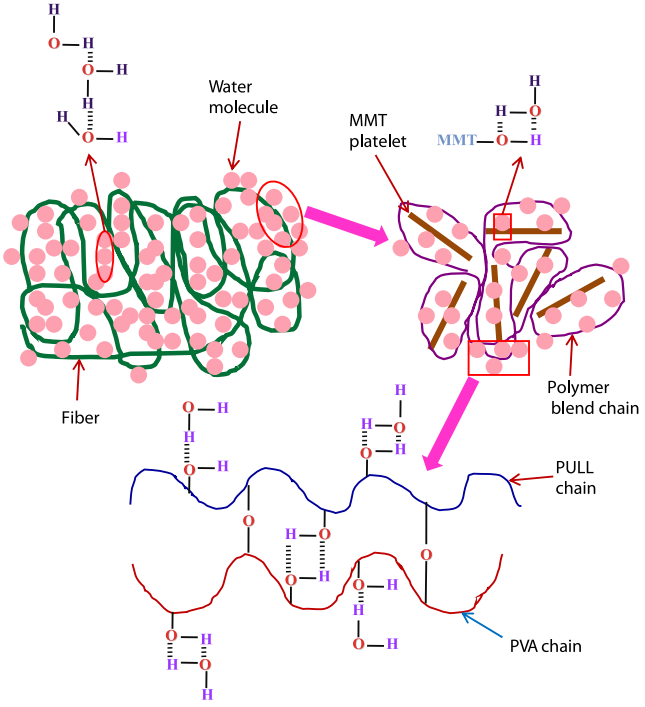


Fig. 7. Water retention of heat treated electrospun PULL/PVA/MMT nanofibers for (a) distilled water and (b) saline water [total polymer concentration = 14%, blend ratio (PULL/PVA) = 60/40, MMT content = 5%, applied voltage = 15 kV, and TCD = 15 cm].

but cannot due to the cross-linking. Thus, the fibers expand as water enters the network. The water is held tightly in the network by hydrogen-bonding interactions between water and polymer chains or MMT platelets.

3.8. Water retention study

The water retention behavior of the heat-treated PULL/PVA with 5 wt% MMT content blend nanofiber mats is shown in Fig. 7. In general, the nanofiber webs showed better water retention ability, as they retained 43% and 38% of the distilled and saline water, respectively, after exposure to air under arid conditions for 7 days. However, percentages of water retention after 1 day were 85% and 89% for distilled and saline water, respectively. From a literature review, after exposure to air under dry conditions for 6 days, pullulan hydrogel can retain water approximately 30% water (Li, 2011),



Scheme 2. A schematic representation of the water absorption mechanism for the electrospun PULL/PVA/MMT composite super-absorbent.

which is less than that of heat-treated PULL/PVA/MMT composite nanofibers. Presumably, the intense water-retentive nature of the composite materials results from the hydrophilic characteristic of each of the constituents.

4. Conclusion

A novel super-absorbent composite was prepared from PULL, PVA, and MMT clay using the electrospinning technique followed by a heat treatment. PVA content increases the thermal stability in the mid-point temperature of the degradation as well as mechanical strength of the polysaccharide, PULL. Incorporation of MMT with PULL/PVA blend makes the PULL/PVA/MMT nanofiber webs as superabsorbent. The water absorbencies of the prepared heat-treated PULL/PVA/MMT composite nanofibers with different MMT contents (0%, 1%, 3%, 5%, and 10%) were investigated. The water absorbencies increased with increasing MMT content, and the 5% MMT content resulted in a significant increase in the water absorbency (143.42 g g^{-1} in distilled water and 39.75 g g^{-1} in saline water). Moreover, the prepared super-absorbent material has the ability to retain 43% distilled water and 38% saline water after 7 days. These data demonstrate that this material possesses excellent water retention behavior. In this report, we also investigate thermal stabilities, and mechanical properties of the PULL/PVA/MMT composite nanofiber webs. Significant improvements in all of these properties of the composite nanofiber webs are observed with increasing MMT content. The characteristic of SAPs can be utilized in many different applications. The largest use of superabsorbent polymers is in personal hygiene products. These consumer products include disposable infant diapers, children's training pants, adult incontinence articles, and feminine sanitary napkins. Because PULL and PVA are biocompatible polymers, their blended system would be a biocompatible material that is very environmentally friendly. Montmorillonite clay is a natural layered silicate nanomaterial, which is a type of green eco-friendly natural product that does not have any toxic environmental effects.

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References

Alexander, M., & Dubois, P. (2000). Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Materials Science and Engineering*, *28*, 1–63.

Brenner, E. K. (2012). Electrospinning of hyaluronic acid nanofibers from aqueous ammonium solutions. *Carbohydrate Polymers*, *87*, 926–929.

Biliaderis, C. G. (1999). Glass transition and physical properties of polyol-plasticized pullulan-starch blends at low moisture. *Carbohydrate Polymers*, *40*, 29–47.

Barber, G. D. (2005). Poly(ethylene terephthalate) ionomer based clay nanocomposites produced via melt extrusion. *Polymers*, *46*, 6706–6714.

Chu, M. (2006). Synthesis of poly(acrylic acid)/sodium humate superabsorbent composite for agricultural use. *Applied Polymer Science*, *102*, 5137–5143.

Chang, J. H. (2003). Poly(vinyl alcohol) nanocomposites with different clays: Pristine clays and organoclays. *Journal of Applied Polymer Science*, *90*, 3208–3214.

Deshpande, M. S. (1992). Aureobasidium pullulans in applied microbiology: A status report. *Enzyme Microbial Technology*, *14*, 514–527.

Duan, B. (2007). Degradation of electrospun PLGA-chitosan/PVA membranes and their cytocompatibility in vitro. *Journal of Biomaterials Science, Polymer Edition*, *18*, 95–115.

Ende, M. (1995). Factors influencing drug and protein transport and release from ionic hydrogels. *Reactive and Functional Polymers*, *25*, 127–137.

Fong, H. (1999). Beaded nanofibers formed during electrospinning. *Polymer*, *40*, 4585–4592.

Fong, H. (2002). Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. *Polymer*, *43*, 775–780.

Han, X. J. (2006). Coaxial electrospinning of PC (shell)/PU(core) composite nanofibers for textile application. *Polymer Composites*, *27*, 381–387.

Hong, K. H. (2006). Preparation of antimicrobial poly(vinyl alcohol) nanofibers containing silver nanoparticles. *Journal of Polymer Science Part B: Polymer Physics*, *44*, 2468–2474.

Hayder, M. N. (2011). Layer-by-layer assembled polyaniline nanofiber/multiwall carbon nanotube thin film electrodes for high-power and energy storage applications. *ACS Nano*, *5*, 8522–8561.

Huang, Z.-M. (2004). Electrospinning and mechanical characterization of gelatin nanofibers. *Polymer*, *45*, 5361–5368.

Islam, M. S. (2012). Effect of pullulan/poly(vinyl alcohol) blend system on the montmorillonite structure with property characterization of electrospun pullulan/poly(vinyl alcohol)/montmorillonite nanofibers. *Journal of Colloid and Interface Science*, *368*, 273–281.

Iwamoto, K. (1991). Polysaccharide-coated oil droplets in oil-in-water emulsions as target able carriers for lipophilic drugs. *Journal of Pharmaceutical Sciences*, *80*, 219–224.

Ji, H. M. (2009). Electrospinning and characterization of mediummolecular-weight poly(vinyl alcohol)/high-molecular-weight poly(vinyl alcohol)/montmorillonite nanofibers. *Colloid and Polymer Science*, *287*, 751–758.

Kamat, M., & Malkani, R. (2003). Disposable diapers: A hygienic alternative. *The Indian Journal of Pediatrics*, *70*(11), 879–881.

Kiatkamjornwong, S. (2002). Synthesis and property characterization of cassava starch grafted poly[acrylamide-co-(maleic acid)]superabsorbent via g-irradiation. *Carbohydrate Polymers*, *43*(14), 3915–3924.

Kristo, E. (2007). Water vapour barrier and tensile properties of composite caseinate–pullulan films: Biopolymer composition effects and impact of beeswax lamination. *Food Chemistry*, *101*, 753–764.

Karim, M. R. (2011). Thermal behavior with mechanical property of fluorinated silane functionalized superhydrophobic pullulan/poly(vinylalcohol) blends by electrospinning method. *Journal of Nanomaterials*, *2011*, 1–7.

Kibiri, K. (2003). Synthesis of fast-swelling superabsorbent hydrogels: Effect of crosslinker type and concentration on porosity and absorption rate. *European Polymer Journal*, *39*(7), 1341–1348.

Li, A. (2007). Utilization of starch and clay for the preparation of superabsorbent composite. *Bioresource Technology*, *98*(2), 119–122.

Lazaridou, A. (2003). Molecular weight effects on solution rheology of pullulan and mechanical properties of its films. *Carbohydrate Polymers*, *52*, 151–166.

Lee, H. W. (2009). Electrospinning fabrication and characterization of poly(vinyl alcohol)/montmorillonite nanofiber mats. *Journal of Applied Polymer Science*, *113*, 1860–1867.

Lu, G. Z. (2010). A novel in situ-formed hydrogel wound dressing by the photocrosslinking of a chitosan derivative. *Wound Repair and Regeneration*, *18*, 70–79.

Li, H. (2011). Superabsorbent polysaccharide hydrogels based on pullulan derivate as antibacterial release wound dressing. *Journal of Biomedical Materials Research A*, *98 A*, 31–39.

Mondal, D. (2013). Effect of poly(vinyl pyrrolidone) on the morphology and physical properties of poly(vinyl alcohol)/sodium montmorillonite nanocomposite films. *Progress in Natural Science: Materials International*, *23*, 579–587.

Pourjavadi, A., & Mahdavinia, G. R. (2006). Superabsorbency, pH-sensitivity and swelling kinetics of partially hydrolyzed chitosan-g-poly (acrylamide)h ydrogels. *Turkish Journal of Chemistry*, *30*, 595–608.

Park, J. H. (2012). Effect of montmorillonite on wettabilityand microstructure properties of zein/montmorillonite nanocomposite nanofiber mats. *Journal of Composite Materials*, *0*, 1–7.

Park, J. H. (2010). Electrospinning fabrication and characterization of poly(vinyl alcohol)/montmorillonite/silver hybrid nanofibers for antibacterial applications. *Colloid and Polymer Science*, *288*, 115–121.

Park, J. H. (2009). Electrospinning and characterization of poly(vinyl alcohol)/chitosan oligosaccharide/clay nanocomposite nanofibers in aqueous solutions. *Colloid and Polymmer Science*, *287*, 943–950.

Qin, X.-H., & Wang, S.-Y. (2006). Filtration properties of electrospinning nanofibers. *Journal of Applied Polymer Science*, *102*(2), 1285–1290.

Ray, S. S., & Bousmina, M. (2005). Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world. *Progress in Materials Science*, *50*, 962–1079.

Ren, G. (2006). Electrospun poly(vinyl alcohol)/glucose oxidase biocomposite membranes for biosensor applications. *Reactive and Functional Polymers*, *66*, 1559–1564.

Ristolainen, N. (2006). Poly(vinyl alcohol) and polyamide-66 nanocomposites prepared by electrospinning. *Macromolecular Materials and Engineering*, *291*, 114–122.

Sadeghi, M., & Hosseinzadeh, H. J. (2008). Synthesis of starch-poly (sodium acrylate coacrylamide)superabsorbent hydrogel with salt and pH-responsiveness properties as a drug delivery system. *Journal of Bioactive and Compatible Polymers*, *23*, 381–404.

Su, C.-I. (2012). PAN-based carbon nanofiber absorbents prepared using electrospinning. *Fibers and Polymers*, *13*(4), 436–442.

Singh, R. S. (2008a). Pullulan: Microbial sources, production and applications. *Carbohydrte Polymers*, *81*, 252–259.

Singh, R. S. (2008b). Pullulan: Microbial sources, production and applications. *Carbohydrate Polymers*, *73*, 515–531.

Shao, C. (2003). Fiber mats of poly(vinyl alcohol)/silica composite via electrospinning. *Materials Letters*, *57*, 1579–1584.

Seo, H. P. (2004). Production of high molecular weight pullulan by *Aureobasidium pullulans* HP-2001with soybean pomace as a nitrogen source. *Bioresource Technology*, *95*, 293–299.

Stepto, R. F. T. (1998). *Polymer networks*. Chichester, England: Wiley.

Tang, X. (2011). Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability. *Carbohydrate Polymers*, *85*, 7–16.

Shen, W. (2014). Biocompatible sodium alginate fibers by aqueous processing and physical crosslinking. *Carbohydrate Polymers*, *102*, 893–900.

Wang, Z., & Liu, Z. (2004). Properties of super water absorbent polymers and their applications in agriculture. *Chinese Journal of Soil Science*, *6*, 355.

Yi, J. Z., & Zhang, L. M. (2008). Removal of methylene blue dye from aqueous solution by adsorption onto sodium humate/polyacrylamide/clay hybrid hydrogels. *Bioresource Technology*, *99*(7), 2182–2186.

Yoshimura, T. (2005). Synthesis and characterization of novel biodegradabl superabsorbent hydrogels based on chitin and succinic anhydride. *Carbohydrate Polymers*, *61*, 322–326.

Yuen, S. (1974). Pullulan and its applications. *Process Biochemistry*, *9*, 7–22.

Yurudu, C. (2006). Preparation and characterization of PVA/OMMT composites. *Journal of Applied Polymer Science*, *102*, 2315–2320.

Zhang, J. (2007). Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgite super-absorbent composites. *Carbohydrate Polymers*, *68*(2), 367–374.

Zhang, J. (2006). Synthesis and characterization of multifunctional poly(acrylic acid-co acrylamide)/sodium humate super-absorbent composite. *Reactive and Functional Polymers*, *66*(7), 747–756.

Zhang, Y. (2007). Preparation of electrospun chitosan/poly(vinyl alcohol) membranes. *Colloid and Polymer Science*, *285*, 855–863.

Zuohao, M. (2011). Synthesis and characterization of a novel super-absorbent based on wheat straw. *Bioresource Technology*, *102*, 2853–2858.

Zhu, J. (2007). Room temperature spontaneous exfoliation of organo-clay in liquid polybutadiene: Effect of polymer end-groups and the alkyl tail number of organic modifier. *Polymers*, *48*, 7590–7597.