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Preparation and Properties of Electrospun Poly(vinyl alcohol) Blended Hybrid Polymer with Aloe vera and HPMC as Wound Dressing

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Abstract

A series of poly(vinyl alcohol) (PVA)/poly(vinyl pyrrolidone) (PVP)/poly(ethylene glycol) (PEG) hybrid nanofibers were fabricated by an electrospinning method, in order to be used as a potential wound dressing material. The effect of Aloe vera was investigated in terms of solution properties such as viscosity, conductivity, pH and surface tension. The nanofibrous wound dressing materials were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) and differential scanning calorimetry (DSC). SEM results revealed that the fiber diameters ranged between 200-500 nm and they were linear, homogenous and free of beads. DSC thermograms indicated that the addition of Aloe vera affects the crystal structure and efficiently cross-links the hybrid polymer, forming an amorphous structure with a melting temperature (Tm) of 219°C at an Aloe vera concentration of 3%. FTIR results clearly resolved the hybrid polymer structure of nanofibers obtained.

INTRODUCTION

Generally, a wound dressing is defined as the protective coverage placed on a wound in order to accelerate the healing process. Many polymers and their hybrids can be used to prepare wound dressing material, such as PVA, PVP and PEG [1]. PVA is a well-known polymer, and has been developed for biomedical applications such as wound dressing materials [2]. PVP is one of the most widely used polymers in medicine because of its solubility in water and its extremely low cytotoxicity [3]. Combination of the properties of PVA and PVP blended hybrid polymer with appropriate mechanical properties has led to the preparation of new biomaterials [4,5]. In this study, PEG was added to PVA/PVP hybrid polymer. Hilmy et al. reported that the addition of poly(ethylene glycol) to the PVP hydrogel composition could improve the performance of the hydrogel barrier against bacteria [6,7].

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Wound dressing nanofibers were prepared by an electrospinning technique. The nanofibers obtained with electrospinning have unique properties, such as high surface area to volume ratio, small pore sizes and high porosity. Electrospinning is a cost effective method of manufacturing wound dressing materials. The addition of several components could facilitate the electrospinning process.

Aloe vera used in this study is one of the oldest known therapeutic herbs and is renowned worldwide as a healing plant. Many of the health benefits associated with Aloe vera, especially for the promotion of wound healing have been attributed to the polysaccharides contained in the gel of the leaves. Among its other healing ingredients for burns, Aloe vera contains salicylic acid, which is the main content of aspirin. The salicylic acid and magnesium in Aloe vera are thought to work together to produce an analgesic effect on burns. To date, 200 nutrients have been found in the gel of the Aloe vera leaf, including eight essential amino acids, twelve non-essential amino acids and anthraquinones, ten enzymes and many minerals and vitamins [8-14]. Hydroxypropyl methylcellulose (HPMC) was also used for its water retention capacity in addition to Aloe vera. The chemical structure of HPMC is given Figure 1.

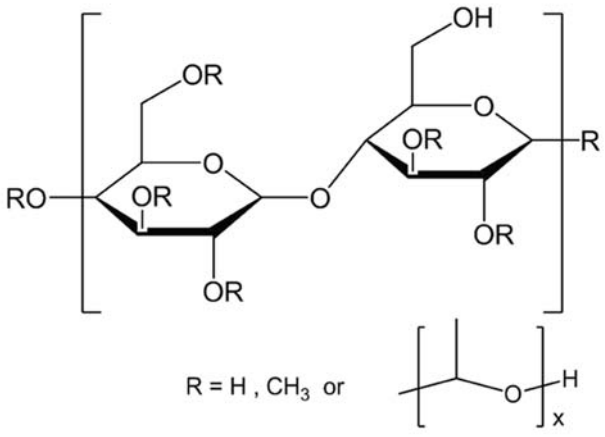

Figure 1. Chemical structure of HPMC.

In the investigation reported here, Aloe vera-loaded PVA/PVP/PEG hybrid polymer fibers were prepared by electrospinning and characterized, demonstrating that they can be used as wound dressing materials [15,16].

EXPERIMENTAL METHOD

Materials

The PVA (M_w: 85000-124000 g/mol, 98% hydrolyzed) and PEG (M_w: 400 000 g/mol) used in the study were purchased from Merck. PVP (M_w: 85000-124000 g/mol) and HPMC were purchased from BASF Chemical Co. (Ludwigshafen, Germany). These polymers were used without further purification. Distilled water was used as a solvent in all experiments. Aloe vera gel solution (50 mL) was supplied by Forever Living Health and Beauty Products Ltd.

Sample Preparation

PVA hydrogel was prepared by fully dissolving 10 g of polymer powder in an appropriate amount of ultra-pure deionized water, under magnetic stirring for two hours, at a temperature of 80 ± 2°C. The 10% PVA solution was then cooled to room temperature. Solution A was prepared by mixing of 100 g PVA, 10 g PVP (10 wt %), 1 g PEG (10 wt %) and 2 g HPMC at 60°C with magnetic stirring for two hours. Solutions B, C and D were prepared by the addition of 1 g, 2 g and 3 g Aloe vera (2 wt %) to solution A, respectively.

Electrospinning of Polymer Solution

Polymeric nanofibers can easily be prepared by an electrospinning process. Electrospinning is based on the use of a strong electric field to draw a polymer solution from the tip of a capillary towards a collector. The voltage of the electrospinning equipment was adjusted with a variable high-voltage power supply from Gamma High Voltage Research

(USA). Nanofiber samples were prepared by electrospinning the four different aqueous solutions described at an electrical voltage of 20 kV at room temperature under atmospheric pressure. The applied voltage causes a jet of the solution to be drawn toward a grounded collector. A syringe needle (8 mm) was used as the electrode connected to the power source. After drying the nano-sized polymeric fibers were formed by the fine jets form and, then, collected as a web-like mass. The collector was a 20 x 40 cm^2 aluminum foil placed horizontally 15 cm away from the tip of the needle. The collector was connected to the power supply as an electrode with opposite polarity to the syringe. A metering syringe pump from New Era pump systems Inc. (USA) was used to supply polymer solution at a constant rate of 0.5 mL/h. Finally, nanofibers were detached from the Al foil collector and dried in a furnace at 70°C overnight under vacuum.

Characterization

pH values of polymer solutions were determined with a pH meter (WTW 315 I Set Sentix 41 electrode, Wissenschaftlich-Technische Werkstätten GmbH & Co., Weilheim, Germany). Solution viscosity and conductivity measurements were performed with an AND SV-10 viscometer. Fourier Transformation Infrared (FT-IR) spectra of the electrospun fibers were obtained using a Thermo Nicolette 6700 spectrophotometer with an ATR module. Fiber formation and morphology of the electrospun PVA/PVP/PEG with Aloe vera and HPMC fibers were determined using a Quanta 400 FEI MK-2 Scanning Electron Microscope (SEM). Differential scanning calorimeter (DSC) studies of the nano-fibers were carried out with a Schimadzu DSC-60, using nitrogen as the carrier gas. The temperature was raised from room temperature to 200°C then cooled to room temperature and the sample was heated again to 500°C at a rate of 10°C/min. Fiber diameters were measured using ImageJ software (Rasband WS 1997-2005 ImageJ, US National Institutes of Health, Bethesda, Maryland, USA). ImageJ is a public domain Java-based program that was originally developed at the National Institutes of Health (NIH). It contains basic digital image processing tools, and includes numerous tools that facilitate quantitative measurements.

RESULTS AND DISCUSSION

Physical Properties of Solutions and Fibers

Solution properties have been found to affect the morphology of the fibers. The pH, viscosity, conductivity and the surface tension of the polymer solutions before the electro spinning experiment are given in Table 1. One of the major parameter influencing the fiber diameter is the solution viscosity. Generally, the viscosity of the solution is releated to the extent of polymer molecule chains entanglement within the solution. A higher viscosity results in a large fiber diameter. In addition, viscosity has a significant effect on whether the electro-spinning jet breaks up into small droplets or whether the resulting electrospun fibers contain beads [17]. At low viscosity, it is common to find beads along the fibers deposited on the collection plate [18]. The addition of Aloe vera increased the viscosity from 546 to 641 mPa.s but the effect of concentration was not prominent, such that a 1% to 3% increase in concentration leads to an increase in viscosity from 641 to 645 mPa.s.

The conductivity of the fiber solution is important to initiate the electrospinning process. The increase in Aloe vera concentration from 1% to 3% leads to an increase conductivity of the solution from 908 µS/cm to 925 µS/cm. As the electrical conductivity of the solution increases, the diameter of the electrospun nanofibers decreases. Although it was expected that increased viscosity would produce an increase in fiber diameter, SEM micrographs indicated a

decrease in fiber diameters. Since these fundamental properties are interacting and influencing each other during the electrospinning process, the effect of solution conductivity dominates the effect of variations in viscosity.

Generally, the initiation of electrospinning requires the charged solution to overcome the surface tension. However, as the jet travels towards the collection plate, surface tension may cause the formation of beads. Surface tension has the effect of decreasing the surface area per unit mass of fluid. At high viscosity, the solvent molecules are distributed over the entangled polymer molecules due to the stretching under the influence of electrical charges. Conversely, lower viscosity leads polymer molecules to congregate in beads under the action of surface tension [18]. The surface tension results were not affected by the change in the concentration of Aloe vera and remained at 80 mN/m. The addition of Aloe vera increased the pH of the hybrid polymer solution from 5.86 to 5.92.

Table 1. Physical Properties of Fiber Solutions.

Solution	Solution viscosity (mPa.s)	Solution conductivity (μS/cm)	pH	Surface Tension (mN/m)
A	546	785	5.80	79
B	641	908	5.86	80
C	644	916	5.88	80
D	645	925	5.92	80

DSC Analysis of Chitosan/PVA Nanofibers

The DSC thermograms of the electrospinning fibers of PVA/PEG/HPMC with Aloe vera are shown in Figure 2. Fibers obtained from PVA/PEG/HPMC solution showed a sharp endothermic curve, with a peak at 216°C. The incorporation of Aloe vera caused a shift in the T_m values from 216 to 219°C, as shown in Figure 2b-2d. This indicates that the addition of Aloe vera affects the crystal structure and efficiently cross-links the hybrid polymer, forming an amorphous structure.

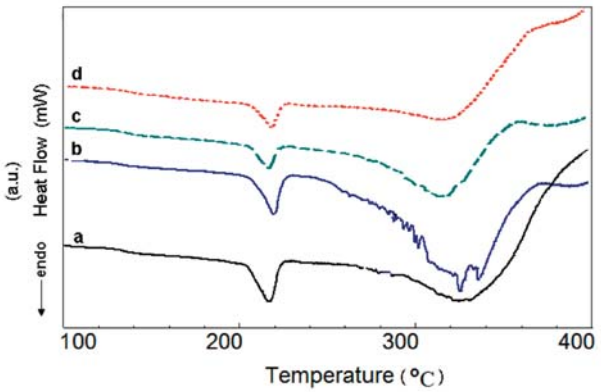

Figure 2. DSC thermograms of the nanofibers obtained from (a) PVA/HPMC/PEG, (b) solution B, (c) solution C, and (d) solution D.

FT-IR Analysis

The FTIR spectra of the nanofibers and the PVA/PEG were within the range 4000-750 cm^{-1}, as shown in Figure 3. The finger print region of the PVA/PEG spectrum shown in Figure 3a indicated a wide and intense band due to the presence of hydroxyl groups (O-H) at 3300-3500 cm^{-1}. The C-H alkyl stretching bands which appeared at 2700-3000 cm^{-1} can be attributed to C-H stretching vibrations. The broad absorption peak at 1143-1090 cm^{-1} is related to C-O stretching. The absorption peaks at 1444 cm^{-1} (CH_2 bending) and 852 cm^{-1} (CH_2 rocking) are characteristic of PVA and appeared with differing intensities in all spectra. The peak at 1263 cm^{-1} is due to the C-H vibration. Carbonyl bonds, which are attached to the pyrrolidone rings, result in stretching modes seen with the absorbance peaks at 1650 cm^{-1} shown in Figure 3 b-e. Intramolecular and intermolecular hydrogen bonding are expected to occur among PVA chains due to high hydrophilic forces. With the addition of Aloe vera, the carbonyl band was shifted from 1656 cm^{-1} to 1660 cm^{-1}. It is assumed that a hydrogen bonded carbonyl is an indication of an intermolecular secondary interaction between the carbonyl oxygen on a PVP chain and a hydroxyl group along a PVA chain.The absorption peak at 1096 cm^{-1} (C-O, 1090-1150 cm^{-1}) is very sharp for the electrospun fiber. This is a carboxyl stretching band (C-O) and is attributed to the crystallinity of the PVA. It is used for the assessment of poly(vinyl alcohol) structure.

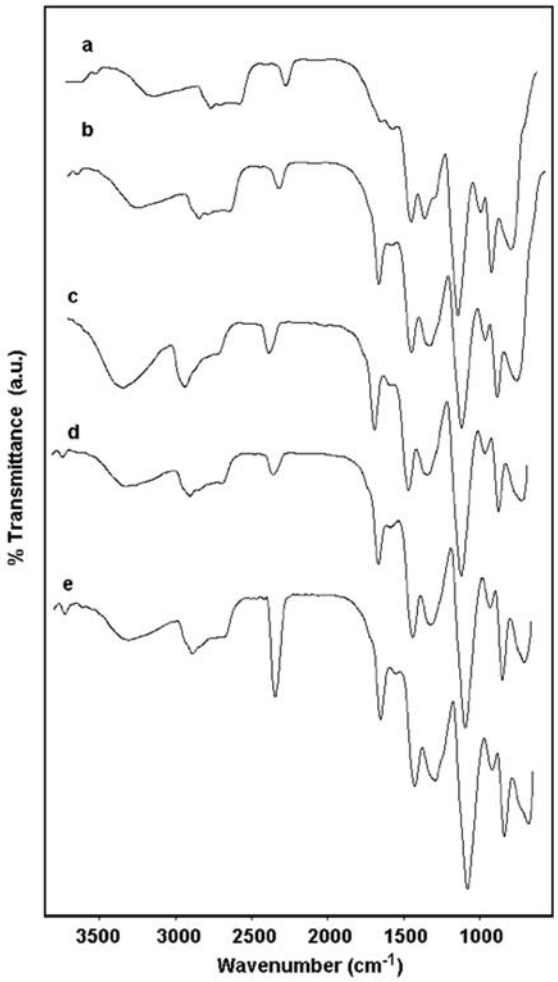

Figure 3. FT-IR spectra of the electrospun fibers of (a) PVA/PEG, (b) solution A, (c) solution B, (d) solution C, (e) solution D.

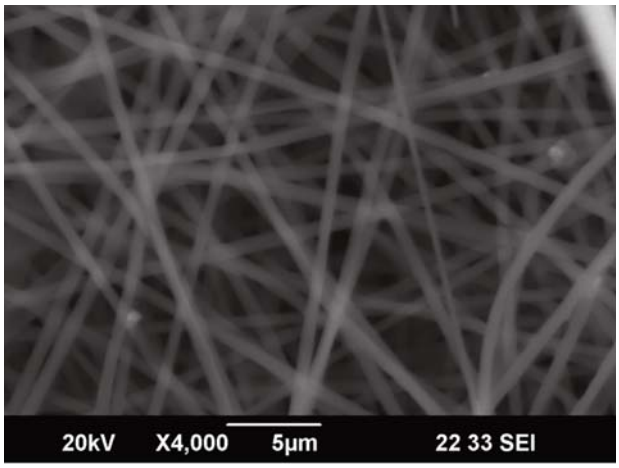

Figure 4. SEM picture of electrospun nanofibers obtained from solution A.

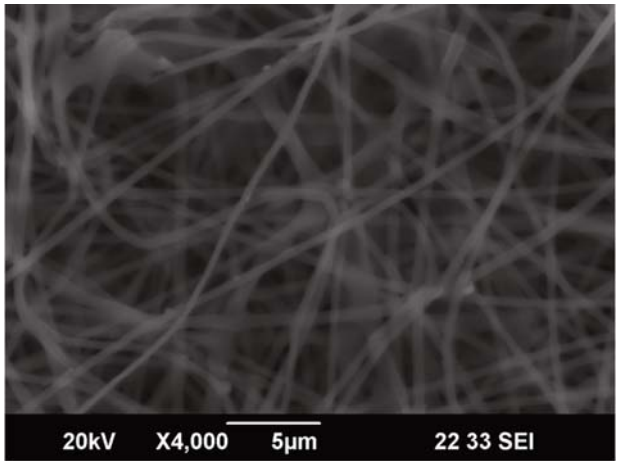

Figure 5. SEM picture of electrospun nanofibers obtained from solution B.

Scanning Electron Microscope (SEM) Analysis

SEM image of the electrospun fibers prepared from solution A is shown in Figure 4. It is clear that the fibers are finely spun and contain no beading. The fibers appear to be homogenous and linear. The IMAGEJ digital image analysis software was used to measure the fiber diameters. The average diameter of the fibers, as estimated from the image, was 660.3 nm. The average diameter of the hybrid polymeric fibers obtained from solution A with 1% Aloe vera was calculated as 596 nm and is shown in Figure 5. The fiber structure appeared to be homogenous and beadless, although a slight distortion from linear structure is evident. Figure 6 illustrates the SEM image of the fibers obtained from solution C. It is seen that the average fiber diameter is reduced to 553 nm. The SEM picture of solution D, given in Figure 7, shows that the linear structure is completely distorted into a curvy structure, and that the fibers are intermingled with each other.

CONCLUSIONS

Electrospun nanofibers were fabricated from PVA/PVP/PEG and the effect of the addition of Aloe vera on structure and morphology were investigated. The addition of Aloe vera affected the solution properties by increasing viscosity and conductivity. Since the viscosity and the conductivity act inversely on the final fiber diameter, the solution conductivity dominates over the effects of viscosity. Therefore, the fiber diameters decreased with the addition of Aloe vera, which was also verified from

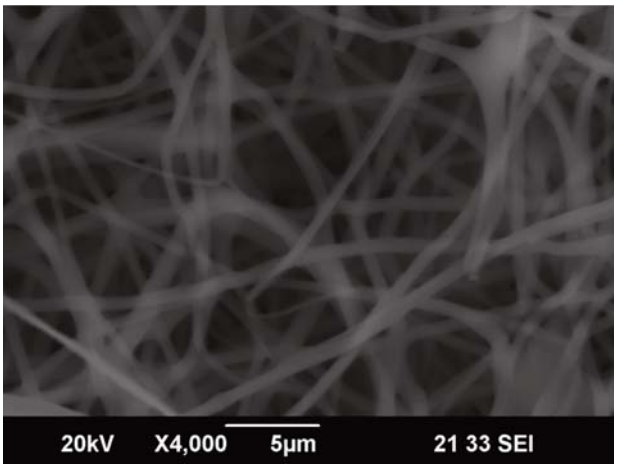

Figure 6. SEM picture of electrospun nanofibers obtained from solution C.

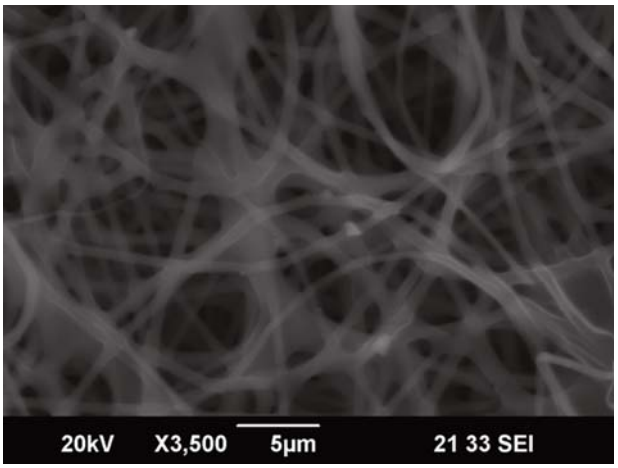

Figure 7. SEM picture of electrospun nanofibers obtained from solution D.

the SEM micrographs. SEM micrographs indicated that the addition of Aloe vera caused the formation of finer fibers without any beading. This beadless structure might lead to an increased porosity and thereby facilitate the penetration of oxygen and moisture to the wound, which are of vital importance for the healing process. The increased porosity of the structure effectively prevents the infiltration of bacteria. The FTIR vibrations confirmed the PVA/PVP/PEG structure by the appearance of characteristic stretching and bending vibrations. DSC thermograms showed an increase in the melting point and the decomposition temperatures. The establishment of an intermingled, porous fiber structure makes the fibers containing 3% Aloe vera a highly promising candidate for wound dressing applications.

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REFERENCES

1. Haijun, Y., Xiaoyi, X., Xuesi, C., Tiancheng, L., Peibiao, Z., Xiabin, J., Preparation and antibacterial effects of PVA-PVP hydrogels containing silver nanoparticles, J. Appl. Polym. Sci., 103(1), 125, 2006.
2. Hong, K.H., Preparation and properties of electrospun poly(vinyl alcohol)/silver fiber web as wound dressings, Polym. Eng. Sci., 47(1), 43, 2007.
3. Razzak, M.T., Zainuddin, E., Dewi, S., Lely, H., Taty, S., The characterization of dressing component materials and radiation formation of PVA-PVP hydrogel, Radiat. Phys. Chem., 55,153, 1999.
4. Cassu, S.N., Felisberti, M.I., Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blends: miscibility, microheterogeneity and free volume change, Polymer, 38, 3907, 1997.
5. Seabra, A.B., Oliveira, M.G., Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blended films for local nitric oxide release, Biomaterials, 25, 3773, 2004.
6. Hilmy, N., Darwis, D., Hardiningsih, L., Poly(*N*-vinyl-pyrrolidone) hydrogels. 2. Hydrogel composites as wound dressing for tropicalenvironment, Radiat. Phys. Chem., 42(4-6), 911, 1993.
7. Ajji, Z., Othman, I., Rosiak, J.M., Production of hydrogel wound dressings using gamma radiation, Nuc. Inst. Met. Phys. Res. B, 229, 375, 2005.
8. Eshun, K., He, Q., Aloe vera: a valuable ingredient for the food, pharmaceutical and cosmetic industries, Crit. Rev. Food Sci. Nutr., 44(2), 91, 2004.
9. Hamman, J.H., Composition and Applications of Aloe vera Leaf Gel, Molecules, 13, 1599, 2008.
10. Tizard, I., Busbee, D., Maxwel, B., Kemp, M.C., Effects of acemannan, a complex carbohydrate, on wound healing in young and aged rats, Wounds: A Compendium of Clin. Res. Pract., 6, 201, 1994.

11. Davis, R.H., Donato, J.J., Hartman, G.M., Haas, R.C., Anti-inflammatory and wound healing activity of a growth substance in Aloe vera, J. Am. Pediatr. Med. Assoc., 84, 77, 1994.

12. Shelton, R.M., Aleo vera. Its chemical and therapeutic properties, Int. J. Dermatol., 30, 679, 1991.

13. Robson, M.C., Heggers, J.P., Hagstrom, W.J.J., Myth, magic, witchcraft, or fact. Aloe vera revisited, Burn Care Rehabil., 3, 157, 1982.

14. Klein, A.D., Penneys, N.S., Aloe vera, J. Am. Acad. Dermatol., 18, 714, 1988.

15. Jensen, J.L., Seeley, J., Gillin, B. Diabetic foot ulcerations. A controlled, randomized comparison of two moist wound healing protocols: Carrasyn Hydrogel Wound dressing and wet-to-moist saline gauze. Adv. Wound Care, 11, 1, 1998.

16. Khil, M.S., Cha, D., Kim, H.Y., Kim, I.S., Bhattarai, N, Electrospun nanofibrous polyurethane membrane as wound dressing, J. Biomed. Mater. Res. Part B: Appl. Biomat., 67B(2), 675, 2003.

17. Shenoy, S.L., Bates, W.D., Frisch, H.L., Wnek, G.E. Role of Chain Entanglements on Fiber Formation during Electrospinning of Polymer Solutions: Good Solvent, Non-specific Polymer-polymer Interaction Limit, Polymer, 46, 3372, 2005.

18. Ramakrishna, S., Fujihara, K., Teo, W.E., Lim, T.C., Ma, Z. An introduction to electrospinning and nanofibers, New Jersey: World Scientific, 1st Ed., pp.91-101, 2005.