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Construction of CaF_2-appended PVA nanofibre scaffold

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Abstract. In this work, a new material, calcium fluoride (CaF_2)-appended poly(vinyl alcohol) (PVA) nanofibre scaffold, was prepared through electrospinning technique successfully. Scanning electron microscopy result showed that the morphology of the fibres was uniform and smooth, and the average diameter of the fibres was about 200 nm. Transmission electron microscopy results showed that many CaF_2 nanoparticles were well dispersed in the PVA fibre matrix. The water-resistant ability of the scaffold was improved through intermolecular crosslinking of PVA by formaldehyde vapour. This novel material seems to be a promising scaffold for bone tissue engineering.

Keywords. Electrospinning; fluoride; nanofibre; PVA; bone tissue engineering.

1. Introduction

Poly(vinyl alcohol) (PVA) is a synthetic polyol polymer with a good water-solubility, which is widely used in medical materials, cosmetics, food engineering, etc. Moreover, because of its good spinnability, biocompatibility and biodegradability, the fibre products of PVA have been widely used in tissue engineering field as a scaffold. Yan *et al* [1] prepared PVA–poly(butylene carbonate) (PBC) core–shell nanofibres by the coaxial electrospinning technology, in which PVA forms the core and PBC forms the shell. Doxorubicin was loaded into this core–shell nanofibres to test the attachment and proliferation of cells. They showed that the material is promising in the application of tissue engineering. Sambudi *et al* [2] synthesized chitosan–PVA fibres loaded with ellipsoidal calcium carbonate with nano-branch network by electrospinning and the various test results showed the potential of this material for use as scaffolds in tissue engineering.

In this work, CaF_2 nanoparticles have been introduced into the PVA nanofibre scaffold by electrospinning. Fluoride is one of the few inorganic ions that are able to stimulate osteoblasts proliferation and calcium ions are necessary for bone formation [3–7]. Therefore, this material seems to be a potential material as a bone tissue engineering scaffold. A transmission electron microscope (TEM) was used to analyse the distribution of CaF_2 nanoparticles in the fibre. Formaldehyde was used as a crosslinking agent to enhance its water-resistance.

2. Materials and methods

2.1 *Materials*

PVA (M_w = 80,000) was purchased from Tong Li Tech Co., Ltd. Sodium fluoride (NaF) was purchased from Beijing Tongguang Fine Chemicals Company. Calcium chloride ($CaCl_2$) was purchased from Tianjin Tanggu Dengzhong Chemical Factory. Formaldehyde solution (50%) was purchased from Shenyang Liaozhong County Fine Chemical Factory. Hydrochloric acid (36–38%) was obtained from Beijing Chemical Works.

2.2 *Preparation of nanofibre scaffold*

$CaCl_2$ (0.0777 g) and 0.0591 g NaF were dissolved in 8 and 2 ml distilled water, respectively, and stirred vigorously for 30 min. Then, 0.8 g PVA was dissolved in the $CaCl_2$ solution and stirred for 24 h at 40°C. The NaF aqueous solution was added into the mixed solution dropwise with vigorous stirring. The mixture was then stirred at room temperature for 6 h. The spinning liquid had been prepared. The facility for the electrospinning experiments was similar to that of the previous report [8]. The spinning liquid was sucked into a glass dropper with the tip of 1 mm inner diameter. The glass dropper was connected to a high-voltage power supplier (TianJin Dongwen High Voltage Power Supply Limited Company, China).

A piece of aluminium foil was placed towards the tip of the glass dropper at a distance of 12 cm as grounded collector.

The fluoride-containing PVA nanofibres were collected on the aluminium foil at 12 kV and then formed a membrane. The membrane was then placed in a vacuum oven for 24 h at 30°C to remove the residual solvent.

2.3 *Crosslinking by acetalization*

The fluoride-containing PVA nanofibre membrane, 10 ml hydrochloric acid (36–38%) in a small beaker, 10 ml formaldehyde solution (50%) in a small beaker and moderate allochroic silica gel (approximate 60 g) were sealed in a dessicator (approximate 5 l). The fluoride-containing PVA nanofibre membrane was crosslinked by formaldehyde vapour with acid catalysis for 48 h at room temperature. The crosslinked membrane was dried in the vacuum oven for 24 h at 30°C to remove residual formaldehyde.

2.4 *Characterization*

The morphology of the fibres scaffold was observed using a scanning electron microscope (SEM; SHIMADZU SSX-550) at an accelerating voltage of 20 kV. The structure of fibres was observed using a TEM (JEM-2000EX). FTIR spectra were obtained from a Fourier Transform Infrared spectrometer (SHIMADZU 8400S).

3. Results and discussion

As shown in the SEM image (figure 1), the fibres of the sample had a uniform morphology and had an average diameter of about 200 nm. The structure of the nanofibres is shown in the TEM image (figure 2). We can see that some nanoparticles are distributed in the PVA fibre matrix homogeneously. These nanoparticles should be CaF_2 from the reaction between NaF and $CaCl_2$ [9,10]. To determine the accurate structure for these nanoparticles, the electron diffraction pattern of these nanoparticles at the TEM-selected area was recorded and it is shown in the inset (figure 2). The diffraction pattern of the nanoparticles in the PVA fibre matrix is consistent with that of single-crystal CaF_2 [11]. This indicates that the CaF_2 crystal nanoparticles have been indeed introduced into the PVA nanofibres successfully.

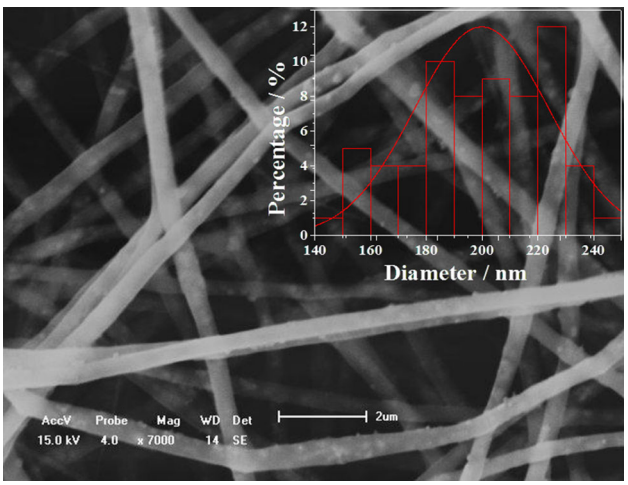

Figure 1. SEM image of CaF_2-appended PVA fibres before crosslinking. Scale bar = 2 μm.

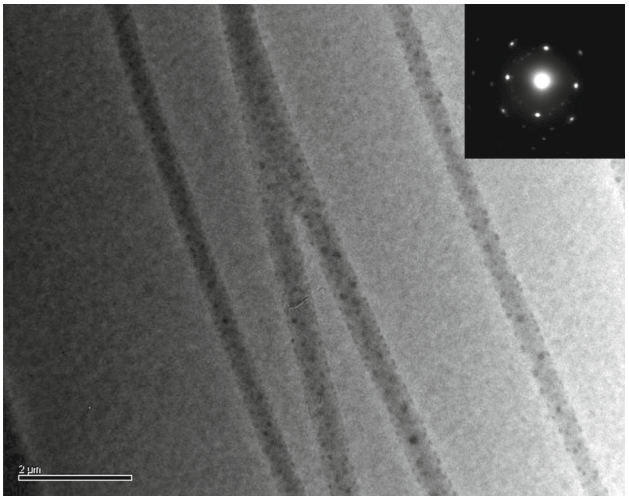

Figure 2. TEM image of CaF_2-appended PVA fibres before crosslinking and electron diffraction pattern of nanoparticles (inset). Scale bar = 2 μm.

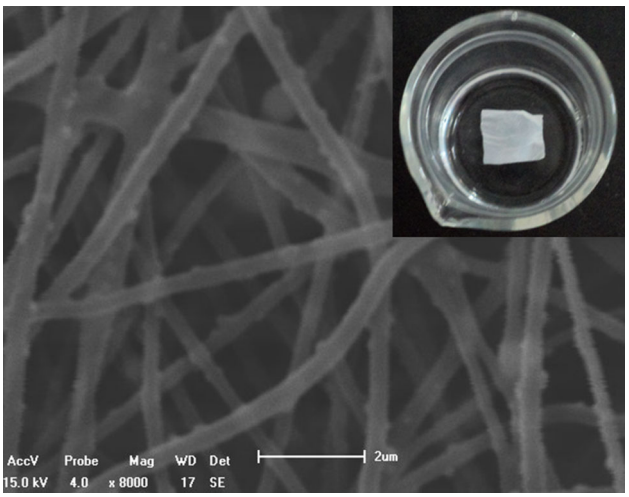

Figure 3. SEM image of CaF_2-appended PVA fibres after crosslinking and immersing in water; camera photographs (inset) of the crosslinked fibre scaffold after soaking for 7 days in a small beaker. Scale bar = 2 μm.

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PVA could be dissolved by water easily. Hence, the PVA nanofibre scaffold disappears immediately after immersion in water due to its particularly high specific surface area. This made it difficult to be used in an aqueous environment. To enhance the water-resistant ability of the scaffold, formaldehyde vapour was used to crosslink the PVA fibre scaffold.

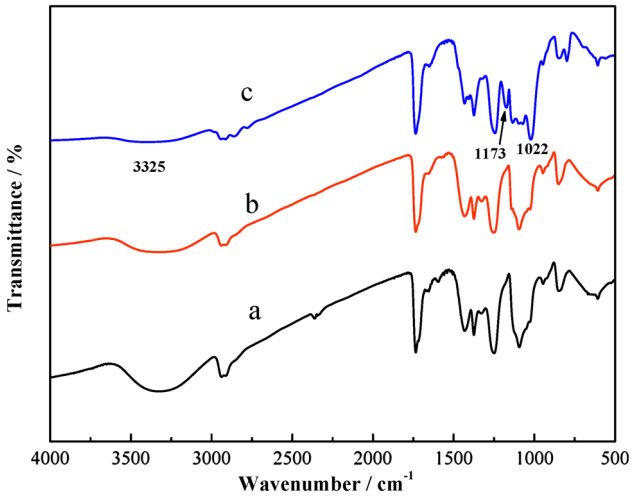

Figure 4. FTIR spectra of (a) PVA and CaF_2-appended PVA fibres (b) before and (c) after crosslinking.

The crosslinked fibre scaffold was immersed in water to test its dissolvability at room temperature. After immersing in a small beaker for 1 week, the scaffold still kept an intact appearance in macroscopic view (figure 3 inset). From figure 3, we can see that the fibre still retains a good micromorphology. Compared with the non-crosslinked scaffold, the water-resistance of the crosslinked scaffold was greatly enhanced. This proves that the crosslinked CaF_2-appended PVA nanofibre scaffold is applicable to the aqueous environment for cell culture as a scaffold.

Figure 4 shows wide-scan FTIR spectra for (a) PVA, (b) CaF_2-appended PVA and (c) CaF_2-appended PVA nanofibres after crosslinking. From these three curves, the stretching vibration of hydroxyl group in PVA can be observed at 3325 cm^{-1}. However, the hydroxyl peak intensity in (c) is weaker obviously compared with (a) and (b), which means the quantity of hydroxyl is reduced. Two new peaks appear in (c) at 1173 and 1022 cm^{-1}, which are the stretching vibration of –C–O–C– group. This proved that the acetalization indeed took place between the hydroxyl in PVA and formaldehyde [12,13]. The peak positions of CaF_2-appended PVA nanofibres are almost the same as the peaks position of PVA nanofibres. This may be understood as the weakness of molecular interaction between CaF_2 and PVA.

4. Conclusions

Electrospinning is an effective method to introduce fluoride into PVA nanofibres with a uniform and smooth morphology. CaF_2 nanoparticles were well dispersed in the PVA nanofibre matrix. The fibre scaffold shows a good water-resistant ability after crosslinking of acetalization with formaldehyde vapour.

Acknowledgements

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References

[1] Yan E Y, Cao M L, Wang Y W, Meng Y, Zheng H, Hao X Y *et al* 2016 *Mater. Lett.* **167** 13
[2] Sambudi N S, Kim M G and Park S B 2016 *Mater. Sci. Eng. C* **60** 518
[3] Fareley J R, Wergedal J E and Baylink D J 1983 *Science* **222** 330
[4] Dequeker J and Declerck K 1993 *Schweiz. Med. Wochenschr.* **123** 2228
[5] Harrison J, Melville A J, Forsythe J S, Muddle B C, Trounson A O, Gross K A *et al* 2004 *Biomaterials* **25** 4977
[6] Kim H W, Lee E J, Kim H E, Salih V and Knowles J C 2005 *Biomaterials* **26** 4395
[7] Cooper L F, Zhou Y, Takebe J, Guo J, Abron A, Holmen A *et al* 2006 *Biomaterials* **27** 926
[8] Badami A S, Kreke M R, Thompson M S, Riffle J S and Goldstein A S 2006 *Biomaterials* **27** 596
[9] Ye Q S, Xu J, He Y and Sandham A 2014 *Ann. R Australas. Coll. Dent. Surg.* **22** 71
[10] Xu J, Yan J, Gu Q, Li J F and Wang H Y 2011 *Mater. Lett.* **65** 2404
[11] Zhao D H, Shen Y L, Zhang Y L, Wei D Q, Gao N Y and Gao H W 2010 *J. Mater. Chem.* **20** 3098
[12] Yang J M, Su W Y, Leu T L and Yang M C 2004 *J. Membr. Sci.* **236** 39
[13] Han B, Li J, Chen C, Xu C and Wickramasinghe S R 2003 *Chem. Eng. Res. Des.* **81** 1385