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Novel poly(vinyl alcohol) nanofibers prepared by heterogeneous saponification of electrospun poly(vinyl acetate)

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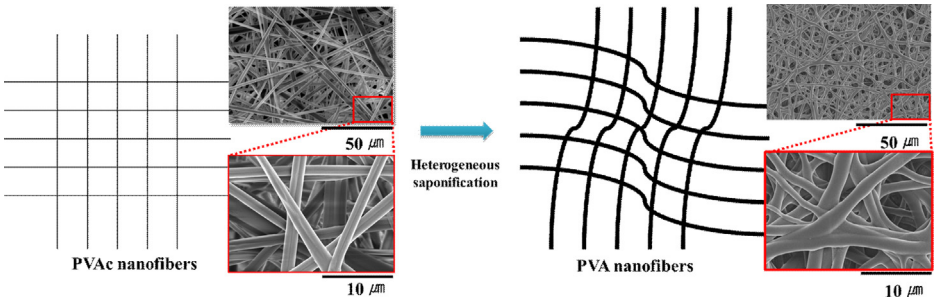
HIGHLIGHTS

- Novel poly(vinyl alcohol) nanofibers were prepared through the heterogeneous saponification of poly(vinyl acetate) nanofibers for the first time.
- It was found that the degree of saponification depended on the temperature and alkali solution concentration.
- The fully saponified PVA nanofibers had the appearance of wrinkled and wound fibers.

GRAPHICAL ABSTRACT

Generally, PVA nanofibers were prepared by the electrospinning of a PVA solution. In this work, we demonstrated a novel and facile technique to prepare PVA nanofibers from PVAc nanofibers, which are considered to be one of the most common precursors of PVA. This is a novel method for preparing PVA nanofibers through the heterogeneous saponification of PVAc electrospun nanofibers.



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ABSTRACT

Novel poly(vinyl alcohol) (PVA) nanofibers were prepared through the heterogeneous saponification of poly(vinyl acetate) (PVAc) nanofibers for the first time. To prepare the saponified PVA nanofibers, the effects of the alkali solution concentration and temperature were studied. It was found that the degree of saponification depended on the temperature and alkali solution concentration. Field emission scanning electron microscopy was utilized to characterize the morphology and properties of mats of the saponified PVA nanofibers, and unusual wrinkled and wound fibers were found. The conversion of PVAc nanofibers to PVA nanofibers was measured using proton nuclear magnetic resonance spectrometry, X-ray diffraction measurements, and Fourier transform infrared spectroscopy.

1. Introduction

Nanofibers have been the subject of vigorous experimentation because they exhibit distinctive characteristics such as a large surface-area-to-volume ratio, flexible surface functionalities, and superior mechanical properties (e.g., stiffness and tensile strength), which give them a fascinating appeal in numerous disciplines. Electrospun nanofibrous mats have been implemented in wound

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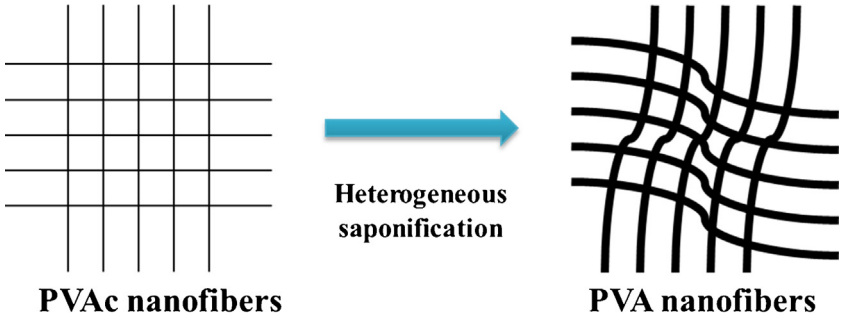

Fig. 1. Schematic illustration of preparation of PVA nanofibers by heterogeneous saponification.

healing, sensor, tissue engineering, drug delivery, and antibacterial applications [1,2].

Poly(vinyl alcohol) (PVA) has generated significant interest, particularly for various pharmaceutical and biomedical applications, because of its many appealing features such as low protein adsorption properties, high water solubility, biocompatibility, and chemical resistance. Soft contact lenses, eye drops, tissue adhesion barriers, embolization particles, and artificial cartilage and menisci are some of the most common medical uses of PVA [3]. Ultrafine PVA fibers, which have high compressive and tensile strengths, and a high tensile modulus, may hold the potentialfor various applications because of their excellent functional properties [4,5]. Therefore, many attempts have been made to develop PVA-based nanofibers and microspheres. Lee et al. reported that in an aqueous alkali solution heterogeneous saponification obstructed the reaction on the surface of poly(vinyl acetate) (PVAc) and preservation of the spherical structure of the PVAc was possible. The PVA skin that adhered to the PVAc core was a hydrogel that was reversely swellable in water, and they used sodium sulfate to prevent the dissolution of this PVA skin during the heterogeneous saponification [6]. In another report, PVAc microspheres were saponified in an aqueous alkali solution containing sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), and methanol (MeOH), which caused PVA to form at the surface of PVA/PVAc skin/core-type microspheres [7,8]. Our research group reported the novel preparation of PVA/clay nanocomposite microspheres via suspension polymerization and saponification [9]. Our group also studied PVAc/PVA/montmorillonite nanocomposite microspheres prepared by suspension polymerization and saponification [10]. All of the above reports were about microspheres prepared by suspension polymerization and saponification. Yang et al. prepared gelatin/PVA nanofibers and found their potential application in the controlled release of drugs [11]. In another study, the fabrication of PVA/chitosan blend nanofibers was studied [12]. Zeng et al. experimented with PVA nanofibers as a protein delivery system [13]. Shalumon et al. prepared carboxymethyl chitin/PVA electrospun nanofibrous scaffolds for tissue engineering applications [14]. The effect of deacetylation on the wicking behavior of a co-electrospun cellulose acetate/PVA nanofiber blend was studied by Khatri et al [15]. Ulvan-based uniform nanofibers were fabricated by blending with PVA [16]. All of these studies were about PVA nanofibers prepared by the electrospinning of a PVA solution. Our research group also fabricated many PVA nanocomposite nanofibers and examined their applications. However, the literature contains no reports on the saponification of PVAc nanofibers to form PVA nanofibers, which were fabricated for the first time in our lab.

In this work, we demonstrated a novel and facile technique to prepare PVA nanofibers from PVAc nanofibers, which are considered to be one of the most common precursors of PVA [17]. This is a novel method for preparing PVA nanofibers through the heterogeneous saponification of PVAc electrospun nanofibers. The prepared nanofibers presented extraordinary wrinkled and wound fiber characteristics, as well as a large surface area compared to ordinary PVA nanofibers. The effects of the temperature and concentration of the alkali solution on the saponification rate were evaluated.

2. Materials and methods

2.1. Materials

Vinyl acetate (VAc) (Sigma Aldrich) was washed with an aqueous solution of $NaHSO_4$ and water; it was then dried with $CaCl_2$ (anhydrous) and subsequently distilled in a nitrogen atmosphere under reduced pressure. PVA (Aldrich) was used as a suspending agent and the number-average molecular weight and the degree of saponification (DS) of PVA are 127,000 g/mol and 88% respectively. 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) (WakoCo.) was recrystallized twice in methanol and used as an initiator. We used NaOH (Duksan), Na_2SO_4 (Duksan), and MeOH (Duksan) to pre-

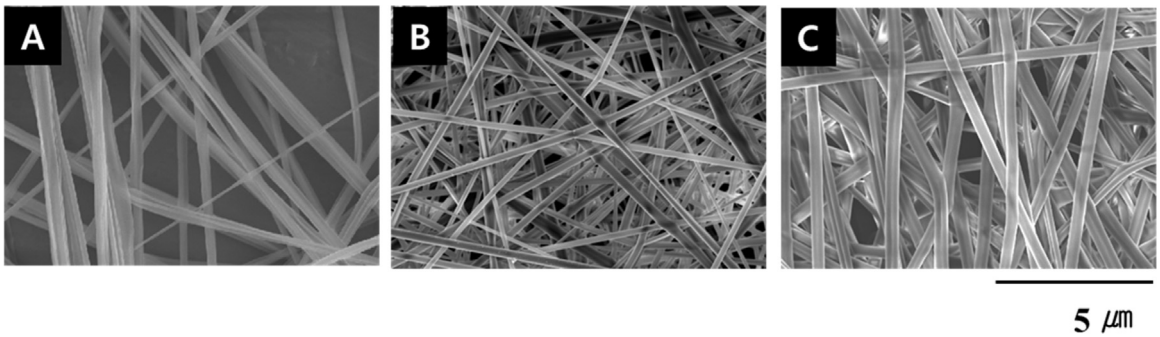

Fig. 2. FE-SEM images of electrospun pure PVAc nanofibers prepared using various solution concentrations: (a) 10 wt.%, (b) 15 wt.%, and (c) 20 wt.% (applied voltage = 15 kV, TCD = 15 cm).