

## THERMAL PROPERTY OF ROCK POWDER-BASED NANOFIBERS FOR HIGH TEMPERATURE FILTRATION AND ADSORPTION

by

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*Rocks have good chemical and thermal properties, which are widely distributed in mountainous areas and contain a great number of chemical elements. Weathered rock powders were used as an additive in an electrospun solution to fabricate rock powder-based nanofibers, and the morphology and thermal property of nanofibers were studied. The results revealed that the rock powder was the most economical approach to fabrication of nanofibers with excellent thermal property and high hydrophilicity. This paper sheds a light on rock powder-based nanofibers with well-defined characteristics for advanced applications for high temperature filtration and absorption, fire prevention and others.*

**Key words:** nanoparticle, color nanofibers, protective clothing, fire prevention, high temperature filter, hierarchical structure, hydrophilicity

### Introduction

Recently, the synthesis and design of organic-inorganic hybrid materials have generated great interests in thermal science, nanotechnology, and material science. Composite nanofibers are attractive for the purpose of creating new materials or enhancing properties compared with single organic or inorganic materials. Generally, the incorporation of a small amount of inorganic nanoparticles can improve the performance of the mechanical, thermal, optical, electrical, antimicrobial, antifouling, and catalytic properties of a polymer matrix [1], those phenomena can be well explained by the geometrical potential theory [2-6]. A small amount of various chemical elements can embody the nanofibers with multi-functional properties for many applications.

Rock comprises approximately two-thirds of the Earth's crust and contains more than 30 bio-essential elements [7-10]. Rocks contain the major elements of Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K, and P and the trace elements S, Cl, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Pb, Th, and U [11]. As a result of external dynamic geological processes, rock masses on Earth's surface are usually severely weathered which are widely distributed in mountainous areas of China. Deeply weathered rocks have been observed in many parts of mountains generally as isolated pockets, but occasionally over large areas. Elsewhere, the weathered rock extends to the surface and forms the parent material of contemporary soils. The weathered rock may be micro/nanoscale. Due to the fact that rock consists of a great many of elements, it may have good thermal properties [12], electrical properties [13, 14], magnetic properties [15], and mechanical property [16,

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17]. Guo *et al.* [18] successfully combined electrospinning and pressure molding to prepare the porous lamellar mullite ceramics with whisker skeletons.

Electrospinning is a simple and versatile technique of fabricating fibers with controllable diameters from micrometers to nanometers [19-23]. Considering the substantial impact on nanotechnology and material science, and extreme richness of rock in resources, it seems to be remarkably economic to fabricate rock powder-based nanofibers with well-defined multi-functional characteristics.

## Experiment

### Materials

Polyvinyl alcohol (PVA) used in this experiment was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), and directly used as received without further purification. PVA's alcoholysis degree was 98-99.0 mol%, and was stored at room temperature. The weathered rocks were taken from a mountain next to Zhejiang Ocean College located in Haiding district, Zhoushan Islands, China (Longitude 122, degrees 30). The collection place is shown in fig. 1.



Figure 1. Weathered rocks and powders; (a) collection place at an island, (b) calcined rock powders

### Preparation of the spun solution

The PVA solution was prepared at room temperature by dissolving the polymer in deionized water with a concentration of 8 wt.%. The PVA solution was stirred in a magnetic heated stirrer (DF-101S, Jintan Xinrui Instrument Factory, Changzhou, China) at 80 °C for two hours to ensure complete dissolution and prepared for a uniform and transparent spun solution. Weathered rocks were grinded to powders and filtered through a 500 mesh screen, the pore size of the mesh is 25 micrometers. The filtered rock powders were calcinated at 700 °C in Muffle (GZ2.5-10TP, Shanghai Grows Precision Instrument Co., Ltd. Shanghai, China) and remained for 1 hour at the required temperature, shown in fig. 1(b). Then, 0.2 g rock powders were added to 10 g PVA solution and stirred using a high speed magnetic homogenizer (HJ-6A, Gongyi Yuhua Instrument co., Ltd. Zhengzhou, China) for 2 hours until a homogeneous magmatic PVA solution was obtained.

### Electrospinning

The electrospinning set-up was shown in fig. 2. The polymer solution was electrospun at room temperature at a voltage of 20 kV. The syringe used in this experiment had a needle tip diameter of 0.7 mm that was positive charged. The negative receptor was placed 15 cm from the tip of the needle. Continuous nanofibers were deposited on the receptor and collected in the form of non-woven fibrous mats. The pristine PVA solution and rock powder/PVA solutions were both electrospun for 6 hours.

### Result and discussion

#### Color of the nanofibers membrane

The color of the rock powder-based nanofibers membrane was rust red, while its PVA nanofibers membrane was white, see fig. 3.

#### Morphological characterization

The morphology and diameters of the rock powder-based nanofibers were determined using a SEM, (Hitachi S-4800, Tokyo, Japan). The SEM images for PVA nanofibers were shown in fig. 4. The SEM images for rock powder-based nanofibers were shown in fig. 5. The electrospun rock powder-based nanofibers exhibited cylindrical morphology and randomly distributed in the fibrous mat with a very uniform and dense structure. Overall, the size and morphology of the nanofibers were affected by the addition of rock powers. The average diameter of the rock powder-based nanofibers was 260 nm, while the average diameter of pristine PVA nanofibers was 226 nm. The addition of the rock powders in the solution increased the nanofiber's diameter.

### Thermogravimetric analysis

Rocks and minerals contain the major elements of Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K, and P, the products of rocks calcined at high temperatures mainly contain the oxide of these elements, such as  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ , and so on [24], which have high resistance to thermal degradation and can be used as additive to increase material's thermal properties.

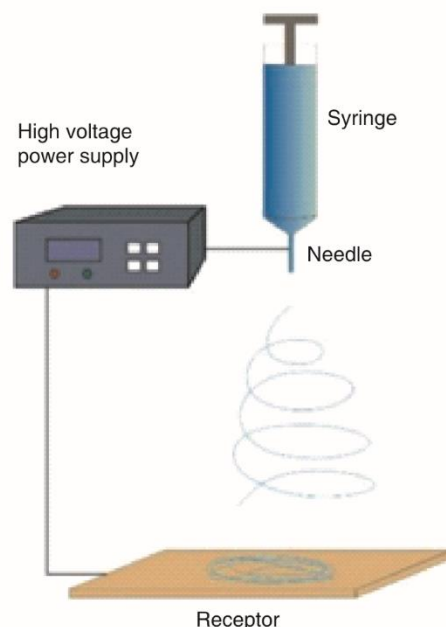


Figure 2. Electrospinning set-up



Figure 3. Nanofibers membrane; (a) PVA nanofibers membrane, (b) color rock powder-based nanofibers membrane

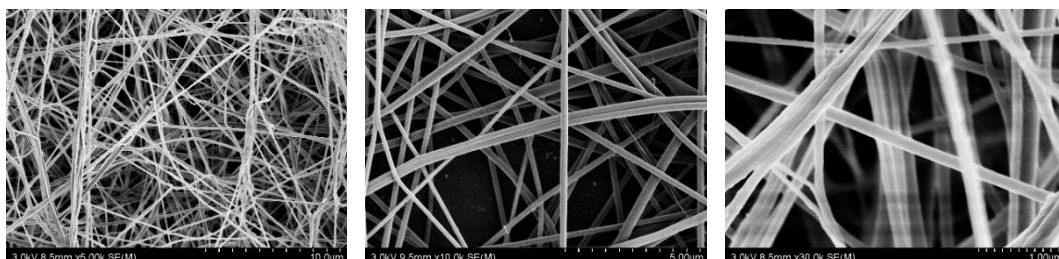


Figure 4. The SEM images for the PVA nanofibers

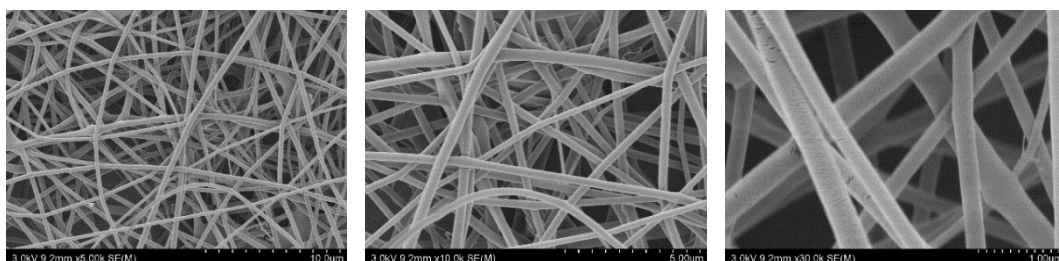


Figure 5. The SEM images for the rock powder-based nanofibers

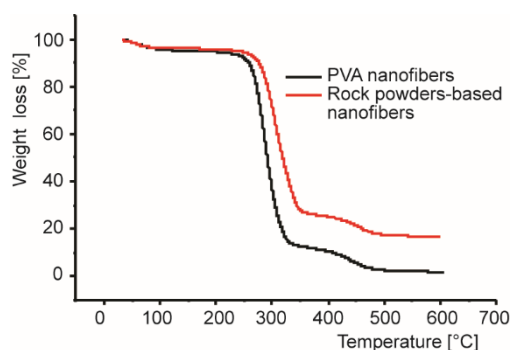


Figure 6. The TGA profiles of a PVA nanofibers and rock powder-based nanofibers

The interaction of rock powders in PVA nanofibers membrane was further evaluated via thermogravimetric/differential thermal analyzer (TGA), (Diamond TG/DTA, Perkin Elmer Instruments, USA), see fig. 6. A temperature correlation with the maximal thermal degradation rate for PVA nanofibers membrane at 329.8 °C was observed. The shifting from 329.8 °C to 351.5 °C for the nanofibers membrane with rock powders, fig. 5, indicated the interaction of nanoparticles with the polymer during the formation of the electrospun process. The rock powders have a good heat resistance, and rock powder-based nanofibers

were more stable than its PVA partner, and can be used in protective clothing, making rock powder-based fibers the best candidate for the fire prevention.

### Mechanical property

The mechanical property was tested by the universal material testing machine (INSTRON-3365, USA). The stress-strain curve was shown in fig. 7. It was clear that the mechanical strength of the rock powder-based nanofibers membrane decreased compared with its PVA partner. It was shown that the curve for rock powder-based nanofibers membrane had two peaks, see fig. 7.

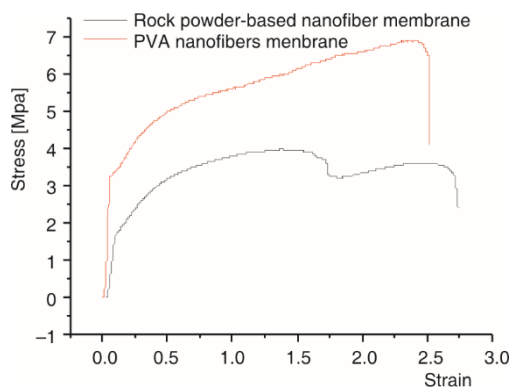
The rock powders were distributed inside nanofibers, due to poor attachment to polymer molecules, the rock powders made the nanofibers brittle, see fig. 8(a). So the rock powder-based nanofibers can be easily broken into parts to make nanoparticles, see fig. 8(b),

which can be used as 3-D filling materials, see fig. 8(c), possessing good thermal property and nanomaterial properties like high surface energy and wetting property. The three dimensional membrane with filling of nanoparticles from rock powder-based nanofibers can be used for a high temperature filtration and adsorption due to their hierarchical structure.

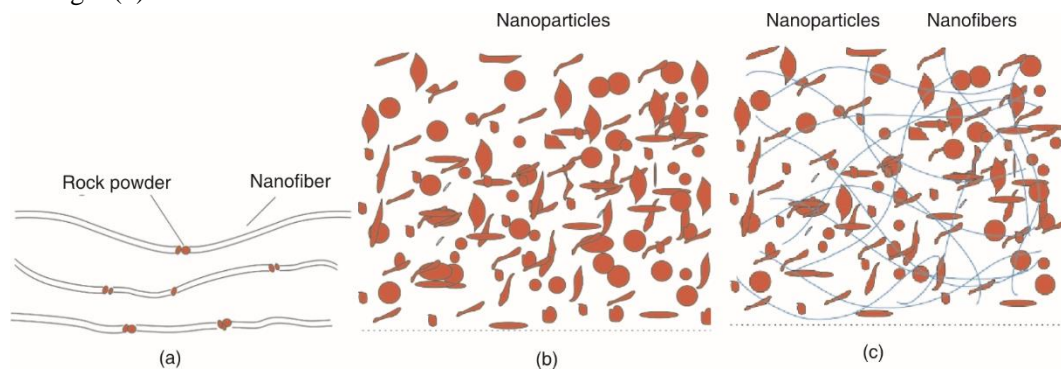
### Wetting property

Contact angle (CA) was analyzed using a Kruss DSA 100 apparatus (Kruss Company Germany). Each samples measured 3 times and its mean value was used.

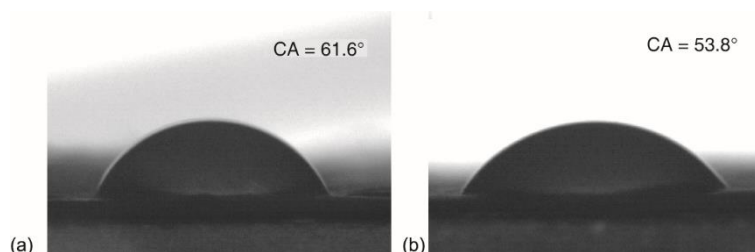
The hydrophilic of alcohol groups in polyvinylalcohol (PVA) always results in hydrophilicity of PVA products as shown in fig. 9(a). The wetting property can be changed after the addition of rock powders. With the addition of the rock powders the contact angle decreased, see fig. 9(b).



**Figure 7. Stress-strain curve for PVA nanofibers membrane and rock powder-based nanofibers membrane**



**Figure 8. From nanofibers to nanoparticles and nanofilling-materials; (a) 1-D nanofiber, (b) 0-D nanoparticles, (c) 3-D membrane with filling of nanoparticles**



**Figure 9. The CA; (a) of PVA nanofibers membrane, (b) of rock powder-based nanofibers membrane**

### Conclusion

Rock powder/PVA nanofibers have been synthesized *via* the electrospinning technology. The diameters of nanofibers are uniform. The presence of a small amount of rock



powders in PVA solution was found to improve the hydrophilicity and thermal properties. The obtained fibers are easy to be broken into nanoparticles which can be used as filling in a membrane for high temperature filtration and absorption. This paper suggests the simplest and most economical way to use weathered rock powders as an additive for fabrication of hybrid nanomaterials.

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