Freeze-Extrusion for Controllable Assembly of 3-Dimensional Ultra-Fine and Amorphous Fibrous Matrices: Potential Applications in Sorption

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Scheme 1 Reaction between PVA and CI Reactive Blue 19

Scheme 1 shows the formation of chemical bond between PVA and the reactive dye. Under alkaline condition, hydroxyl group on PVA reacts with vinyl sulfone group on CI Reactive Blue 19.

Preparation of chitin nanocrystals.

Chitin nanocrystals were prepared by hydrolyzing purified chitin in 3 M HCl for 4.5 h at 90 °C according to method reported by Jacob et al¹.

Preparation of oxidized sucrose

About 3.3 g of sucrose and 6.4 g of sodium periodate were dissolved in 100 mL of distilled water. After the solution was stirred at room temperature for 26 h, 24 about 3.5 g of barium dichloride was added and the mixture was stirred at 5 °C for 1 h to allow complete precipitation. The mixture was filtrated to obtain the liquid containing polyaldehyde derivatives of sucrose.

Chitin reinforced keratin adsorbent was fabricated freeze-drying method. Chitin nanocrystals (25% weight ration of keratin) was added into keratin solution and the dispersion was sonicated for 5 min in an ice bath using an ultrasonic processor (VCX 500:500 W, Sonics & Materials, Newton, CT). After that crosslinking agent oxidized sucrose (10% based on the weight of keratin) solution at pH 6.5 was added into the obtained dispersion. The mixture was stirred for 5 min and then putting into -80 °C refrigerator for 2 h before freeze-dried for 70 h. The freeze-dried keratin adsorbent was put into 70 °C oven for 1 h to allow the crosslinking reaction.

Preparation of Ba-a

0.1mol of bisphenol-A, 0.4 mol paraformaldehyde, and 0.2 mol aniline were added into a flask with stirring for 20 min at room temperature. After that, temperature was gradually increased to 100 °C for 4 h. The resultants were cooled to room temperature and dissolved in 200 mL of tricholoromethane. The solution was purified by washing with 1 wt% sodium hydroxide and pure water, then treated with anhydrous magnesium sulfate and filtered, and dried at 60 °C for 2 h to obtain BA-a powders.



Fig. 1 Observation of 3-D fibrous (a) and non-fibrous (b) PVA matrices via SEM (scale bar = 50 μ m). Solutions contained 0.1 wt.% of PVA in water (a) and in DMSO (b) and were frozen at -80 ^oC. Large solubility of PVA in water ensured late precipitation of PVA after the gaps between ices reduced to fibrous level, therefore, fibrous PVA matrix was formed in Figure 1(a). Small

solubility of PVA in DMSO led to the early precipitation of polymer when the gaps between ices were still large, therefore, ribbon-like matrix was formed in Figure 1(b).



Fig. 2. Controlled alignment of fibers in UFMs by changing temperature gradients (Scale bar = 2 cm). Fibers are aligned from the bottom up (a), towards center of circular plate (b) and center of sphere (c). PVA was used as the polymer with concentration of 0.1% in water. Freezing temperature was -80 °C. Blue arrows indicate directions of fiber orientations in matrices. For a) and b), containers of PVA solution were inserted into coolant at a controlled rate of 2 mm/min and dipped into coolant immediately, respectively. For c), a spherical vessel holding PVA solution was dipped into coolant immediately to ensure whole PVA solution to be covered by coolant.



Fig. 3 Sizes of freeze-extruded PVA matrices at a) -80 ^oC and b) -20 ^oC. Container of RB 19 dyed PVA solution (0.2 g/L) was dipped into cooling fluid immediately. Size of matrices under high freezing rate is larger than that under low freezing rate.

Fig. 3 shows sizes of extruded matrix are affected by freezing temperatures. Precipitation rate of polymer was slow under low freezing rate. Lots of unsolidified polymers moved along with the temperature gradient. Concentration of polymer at the rim of container was very small. As a result, there was no precipitated polymers in the gaps of ices at the rim of container, as shown in Fig. 3b. Alternatively, under high freezing rate, plenty of polymer precipitated at the rim of container because not all dissolved polymer molecules could migrate along with the temperature gradient before they precipitated. Fig. 3a show matrices stretched in every corner of the container.



Fig. 4 Observation of keratin matrices via SEM (scale bar = 50 μ m) after freezing at a) -80 0 C and b) -196 0 C. Solutions contained 0.1 wt.% of keratin were frozen and freeze-dried.

Fig. 4 shows only polymer extruded from ices along with solvent could form fibrous matrices. Fig. 4a shows the formation of fibrous matrices at appropriate freezing rate. On the contrary, polymer could be encapsulated in the ice under extreme high freezing rate. As a result, irregular aligned matrices were formed, as shown in Fig. 4b.

Table 1 Comparison of degree of crystallinity for polymer fibers between different preparation method.

Polymer	Wet-spun fiber	Freeze-extruded fiber
PVA	46%	21%
Feather keratin	22%	<5%

Table 1 shows that fibers via freeze-extrusion have a low degree of crystallinity. There are several reasons for this. During freezing, polymer precipitates at very low temperature. Molecular chains of polymer cannot line up in a regular arrangement at such temperature. Moreover, some ice crystals stay in precipitated polymers and thus hamper interactions among polymer chains. After the sublimation of ices, distance between polymer chains is large, so that interactions between polymer chains are limited. As a result, degree of crystallinity of fibers via freeze-extrusion is low.

Diameter of fiber in UMFs	Spacific surface area (m2/g)	Dye sorption capacity	
(μm)	specific surface area (iii /g)	(mg/g)	
6.8 ± 4.0	720	1200	
$\textbf{2.3} \pm \textbf{1.0}$	760	1250	

Table 2 Relationship among fiber diameter, surface area and dye sorption capacity

Reactive Black 5 was used for sorption measurement.



Fig. 5 Sorption isotherm of RB5 and DR80 at room temperatures. Lines are the Langmuir regression fit.

Table 3. Langmuir isotherm parameters for the sorption of RB5 and DR80 by keratin UFMs

	$K_L (L mg^{-1})$	$[S]_{f} (mg g^{-1})$	R ²
RB5	0.03	1250	0.9925
DR80	0.04	1111	0.9946



Fig. 6 Sorption kinetics for DR 80 and RB 5 on keratin UFMs.

Table 4. Kinetic parameters of pseudo-first-order, pseudo-second-order models for the sorption of RB5 and DR80 by keratin UFMs.

	Pseudo-First-Order		Pseudo-Second-Order	
-	$k_1 (min^{-1})$	R ²	k_2 (g mg ⁻¹ min ⁻¹)	R ²
RB5	0.017	0.9609	2.2*10-5	0.9964
DR80	0.014	0.9742	3.1*10-5	0.9968



Fig. 7 Effect of the variation of $V_{sorption}/V_{desorption}$ on concentration factor and desorption efficiency. – Optimization of desorption step (sorption step: dye solution pH = 2, dye concentration 200 mg/L, 0.5 g/L keratin UFMs; contact time: 600 min, desorption step: 0.1 g L⁻¹ NaOH solution, contact time: 600 min).



Fig. 8 Effect of salt concentration on removal efficiency of RB5 and DR80 by keratin UFMs. (dye solution pH = 2, dye concentration 200 mg/L, 0.5 g/L keratin UFMs; contact time: 600 min)

1. J. D. Goodrich and W. T. Winter, *Biomacromolecules*, 2007, **8**, 252-257.