Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Electrospinning Fibrous Membrane Reinforced Hydrogels with Preferable Mechanical and Tribological Performance for Cartilage Substitute

Qin Chen [a,1]; Xiaodong Yan [a, 1]; Kai Chen [a, b, c, *]; Cunao Feng [a]; Dagang Wang [a]; Xiaowei Li [a]; Xiaoduo Zhao [b]; Zhimin Chai [c]; Qingliang Wang [a, *]; Dekun Zhang [a], Hongbo Zeng [d]

a. School of Chemical Engineering and Technology, School of Materials Science and Physics, School of Mechatronic Engineering, China University of Mining and Technology, Xuzhou 221116, China

b. State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

c. State Key Laboratory of Tribology in Advanced Equipment, Tsinghua University, Beijing 100084, China

d. Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada

1. The effect of PVA/PAA ratio on the mechanical properties of the fibrous membrane

we have added the content of effect of PVA/PAA on properties in Supporting Information. According to the literature, the optimal mass ratio of water and solute in the spinning solution is 9:1, the mass ratio of the solute was 10 wt.%. In the solute, PVA was the matrix, PAA-GO was added to PVA as an enhanced phase. As shown in Figure S2, the optimal mass ratio of PVA to PAA-GO is 8.5:1.5. It was observed that the spinning film could not be formed when the mass fraction of PAA exceeded 3%, the influence of PAA mass fraction on the performance of spinning film was explored.

---

[1] The authors equally contribute to manuscript.

***Corresponding author**: Kai Chen and Qingliang Wang

E-mail address: cumtck@cumt.edu.cn; wql889@cumt.edu.cn

The addition of PAA can significantly enhance the mechanical properties of electrospinning fibrous membrane, with the increase of the mass ratio of PAA in the spinning solution, the tensile strength and modulus of the electrospinning membrane first increased and then decreased. This is because with the increase of the mass ratio of PAA in the spinning solution, the number of hydrogen bond formed between the PVA molecular chain increased, and the carboxyl group in PAA and hydroxyl group in PVA molecular chains can form bonding, which promotes the formation of new entanglement points between polymer chains and increases the degree of cross-linking, thereby increasing the elastic modulus and strength of the fibrous membrane. However, when the PAA content increased to a certain value, the viscosity of the spinning liquid will be too high, and discontinuous fibrils will easily be formed on the membrane during the spinning process, and this stress concentration effect will reduce the mechanical properties of the fibrous membrane.

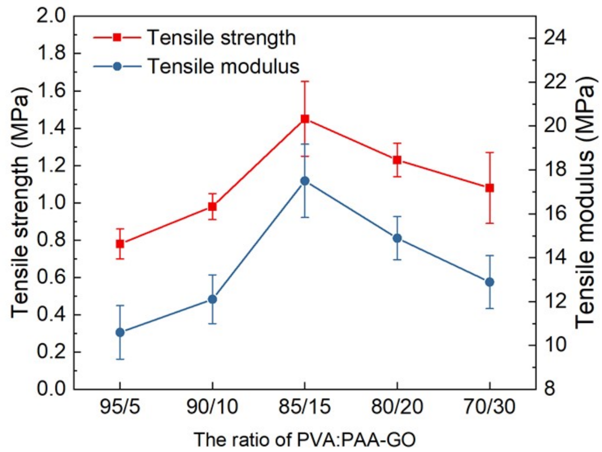

Figure S1. The tensile strength and modulus of the fibrous membrane with different ratio of PVA:PAA-GO (the total mass ratio of solute was 10wt%, the GO content was 0.1wt%).

2. The SEM images of the Electrospinning PVA/PAA/GO Fibrous Membranes

The optimal parameters are determined by the influence of the parameters on the spinning morphology as the receiving distance of 15 cm, the voltage of 12 kV, and the jetting speed of 0.1 mm/min. As shown in **Figure S2a-b,** the spinning voltage was set as 12 kV, the injection rate as 0.1 mm/min, and the receiving distance as (a) 9 cm, (b)

12 cm and (c) 15 cm, respectively. With the increase of receiving distance, the adhesion of hydrogel fibers decreased obviously. The receiving distance of 15cm can be determined from the fiber morphology and spinning process. Moreover, the fiber needs more electric field force to deposit on the receiving device smoothly if the receiving distance was too large.

Generally, with the increase of voltage, the jet radius will decrease, resulting in a finer spinning fiber. However, when the voltage was too high, the jet will become unstable and often break. The Taylor cone at the end of the nozzle was easy to spin and flit, which is not conducive to the smooth spinning. As shown in **Figure S2d-f**, the receiving distance was set at 15 cm, the injection rate at 0.1 mm/min, and the spinning voltages were (d) 10 kV, (e) 12 kV, and (f) 14 kV, respectively. With the increase of the spinning voltage, the fibers were more densely distributed, and the spinning voltage was determined to be 12 kV based on the morphology of fibers and the spinning process.

If the injection speed is too slow, the spinning will be incoherent and the injection flow will be greater than the supply, which will affect the normal spinning. If the injection speed is too fast, the solution will be wasted, and the ejected solution will drop due to gravity before it completely falls on the receiving device. As shown in **Figure S2g-i,** the spinning voltage was set at 12 kV, the receiving distance at 15 cm, and the injection rate at (g) 0.05 mm/min, (h) 0.1 mm/min, and (i) 0.2 mm/min, respectively. With the increase of the spinning voltage, the diameter of the fiber increased, so the injection rate was determined to be 0.1 mm/min.

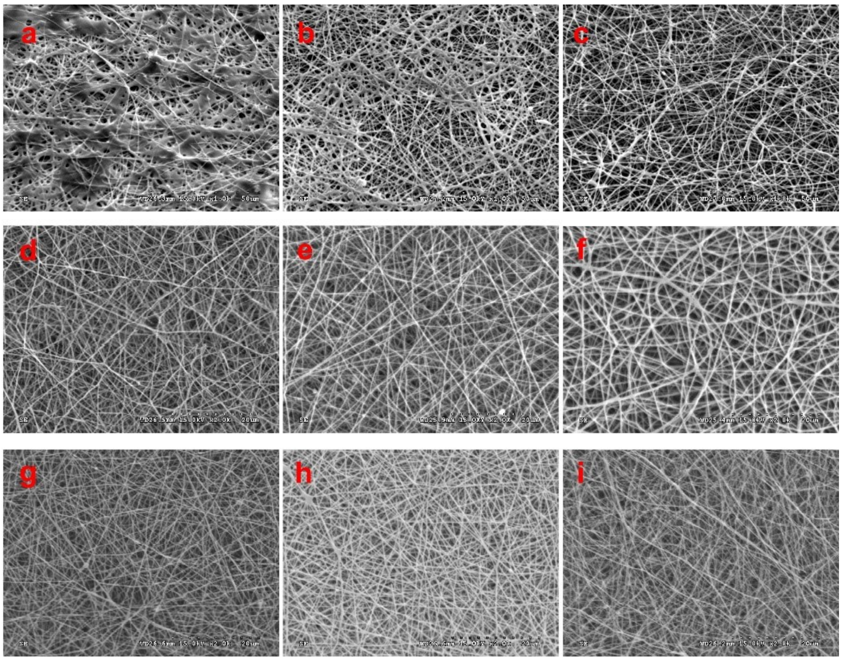

Figure S2. The SEM images of the electrospinning PVA/PAA/GO fibrous membranes under different receiving distance at (a) 9cm, (b) 12cm and (c) 15cm, respectively. The SEM images when receiving distance was set at 15cm, the injection rate at 0.1mm/min, and the spinning voltages were (d) 10V, (e) 12V, and (f) 14V, respectively. The SEM images when spinning voltage was set at 12V, the receiving distance at 15cm, and the injection rate at (g) 0.05mm/min, (h) 0.1mm/min, and (i) 0.2mm/min, respectively.

Table S1. The friction coefficient of the PPG-4 hydrogel and other low friction for cartilage substitute.

Hydrogels	COF	Reference
PVA	0.18	[1]
BC-PVA-PAMPS	0.06	[2]
PAA-G8	0.05	[3]
PEG-G8	0.04	[3]
PAA	0.06	[4, 5]
PAMPS-PDMAAm	0.09	[2]
PVA/SA/NaCl	0.05	[6]
TPCS	0.044	[7]
PVA/MZFA	0.07	[8]
P(AAm-co-AAc)/Fe^{3+}	0.06	[9]
Hydrogel-Elastomer hybrid	0.05	[10]
PVA/PEG/GO	0.04	[11]
PVA-HA/HACC-Cit	0.038	[12]
PVA/PVP/PAA-TN	0.15	[13]
Annealed PVA-HA/PAA	0.071	[14]
PMPC TN	0.05	[15]
Bilayer hydrogel	0.055	[16]
PPG-4 Hydrogel	**0.039**	**This work**

3. Anisotropic properties

The anisotropic mechanical and tribological properties of PPG-4 hydrogel were further studied. The presence of ordered electrospinning fibrous membrane improved the performance of PVA/PAA/GO hydrogels in an anisotropic manner. As shown in Figure S3a-b, the tensile strength of the PPG-4 hydrogel was 13.75±1.51 MPa, and the tensile modulus was 27.5±3.2 MPa when stretched in the direction of the parallel orientation of the electrospinning fibrous membrane; While the tensile strength and tensile modulus were 7.05±0.67 MPa and 16.23±1.78 MPa in the vertical orientation. And when the electrospinning fibrous membrane was disordered, the tensile strength and modulus of the hydrogel are between those of ordered PPG-4 hydrogel in parallel and vertical direction, but it is significantly better than those of PPG hydrogel. The above results showed that the electrospinning fibrous membrane can effectively enhance the mechanical properties of the hydrogel, and the tensile properties of the hydrogel showed anisotropy when the electrospinning membrane present an ordered structure. On the one hand, the electrospinning fibrous membrane formed a reinforcing network inside the hydrogel. On the other hand, the ordered electrospinning fibrous membranes endowed the hydrogel with orientation structure, similar to the collagen fibrils arranged in cartilage, which gives the hydrogel higher mechanical properties.

The tribological properties of PPG-4 hydrogel are also influenced by the oriented structure (Figure S3c-d). When the electrospinning fibrous membrane was horizontally oriented, the friction coefficient of the hydrogel is as low as 0.039. The excellent tribological properties are mainly attribute to the fact that the dense horizontally oriented ordered fibrous membrane hinders the seepage of the liquid phase, and the hydrostatic pressure formed can disperse most of the load, which can significantly reduce the friction coefficient of the hydrogel. In the vertical orientation, the coefficient of friction of the hydrogel is 0.068.

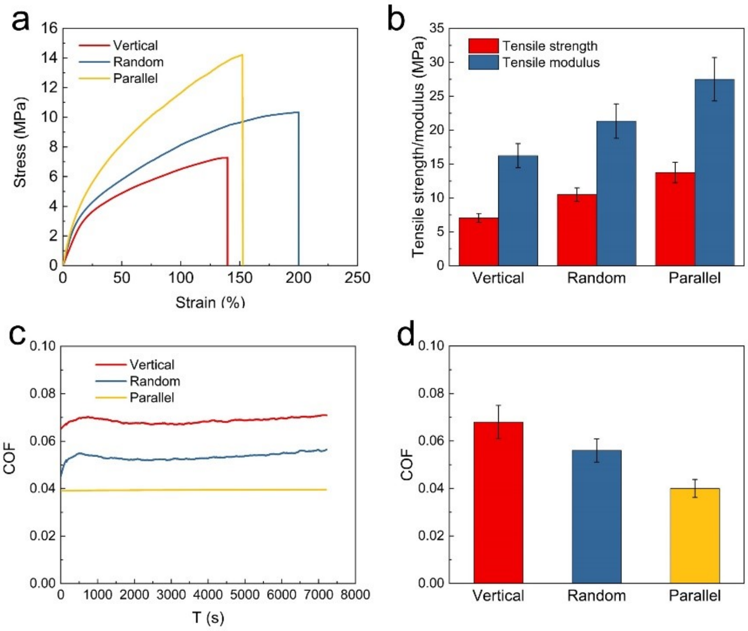

Figure S3. Anisotropic mechanical and tribological properties of the PPG-4 hydrogel. (a) The tensile stress-strain curves, (c) COF-t curves, and (d) average COF of the PPG-4 hydrogel with ordered electrospinning fibrous membrane in parallel and vertical direction, PPG-4 hydrogel with disordered electrospinning fibrous membrane.

References

[1] Stammen, J. A.; Williams, S.; Ku, D. N.; Guldberg, R. E., Mechanical properties of a novel PVA hydrogel in shear and unconfined compression. *Biomaterials* **2001,** *22* (8), 799-806.

[2] Yang, F.; Zhao, J.; Koshut, W. J.; Watt, J.; Riboh, J. C.; Gall, K.; Wiley, B. J., A Synthetic Hydrogel Composite with the Mechanical Behavior and Durability of Cartilage. *Advanced Functional Materials* **2020,** *30* (36).

[3] Lei, H.; Dong, L.; Li, Y.; Zhang, J.; Chen, H.; Wu, J.; Zhang, Y.; Fan, Q.; Xue, B.; Qin, M.; Chen, B.; Cao, Y.; Wang, W., Stretchable hydrogels with low hysteresis and anti-fatigue fracture based on polyprotein cross-linkers. *Nature Communications* **2020,** *11* (1).

[4] Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y., Double-network hydrogels with extremely high mechanical strength. *Advanced Materials* **2003,** *15* (14), 1155-+.

[5] Wei, J.; Wang, J.; Su, S.; Wang, S.; Qiu, J.; Zhang, Z.; Christopher, G.; Ning, F.; Cong, W., 3D printing of an extremely tough hydrogel. *Rsc Advances* **2015,** *5* (99), 81324-81329.

[6] Zhang, R.; Zhao, W.; Ning, F.; Zhen, J.; Qiang, H.; Zhang, Y.; Liu, F.; Jia, Z., Alginate Fiber-Enhanced Poly(vinyl alcohol) Hydrogels with Superior Lubricating Property and Biocompatibility.

Polymers **2022,** *14* (19).

[7] Luo, C. H.; Guo, A. D.; Zhao, Y. F.; Sun, X. X., A high strength, low friction, and biocompatible hydrogel from PVA, chitosan and sodium alginate for articular cartilage. *Carbohydrate Polymers* **2022,** *286*.

[8] Darwish, M. A.; Zubar, T. I.; Kanafyev, O. D.; Zhou, D.; Trukhanova, E. L.; Trukhanov, S. V.; Trukhanov, A. V.; Henaish, A. M., Combined Effect of Microstructure, Surface Energy, and Adhesion Force on the Friction of PVA/Ferrite Spinel Nanocomposites. *Nanomaterials* **2022,** *12* (12).

[9] Huang, S. T.; Wang, B. B.; Zhao, X. Y.; Li, S. J.; Liang, X. C.; Zeng, R.; Li, W.; Wang, X. J., Phospholipid reinforced P(AAm-co-AAc)/Fe3+ hydrogel with ultrahigh strength and superior tribological performance. *Tribology International* **2022,** *168*.

[10] Huang, Y.; Wang, J.; Yu, W.-j.; Yu, Y.; Li, R.-y.; Gao, Q.; Ren, K.-f.; Ji, J., A Bioinspired Hydrogel-Elastomer Hybrid Surface for Enhanced Mechanical Properties and Lubrication. *Acs Applied Materials & Interfaces* **2021,** *13* (42), 50461-50469.

[11] Hu, F.; Lu, H. L.; Ye, Z. S.; Zhang, S. J.; Wang, W. B.; Gao, L., Slow-release lubrication of artificial joints using self-healing polyvinyl alcohol/polyethylene glycol/ graphene oxide hydrogel. *Journal of the Mechanical Behavior of Biomedical Materials* **2021,** *124*.

[12] Gan, S.; Lin, W.; Zou, Y.; Xu, B.; Zhang, X.; Zhao, J.; Rong, J., Nano-hydroxyapatite enhanced double network hydrogels with excellent mechanical properties for potential application in cartilage repair. *Carbohydrate Polymers* **2020,** *229*.

[13] Li, X. F.; Qin, H. L.; Zhang, X. L.; Guo, Z. G., Triple-network hydrogels with high strength, low friction and self-healing by chemical-physical crosslinking. *Journal of Colloid and Interface Science* **2019,** *556*, 549-556.

[14] Chen, K.; Chen, G.; Wei, S.; Yang, X.; Zhang, D.; Xu, L., Preparation and property of high strength and low friction PVA-HA/PAA composite hydrogel using annealing treatment. *Materials Science & Engineering C-Materials for Biological Applications* **2018,** *91*, 579-588.

[15] Milner, P. E.; Parkes, M.; Puetzer, J. L.; Chapman, R.; Stevens, M. M.; Cann, P.; Jeffers, J. R. T., A low friction, biphasic and boundary lubricating hydrogel for cartilage replacement. *Acta Biomaterialia* **2018,** *65*, 102-111.

[16] Lin, P.; Zhang, R.; Wang, X.; Cai, M.; Yang, J.; Yu, B.; Zhou, F., Articular Cartilage Inspired

Bilayer Tough Hydrogel Prepared by Interfacial Modulated Polymerization Showing Excellent Combination of High Load-Bearing and Low Friction Performance. *Acs Macro Letters* **2016,** *5* (11), 1191-1195.