Electronic Supplementary Materials

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3D printing of wet-bonded multilayer scaffolds for skin wound repair

Kangning SHEN[1,2], Jingyi GU[3], Ximin YUAN[4], Nian LIU[4], Yinglin WANG[3], Jiabin CAI[1,2], Yang SHI[3], Kaiyang WANG[4], Xinghua YE[2], Minghao YANG[2], Zhiyong MA[1,2]✉, Zhijian XIE[3]✉

[1]*Zhejiang Key Laboratory of Industrial Solid Waste Thermal Hydrolysis Technology and Intelligent Equipment, Huzhou University, Huzhou 313000, China*
[2]*School of Engineering, Huzhou University, Huzhou 313000, China*
[3]*Stomatology Hospital, School of Stomatology, Zhejiang University School of Medicine, Zhejiang Provincial Clinical Research Center for Oral Diseases, Zhejiang Key Laboratory of Oral Biomedical, Zhejiang-Singapore International Joint Laboratory of Oral Bioengineering, Zhejiang Clinovation Pride, Hangzhou 310016, China*
[4]*State Key Laboratory of Fluid Power and Mechatronic Systems, School of Mechanical Engineering, Zhejiang University, Hangzhou 310058, China*

✉ Zhiyong MA, 02641@zjhu.edu.cn

Zhijian XIE, xzj66@zju.edu.cn

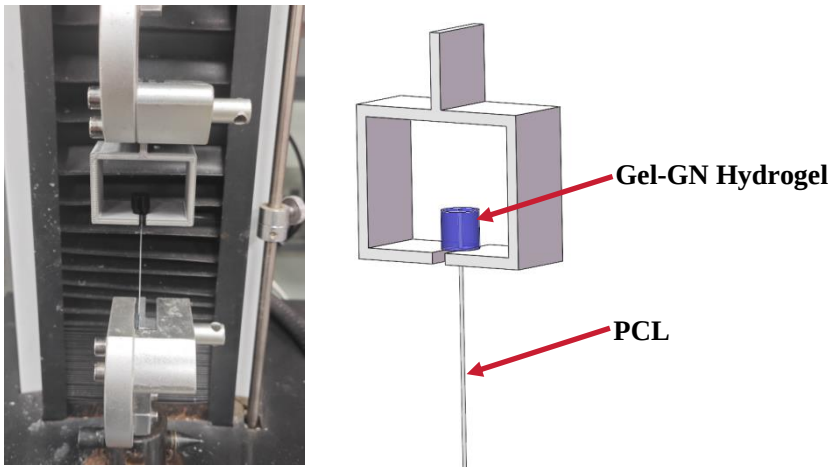

Fig. S1 Interfacial toughness test diagram

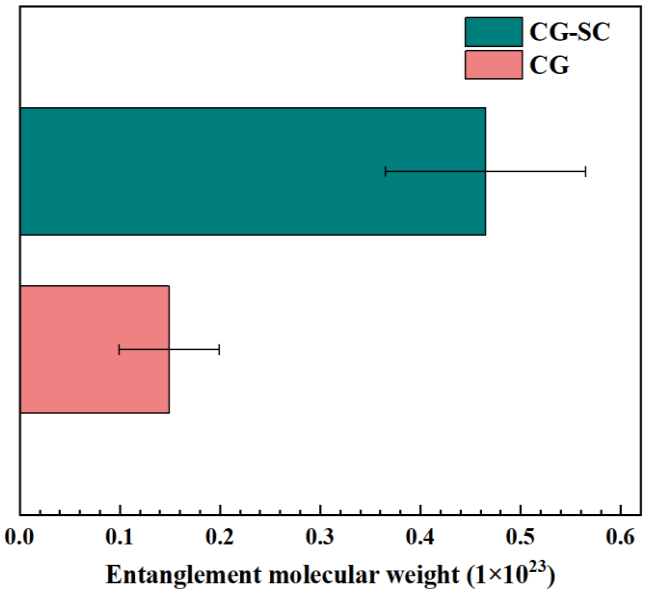

Fig. S2 Histogram of tangled molecular weight

The modulus G_e of the testing platform is the storage modulus at a frequency of 10^{-2} rad/s. The number density N of entangled chains is calculated using the formula:

$$G_e=\Phi_i N k_T$$

Φ_i is the volume fraction of the polymer in the dough, and k_T is the temperature in energy units.

The formula for calculating the entanglement molecular weight is:

$$Me=\rho N_A N^{-1}$$

where ρ is the density of the polymer, and N_A is Avogadro's number.

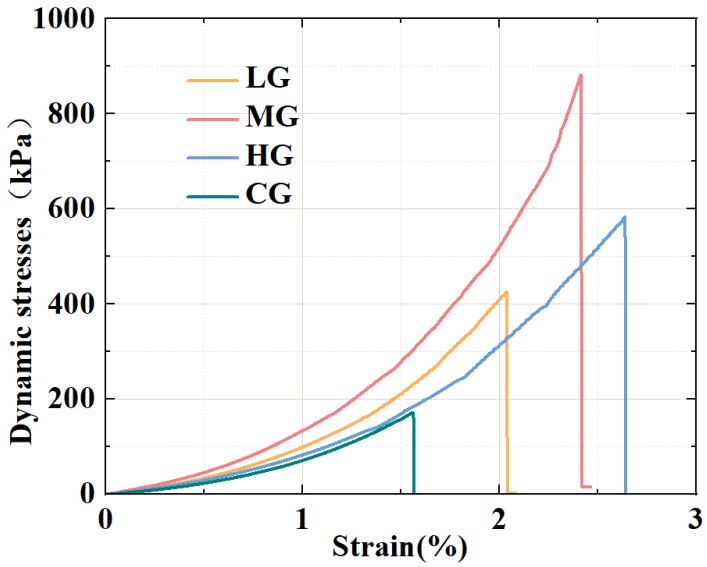

Fig. S3 Dynamic stresses of hydrogels of different compositions

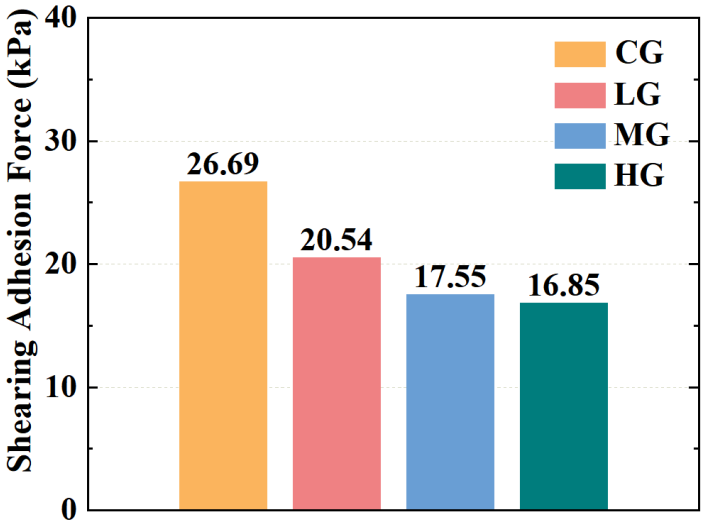

Fig. S4 Tangential adhesion of Gel-GN hydrogels

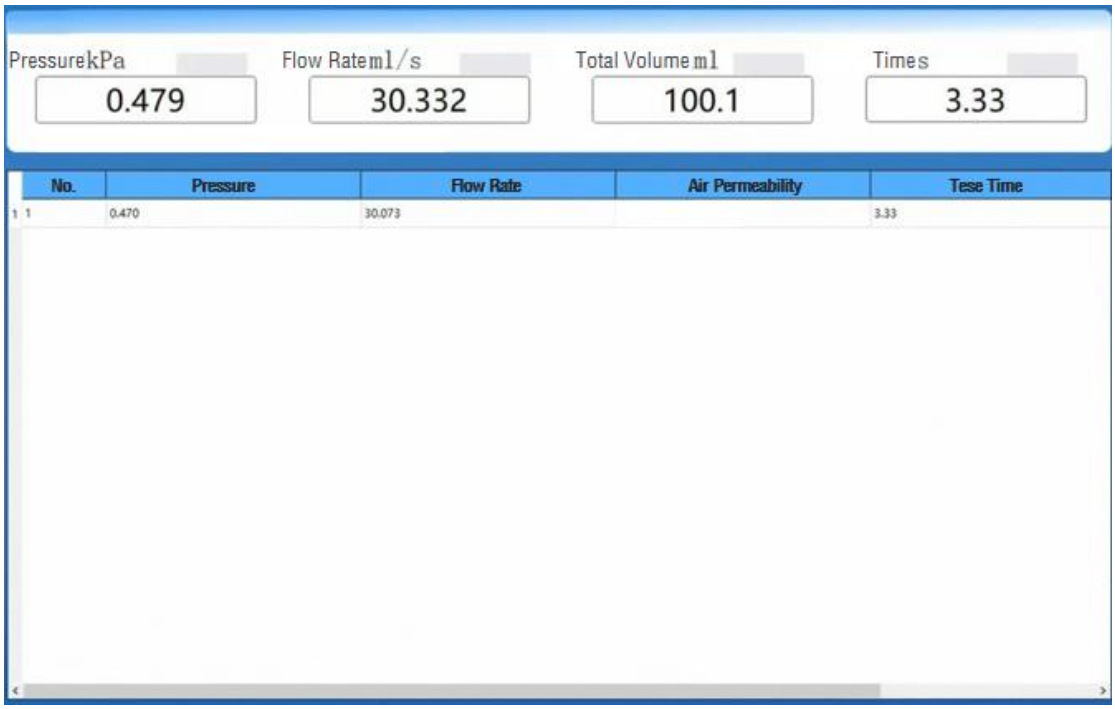

Fig. S5 SL layer Air permeability test

We prepared a 50×50 mm SL layer and measured its gas permeability using the pressure differential method. The measurement was conducted with a PAPT-B02 membrane air permeability tester, using air as the test gas. It can be observed that under a pressure of 0.479 kPa, a flow rate of 30 ml/s was achieved, demonstrating that the SL layer has excellent air permeability.

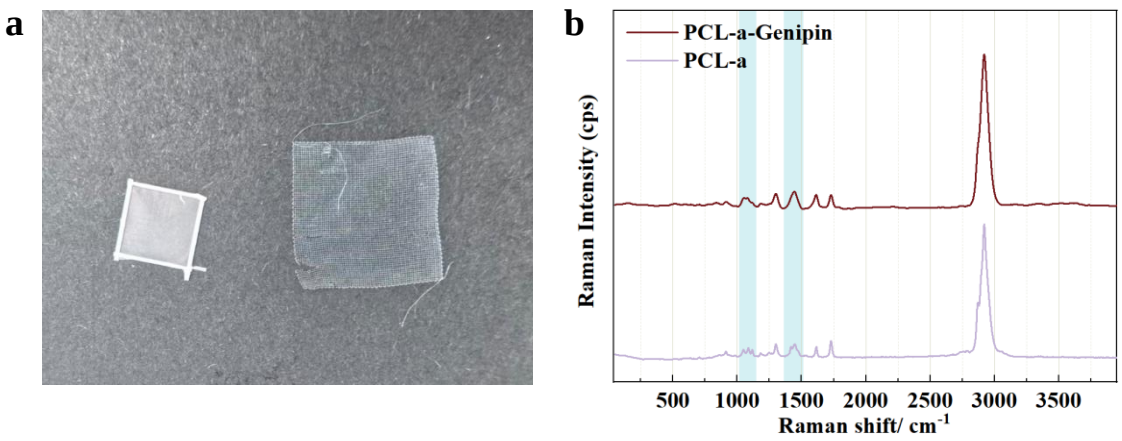

Fig. S6 Comparative illustration of PCL fiber surface amination and cross-linking with genipin. (a) Schematic diagram of the preparation process of SL and PL. (b) SEM morphology of SL and PL.

To verify the crosslinking reaction between genipin and aminated PCL (PCL-a), PCL-a samples were immersed in a 1% genipin solution at room temperature for 24 hours to ensure sufficient reaction. After removal, the samples were thoroughly rinsed with deionized water to eliminate surface residues, yielding the experimental group (PCL-a-Genipin) and the control group (PCL-a). Macroscopically, PCL-a-Genipin exhibited a distinct blue color, consistent with the characteristic coloration resulting from genipin crosslinking (Fig. S6a). Raman spectroscopy further confirmed the occurrence of surface crosslinking (Fig. S6b). After genipin treatment, the characteristic doublet peaks of PCL fibers at ~1417 cm^{-1} and ~1458 cm^{-1} merged into a broadened single peak. Specifically, the vibrational peak at ~1417 cm^{-1}, attributed to $-NH_3^+$, significantly weakened, indicating the consumption of surface amino groups. The sharp peak at ~1458 cm^{-1}, corresponding to the CH_2 bending vibration in the crystalline phase of PCL, broadened noticeably, suggesting that the ordered structure of the fiber surface was disrupted due to crosslinking. Additionally, in the C-O-C vibrational region between 1000–1150 cm^{-1}, the originally separated multiple peaks broadened and tended to merge, reflecting that the formation of the crosslinked layer restricted the motion of PCL molecular chains and introduced chemical heterogeneity. These spectral changes collectively demonstrate that an effective crosslinking reaction occurred between genipin and the surface of PCL-a.

Table S1 RT-PCR genes and primer sequences

Gene	Primer	Sequence (5' - 3')
Fn1	Forward	AGAGGCATAAGGTTCGGGAAGAGG
	Reverse	CGAGTCATCCGTAGGTTGGTTCAAG
ITGB	Forward	TGGGCTTTACGGAGGAAGTAGAGG
	Reverse	GACACTTGGGACTTTCAGGGATGC

VCL	Forward	GCTCTGCTGATGGCTGAGATGTC
	Reverse	GGCGATGTCCTTGGCACACTG
GAPDH	Forward	GCTCTCTGCTCCTCCTGTTC
	Reverse	GACTCCGACCTTCACCTTCC
α-SMA	Forward	GTCCCAGACATCAGGGAGTAA
	Reverse	TCGGATACTTCAGCGTCAGGA
Col I	Forward	TGGGGCAAGACAGTGATCG
	Reverse	GGAGGGAGTTTACAGGAAGCAG
Ki67	Forward	GGGCAGCTTCTACCAAGAGG
	Reverse	GCATCAACTTGGGGCTGG