Multifunctional 3D sponge-like macroporous cryogel-modified long carbon fiber reinforced polyetheretherketone implant with enhanced vascularization and osseointegration

Wenying Dong<sup>1</sup>, Wendi Ma<sup>1</sup>, Shanshan Zhao<sup>1</sup>, Xingyu Zhou<sup>1</sup>, Yilong Wang<sup>1</sup>,

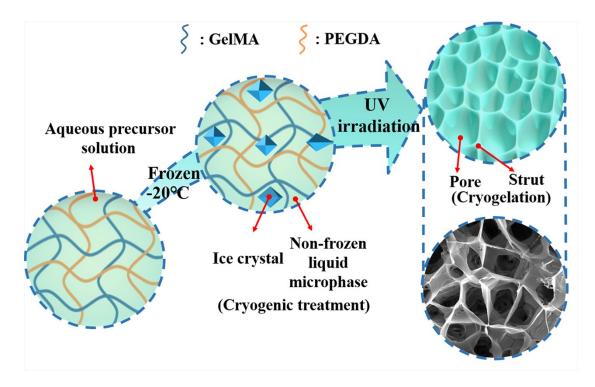
## Zhewen Liu<sup>2</sup>, Dahui Sun<sup>2</sup>, Mei Zhang<sup>1\*</sup>, Zhenhua Jiang<sup>1</sup>

1. Key Laboratory of High Performance Plastics, Ministry of Education, College of Chemistry, Jilin

University, Changchun 130012, P. R. China;

2. Norman Bethune First Hospital, Jilin University, Changchun 130021, P. R. China

\*Corresponding author: <u>zhangmei@jlu.edu.cn</u>



**Fig. S1.** Schematic depiction of the GelMA/PEGDA cryogel on the surface of the sulfonated LCFRPEEK formation.

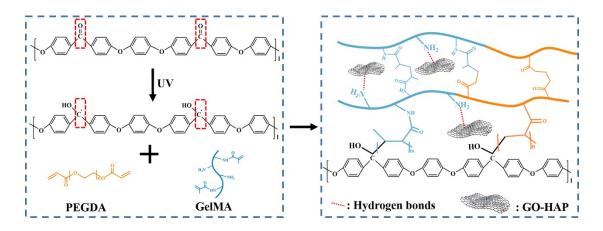
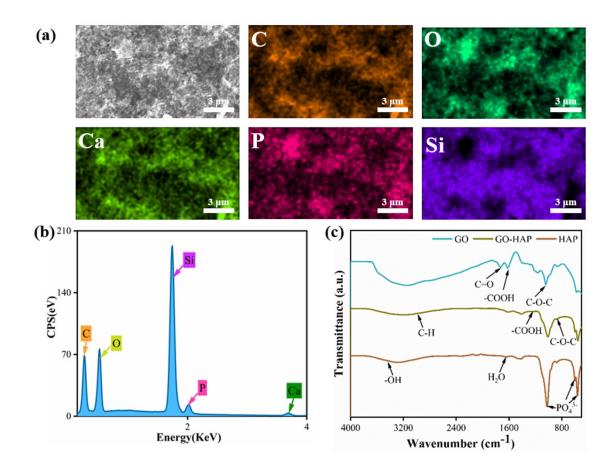
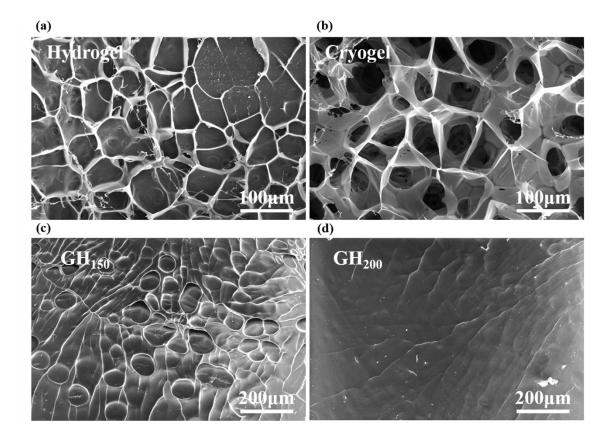


Fig. S2. Schematic illustration of the free radical polymerization on the surface of LCFRPEEK.



**Fig. S3.** (a) EDS images and (b) spectra of GO-HAP nanocomposite. (c) ATR-FTIR spectra of GO, HAP, and GO-HAP.



**Fig. S4.** (a) SEM images of GelMA/PEGDA hydrogel on the surface of sulfonated LCFRPEEK. [GelMA: PEGDA=10:5 wt%, the preparation method of GelMA/PEGDA hydrogel on the surface of sulfonated LCFRPEEK was similar to cryogel whereas without the freezing step.] (b) SEM images of GelMA/PEGDA cryogel on the surface of sulfonated LCFRPEEK. [GelMA: PEGDA=10:5 wt%] (c) SEM images of GH<sub>150</sub>. [The preparation of GH<sub>150</sub> was consistent with GH<sub>100</sub> whereas the concentrations of GO-HAP were 150 ng mL<sup>-1</sup>.] (d) SEM images of GO-HAP were 200 ng mL<sup>-1</sup>.]

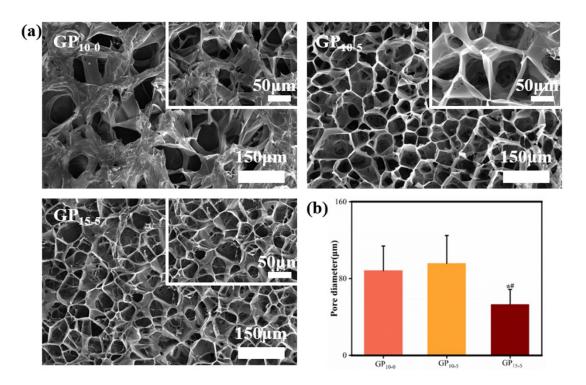
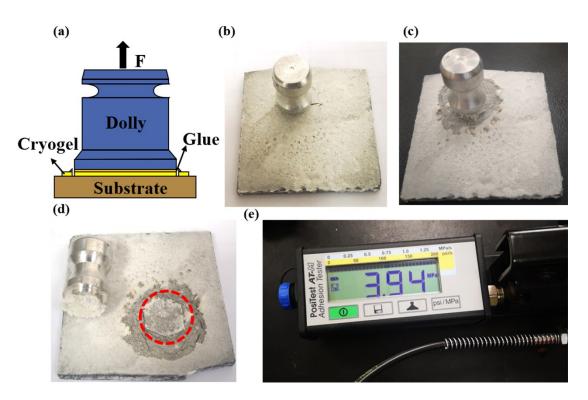


Fig. S5. (a) SEM images of: GP10-0, GP10-5 and GP15-5 at high and low magnifications. Scale bars = 50  $\mu$ m and 150  $\mu$ m. (b) The pore diameters of GP10-0, GP10-5 and GP15-5, \* and # represented p < 0.05 when compared with GP10-0 and GP10-5, respectively.



**Fig. S6.** (a) Diagram of the experimental device of the pull-off method. (b) Image of  $GP_{10-5}$  after adhering the dolly with epoxy glue. (c) Image of  $GP_{10-5}$  after cutting by the cutter. (d) Image of  $GP_{10-5}$  and the dolly after pull-off test. (e) Adhesion data of  $GP_{10-5}$ .

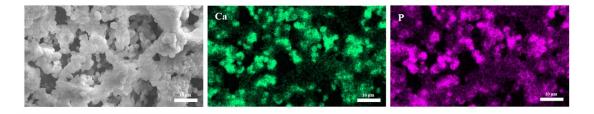


Fig. S7. EDS images of  $GH_{100}$  after soaking in SBF for 7 days. Scale bars = 10  $\mu$ m.

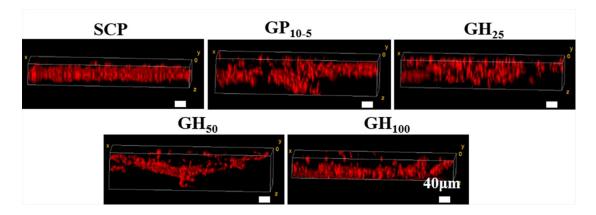


Fig. S8. Representative 3D CLSM images of HUVEC migration into different scaffolds stained using TRITC-phalloidin for cytoskeletal organization. Scale bars = 40 µm.

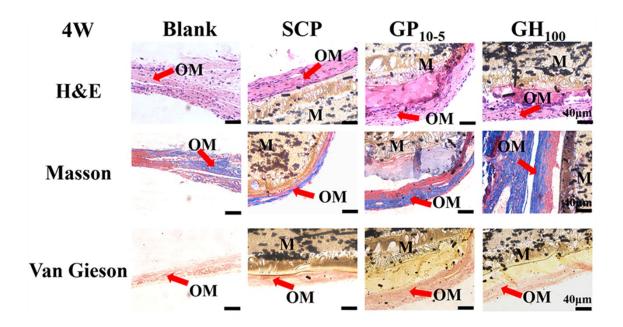


Fig. S9. H & E, Masson and Van Gieson staining of the calvarial defect regions after treatment with different samples for 4 weeks. Scale bars =  $40 \mu m$ . [M, Materials; OM, osteoid matrix (red arrows)].

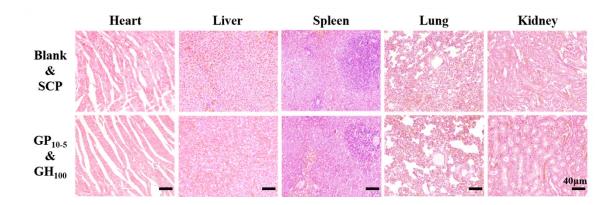


Fig. S10. Histological observation of H & E staining of tissues (heart, liver, spleen, lung, and kidney) after 12 weeks of treatments. Scale bar =  $40 \mu m$ .

Genes	Forward primer sequence (5'-3')	Reverse primer sequence (5'-3')
BMP-2	ATTAGCAGGTCTTTGCACCA	ACGCTTTTCTCGTTTGTGGA
Runx2	GGCAGCACGCTATTAAATCCA A	GACTCATCCATTCTGCCGCTA
ALP	ATCGGAACAACCTGACTGACC	CTGCCTCCTTCCACTAGCAA
COL-I	ATGCCATCAAGGTCTACTGCAA	GAACCTTCGCTTCCATACTCG
GAPDH	TATGACTCTACCCACGGCAAG	ATACTCAGCACCAGCATCACC

Table S1 Primer pairs used in RT-PCR analysis.

Material	C (%)	N (%)	O (%)	S (%)	Ca (%)	P (%)
SCP	58.84		40.06	1.09		
GP <sub>10-5</sub>	41.17	10.11	48.72			
$\mathrm{GH}_{100}$	44	12.46	40.97		1.6	0.96

 Table S2 Elemental composition of different substrate surfaces as determined by XPS.

Table S3 Changes in Ca and P content of  $GH_{100}$  sample before and after immersion in

## SBF by EDS.

Sample	Ca (%)	P (%)	Ca/P
Before immersion in SBF	1.6	0.96	1.67
After immersion in SBF	3.87	2.1	1.84
New bone-like apatite	2.27	1.14	1.99