

Electronic Supplementary Information

A shear-thinning adhesive hydrogel reinforced by photo-initiated crosslinking as a fit-to-shape tissue sealant

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The calculation process to determine the molar ratio of NH₂/CHO

Chitosan is a natural polymer comprised of N-acetylglucosamine and glucosamine. After maleic modification, the degree substitution (DS) of MCS is around 0.455 and the deacetylation degree of chitosan is about 80%. Thus, the quantity ratio of maleic modified glucosamine (relative molecular weight is 259), glucosamine (relative molecular weight is 161) and N-acetylglucosamine (relative molecular weight is 203) was 4.55 : 3.45 : 2. On one hand, there are 3.45 free amino groups of glucosamine in every 10 sugar rings, and the relative molecular weight of these 10 sugar rings is 2139.9 (259×4.55 + 161×3.45 + 203×2). On the other hand, there are 2 benzaldehyde groups per one PEGDF_{4k} molecule (relative molecular weight is 4264). Therefore, the molar ratio between amines and aldehyde can be determined by adjusting the mass ratio between MCS and PEGDF. For example, if the molar ratio of NH₂/CHO = 1, the mass ratio between MCS and PEGDF was about 1 : 3.44 ((2139.9/3.45×2) / 4264). Thus, if the molar ratio of NH₂/CHO was determined as 1 and the concentration of MSC was set as 0.5% w/v, the concentration of PEGDF_{4k} could be calculated as 1.72% w/v. The detailed contents of MCS and PEGDF_{4k} was shown in Table S1 below.

Supplementary Figure

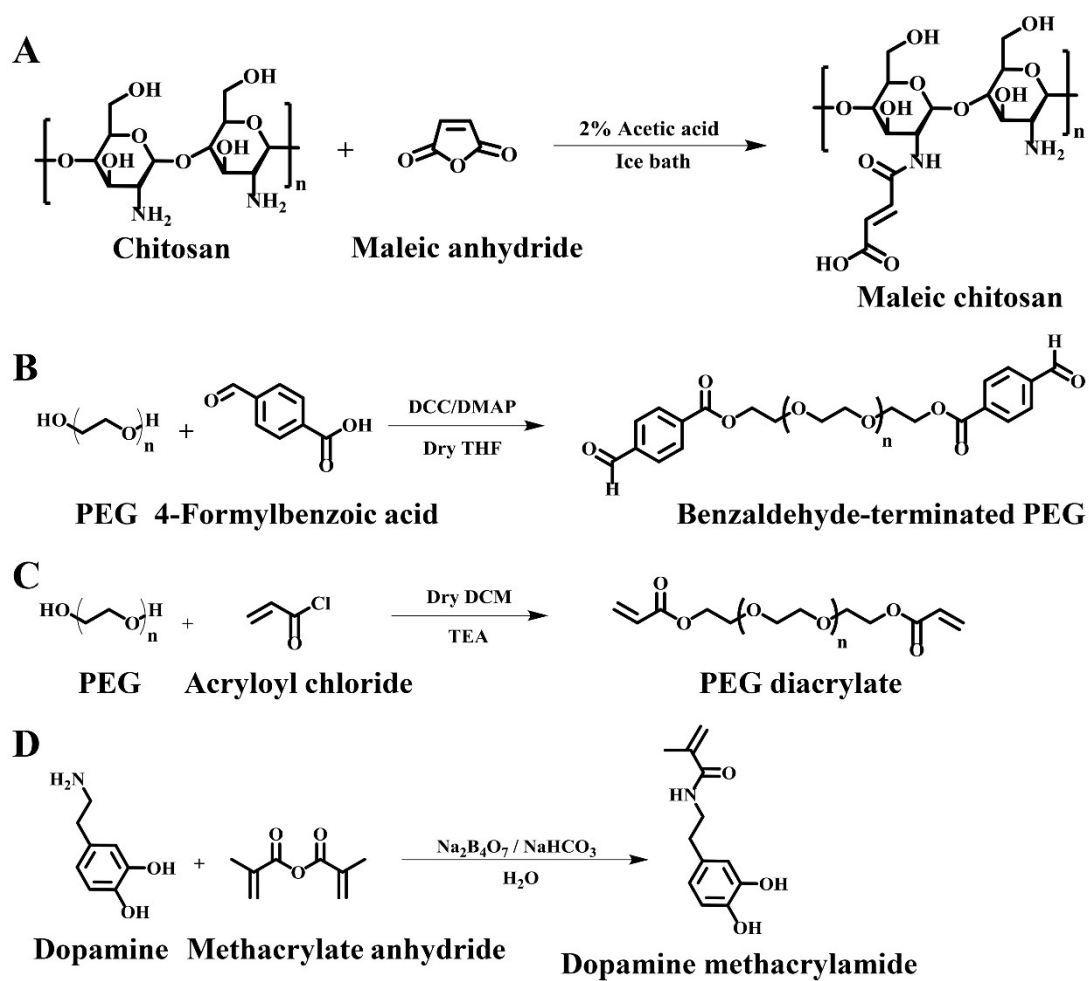


Figure S1. The synthesis scheme of MCS, PEGDF, PEGDA and DMA

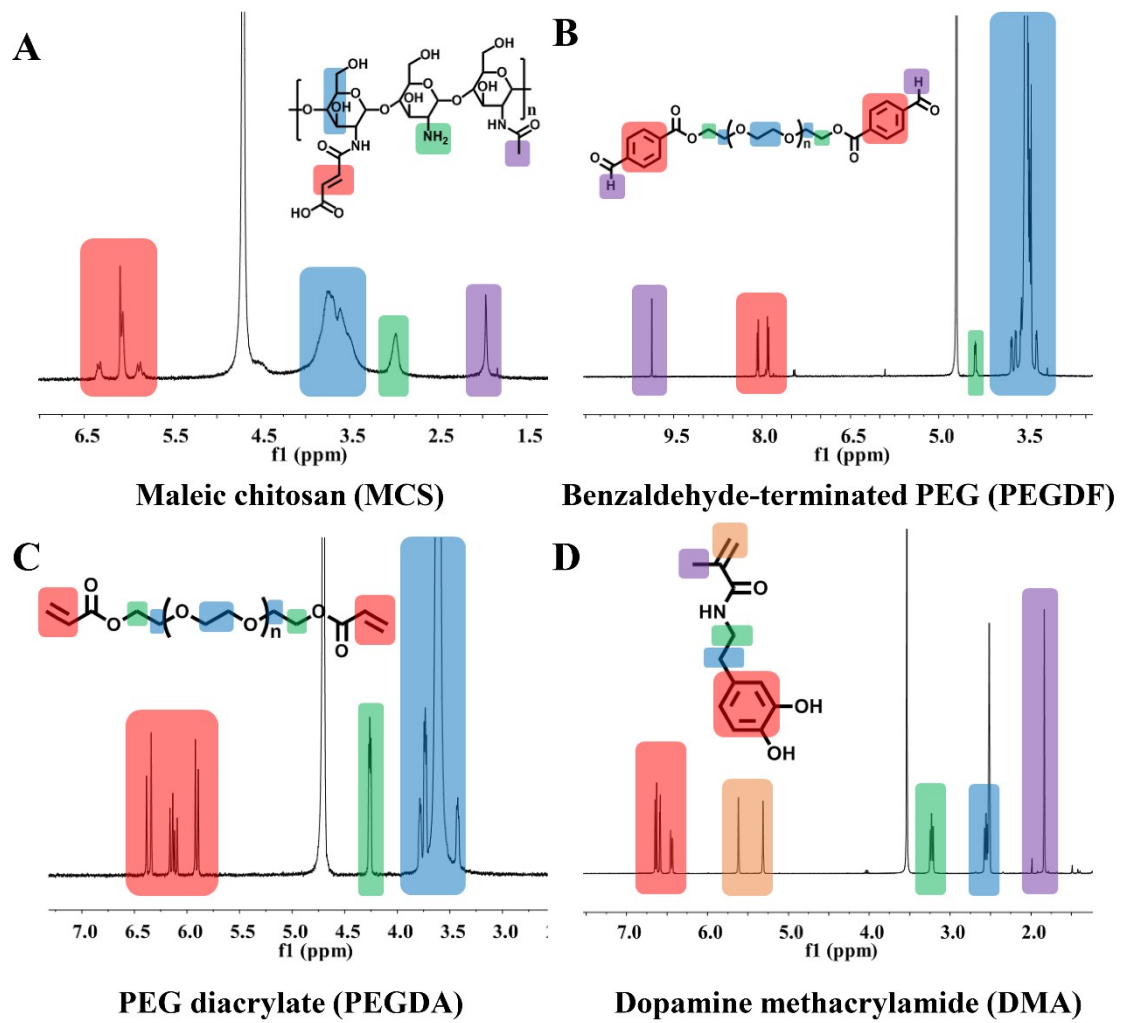


Figure S2. The NMR spectrum of MCS, PEGDF, PEGDA and DMA.

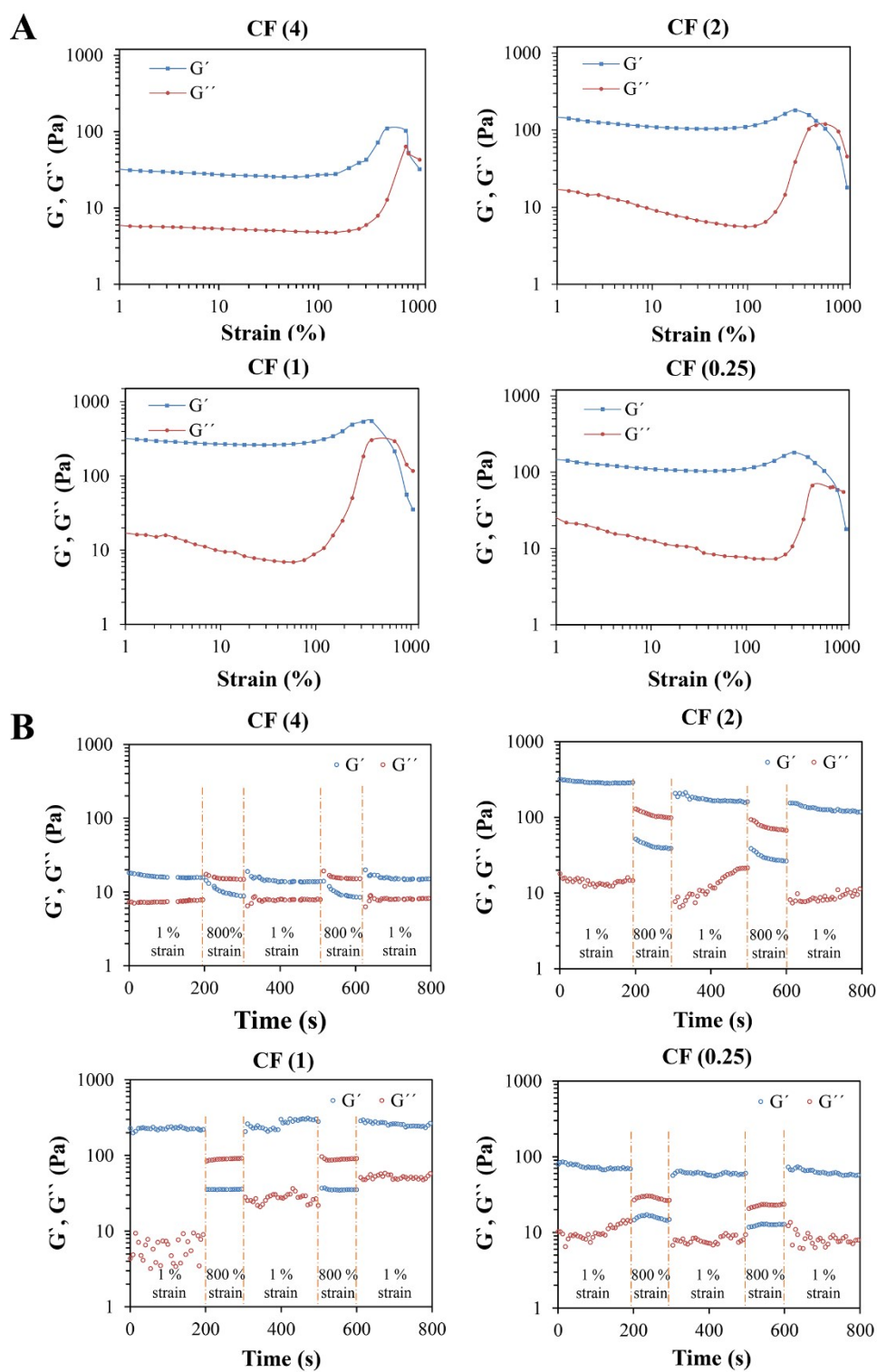


Figure S3. Rheological properties of CF gels. A) G' and G'' of CF gels with different ratios between amino and benzaldehyde on strain amplitude sweep ($\gamma = 1\%–1000\%$) at a fixed angular frequency (10 rad/s). B) Cyclic G' and G'' of different CF gels for small strain ($\gamma = 1\%$) and large strain ($\gamma = 800\%$) with different loading time of 200 and 100 s, respectively.

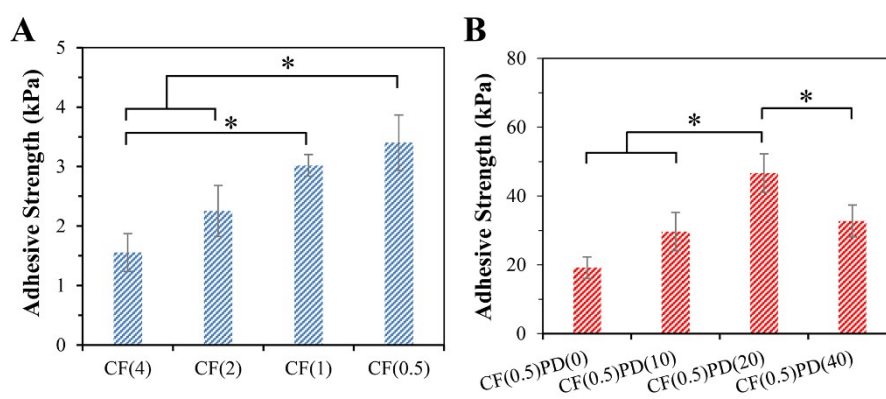


Figure S4. The adhesive strength of different hydrogels. A) The adhesive strength of different CF gels with different ratio between amino group and benzaldehyde group (* represent $p < 0.05$). B) The adhesive strength of CFPD gels with different amounts of DMA (* represent $p < 0.05$).

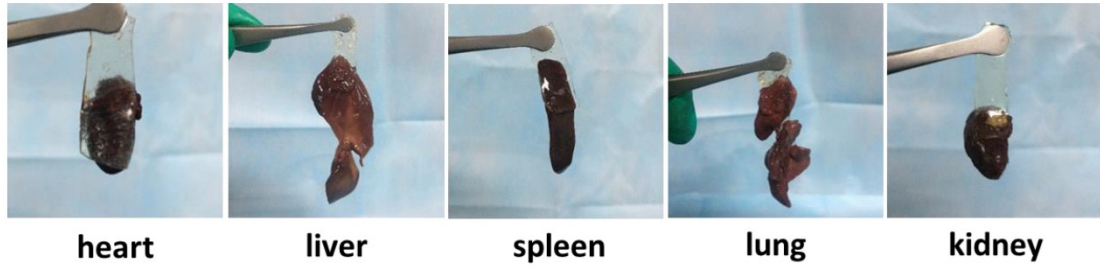


Figure S5. The bioadhesion of CF(0.5)PD(20) gel to different soft organs.

Supplementary Table

Table S1. The gelation time of CF hydrogels at room temperature with different concentrations and ratio between amino group of MCS and benzaldehyde group of PEGDF.

| Sample | CS-MAH (w/v %) | PEGDF (w/v %) | Molar ratio of NH ₂ /CHO | Gelation time (second) |
|-------------------------|-------------------|------------------|--|---------------------------|
| CF(1)-0.5 ^{a)} | 0.5 | 1.72 | 1:1 | ~ 200 |
| CF(1)-0.75 | 0.75 | 2.58 | 1:1 | ~ 95 |
| CF (1)-1.0 | 1.0 | 3.44 | 1:1 | ~ 45 |
| CF(1)-1.5 | 1.5 | 5.16 | 1:1 | ~ 10 |
| CF(4)-0.75 | 0.75 | 0.645 | 4:1 | ~ 190 |
| CF(2)-0.75 | 0.75 | 1.29 | 2:1 | ~ 145 |
| CF(0.5)-0.75 | 0.75 | 5.16 | 0.5:1 | ~ 55 |
| CF(0.25)-0.75 | 0.75 | 10.32 | 0.25:1 | ~ 70 |

a) Taking CF (1)-0.5 as an example, (1) means the ratio between amino and benzaldehyde was 1, and the concentration of MCS was 0.5% w/v.

Table S2. The adhesive strength of different hydrogels and fibrin glue

| Sample | Adhesive strength (kPa) |
|---------------|--------------------------------|
| CF(0.5) | 3.40 ± 0.47 |
| CF(0.5)PD(0) | 23.35 ± 3.6 |
| CF(0.5)PD(20) | 46.6 ± 5.6 |
| Fibrin glue | 4.84 ± 0.89 |