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

Supporting Information

for

Diffusion-Reaction Models of Genipin Incorporation into Fibrin Networks

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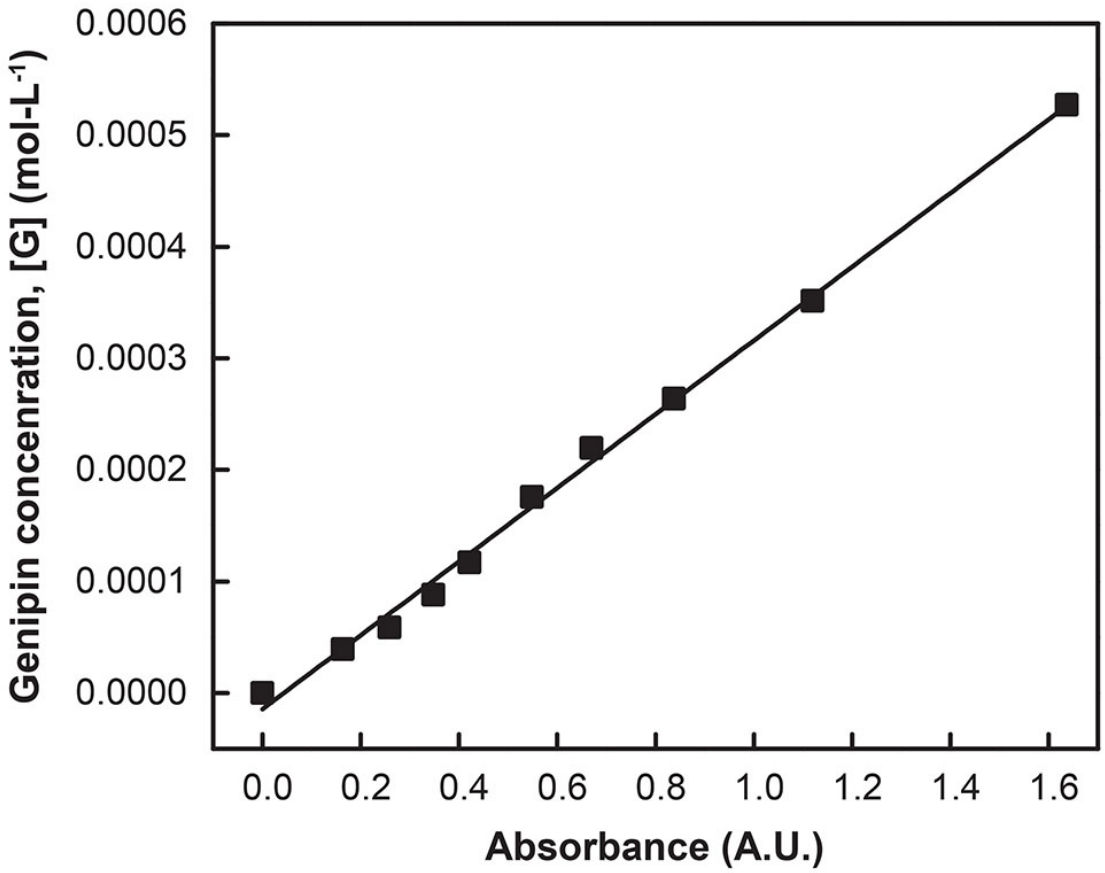

Figure S1. Standard curve relating absorbance at λ_{Abs} = 240 nm to the genipin concentration. The fit is used to determine the concentration of genipin at different time points during reaction of genipin with ethyelene diamine.

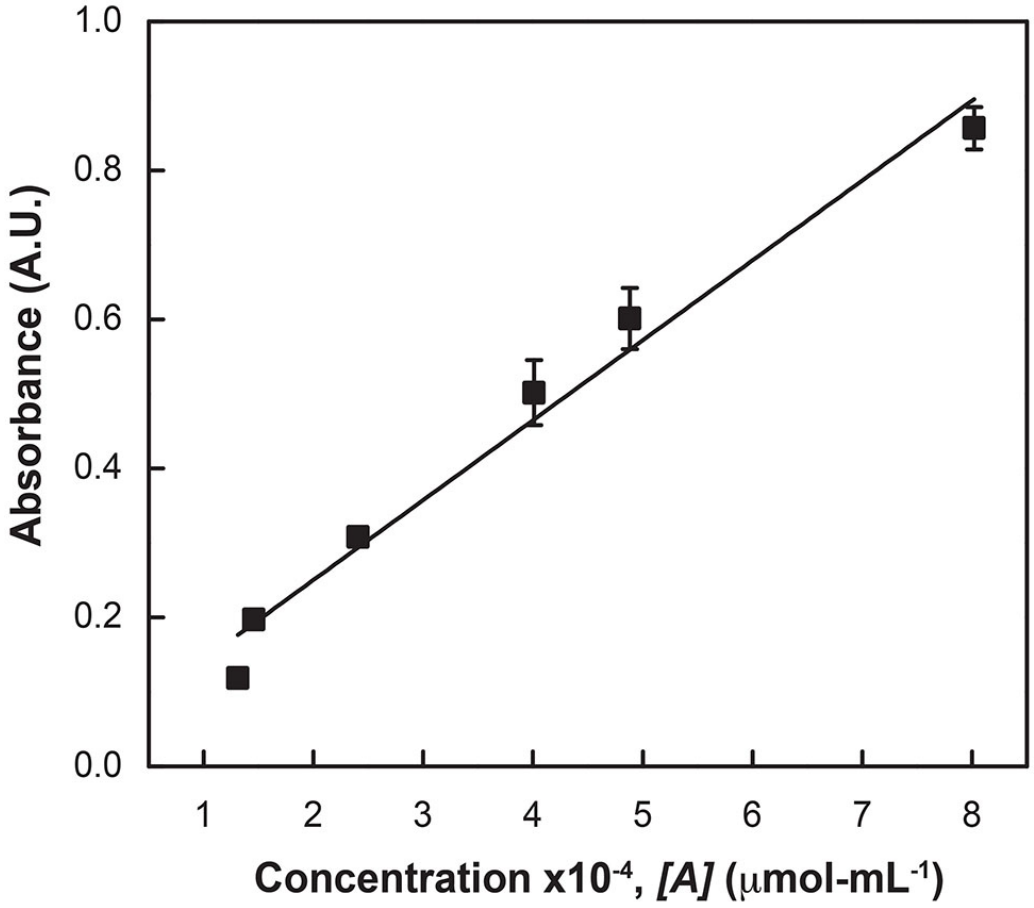

Figure S2. Standard curve relating absorbance at λ_{Abs} = 570 nm to concentration of primary amine groups using tyramine.

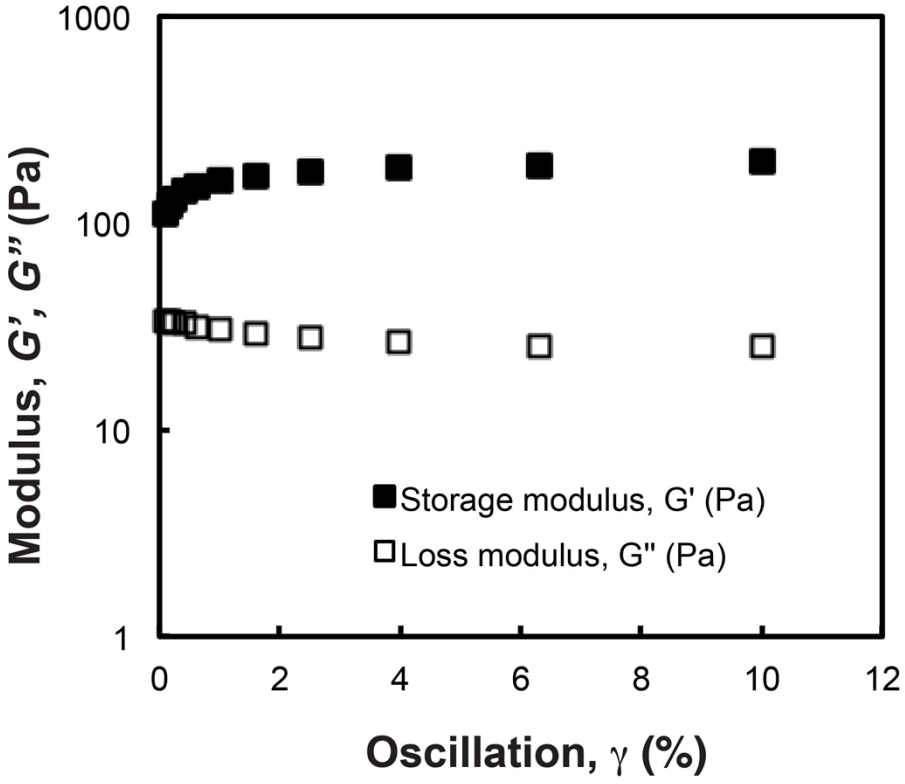

Figure S3. Amplitude sweep of fibrin gels from γ = 0.1% to 10%. Frequency sweeps were conducted from ω = 0.1—10 rad-s^{-1} using a strain amplitude of γ = 2% for subsequent characterization to ensure viscoelastic region (See Text).

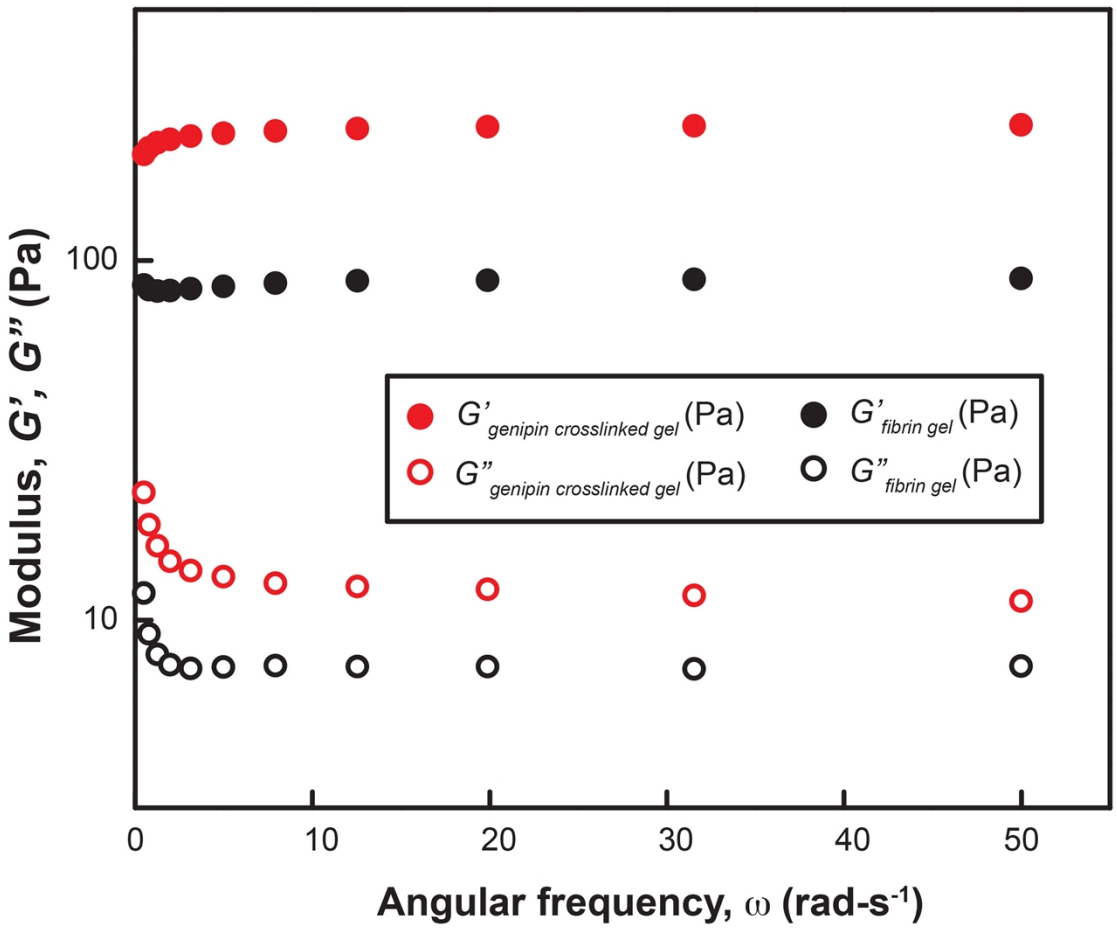

Figure S4. Frequency sweep of fibrin hydrogel and fibrin hydrogel incubated in genipin solution for 24 hours at 37 ^{0}C using a strain amplitude of γ = 2%.

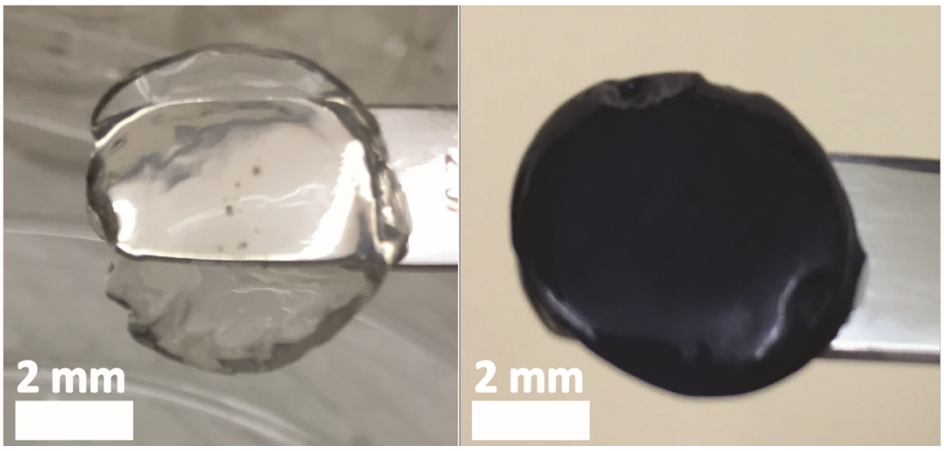

Figure S5. Macroscale images of the pristine fibrin gel (left) and genipin-crosslinked fibrin gel (right).

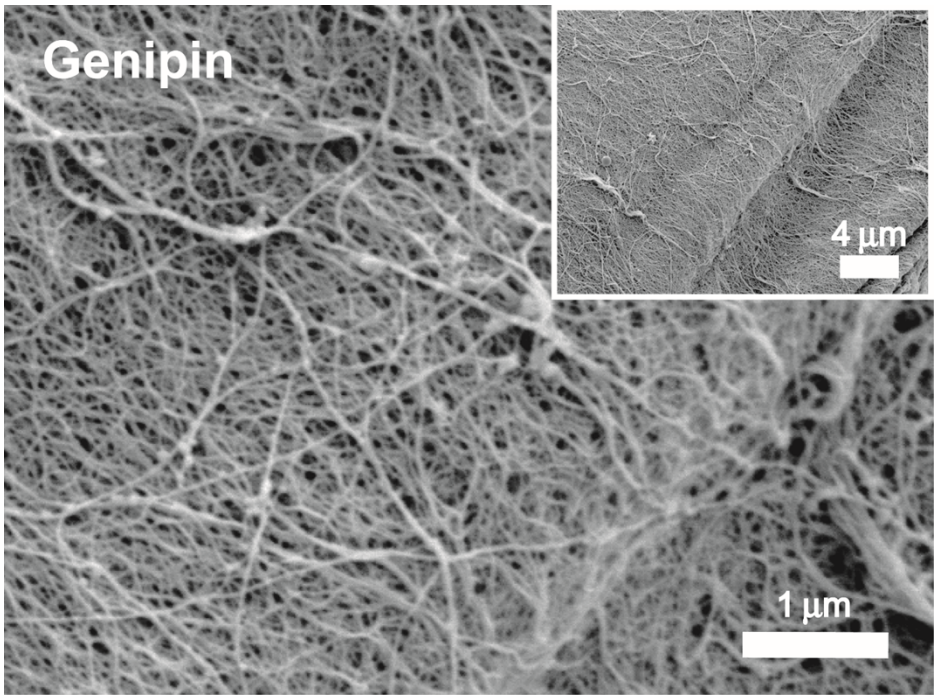

Figure S6. Scanning electron micrograph depicting morphology of genipin-crosslinked fibrin gel.

Detailed Analysis for Time Evolution of Genipin Concentrations (Figure 10)

Predicted time profile of genipin concentration within hypothetical fibrin networks ($[G]_{fibrin}$) is illustrated in Figure 10 for different genipin:PLGA loadings ($m_{genipin-PLGA,t_\infty}$) using previously determined kinetics data. The hypothetical fibrin network was taken as a cylindrical reactor with radius of 7.95 mm and height of 1 mm. Eqn. 5 was used to interpolate the total mass of genipin released into fibrin network at each time point with step time Δt = 1 hr. The concentration of genipin supplied to fibrin networks from the PLGA network (mol-mm^{-3}) ($[G]_{PLGA}$) was determined knowing the molecular weight of genipin (226.2 mg-mol^{-1}), and the volume of the fibrin reaction (calculated as 198.45 mm^3).

The concentration of genipin within fibrin networks ($[G]_{fibrin}$) at t = n +1 (n is an integer from 0 to 400 hr) is a function of the concentration of genipin supplied from PLGA networks and the concentration of genipin consumed by reaction with amines within fibrin networks, i.e.

$$[G]_{fibrin,t=n+1} = [G]_{PLGA,t=n+1} + ([G]_{PLGA,t=n} - [G]_{rxn,t=n})$$

The concentration of genipin consumed was predicted from the reaction kinetics (Eqn. 7) in mol-mm^{-3}h^{-1}

$$-\frac{d[G]}{dt} = 1.116[G]^2[A]^{1.4}$$

Integration of Eqn. 7 gives the relationship to determine $[G]_{rxn,t=n}$ as

$$[G]_{rxn,t=n} = \frac{[G]_{t=n-1}}{1+1.116\Delta t[A]^{1.4}_{t=n-1}}$$

$[G]_{t=0}$ was set as 0 mol-mm^{-3} and $[A]_{t=0}$ was measured using the ninhydrin assay as 1.99 mol-mm^{-3} (See Text). The concentration of amines $[A]_{t=n}$ was predicted by assuming that every mole of reacted genipin consumes one mole of amines via the following relationship:

$$[A]_{t=n} = [A]_{t=n-1} - [G]_{rxn,t=n-1}$$