Solutions to Soft Matter exercise, Chapter 7: Gels

1. Sol-gel process

Sol: A sol is a solution or dispersion that behaves like a liquid (G''>G')
Gel: A gel is a percolating network of polymers or colloids that displays an elastic behavior. Hence, a gel behaves as a solid (G' > G'').

2. Gel

a. Probably the best choice would be a covalently linked, biocompatible hydrogel. Covalent linkages ensure that the shape of the hydrogel is maintained even if it is repetitively sheared. The entrapped water ensures moistening of the wound (maintenance of a high moisture level). The hydrogel must be biocompatible and ideally, it should act as a barrier for bacteria or other infectious specimen because the skin, which typically is the protective layer, is partially destroyed.
b. A material that displays a very good biocompatibility and is highly hydrated is poly(ethylene glycol), PEG, that has at least two functional groups that can form bonds with neighbors, such as acrylates or methacrylates.
c. The hydrogel swells due to differences in osmotic pressures. Inside the hydrogel, the monomer concentration, and very often also the ion concentration is much higher than outside the gel. Hence, water diffuses into the hydrogel.
d. With the choice of the monomers hydrogels are made from: The mechanical properties of hydrogels strongly depend on the crosslinking density (the molecular weight of the chains between two adjacent crosslinks, number of functional groups). The higher the crosslinking density, the stiffer the gel and the lower is the degree of hydration (less water is incorporated in the gel per unit volume).

3. Percolating network

a. The most efficient way to form a percolating network within a few generations is to use monomers with as many chemically reactive groups as possible. For example, monomers with 4 reactive groups easily form percolating networks.
b. To determine if we form a percolating network at any point, we determine the percolation threshold as

$$f_c = \frac{1}{z-1} = \frac{1}{4-1} = \frac{1}{3}$$

In this case, f_c is smaller than 0.4 such that we form a percolating network.
The number of bonds formed, N, in the nth generation can be described as $N \approx \left[f(z-1)\right]^n$ ➔

$$n = \frac{\log N}{\log\left(f(z-1)\right)} = \frac{\log 1000}{\log\left(0.4(4-1)\right)} \approx 38$$

c. In this case, $f < f_c$=1 such that we will never form a percolating network.

d. The rigidity is inversely proportional to the molecular weight between two crosslinking points ($G = \frac{\rho RT}{M_x}$). To increase the shear modulus, the crosslink density must be increased. This can for example be achieved by taking trifunctional low molecular weight monomers (or monomers with four or more reactive groups).

4. Crosslink rate

a. A sol transitions into a gel if the degree of reaction, f, is equal to the percolation threshold, f_c. Hence, to determine the time needed for $f = f_c$, we determine f_c using:

$$f_c = \frac{1}{z-1} = \frac{1}{2}$$

To determine the time, the equation given in the exercise must be integrated

$$\frac{df}{(1-f)^2} = kdt$$

By integrating the two sites we obtain

$$\frac{1}{1-f} = kt + A$$

For $t = 0$ we must have $f = 0$ such that $A = 1$

Hence, we find

$$t = \frac{\frac{1}{1-f} - 1}{k} = \frac{\frac{1}{1-\frac{1}{2}} - 1}{k} = \frac{1}{4 \times 10^{-4} s^{-1}} = 2500s \approx 42\ min$$

b. From the text, we know $f = 0.75$

Using the equation derived for (a), one finds

$$t = \frac{\frac{1}{1-f} - 1}{k} = \frac{\frac{1}{1-\frac{3}{4}} - 1}{k} = \frac{3}{4 \times 10^{-4} s^{-1}} = 7500s \approx 2.1h$$

c. The probability that a site is connected to the percolation network is $P = 1 - Q$, where Q is the probability that a site is not connected to the percolating network.

From the text we know that $P = 0.75$

Q is the probability that a site is not connected to its neighbors ($1-f$) plus the probability that the site is connected to one of its neighbors but that this neighbor is not connected to the percolating network ($fQ^{(3-1)}$). Hence we obtain

$$Q = 1 - f + fQ^2$$

we can re-write this equation as

$$f\left(Q^2 - 1\right) = Q - 1$$

$$f = \frac{Q-1}{Q^2-1}$$

with
$Q = 1 - P = 1 - 0.75 = 0.25$
we find
$$f = \frac{Q-1}{Q^2-1} = \frac{0.25-1}{0.25^2-1} = 0.8$$
Using the equation derived for (a) one finds
$$t = \frac{\frac{1}{1-f} - 1}{k} = \frac{\frac{1}{1-0.8} - 1}{k} = \frac{4}{4 \times 10^{-4} s^{-1}} = 10000s \approx 2.8h$$

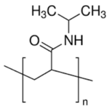
5. Self-healing hydrogels

a. The hydrogel should be crosslinked using ionic bonds because they form reversibly, thereby imparting self-healing properties to the hydrogel.
b. One should increase the relaxation time of the hydrogel. This can be done by choosing a chelator-ion pair with a higher complexation constant and thus longer relaxation times. Alternatively, larger crosslinking agents that can bind more chelators per crosslinking agent can be employed. For example, if ions are re-placed by nanoparticles, relaxation times are significantly increased because it takes much longer to simultaneously break multiple bonds (which is required for the hydrogel to flow) than it takes to break a single bond or, as is the case for conventional chelators, to simultaneously break two bonds.
c. The relaxation time is the time over which a hydrogel relaxes stress and is directly related to the dissipation time of the ion-chelator pair used to crosslink hydrogels. Weak ionic bonds have short relaxation times, strong ionic bonds have long relaxation times.
d. The relaxation time is coupled to the transition from a gel to a sol behavior. One can use oscillatory rheology to determine G' and G'' as a function of the shear rate. The shear rate where G'' ≈ G' is the inverse time scale where a sol transitions into a gel.

Working principle of oscillatory rheology: One applies a sinoidal stress and measures the response of the material. If the material is perfectly elastic, there is no lag between the stress and the material response. If the material is viscoelastic, there is a lag of its response to the stress that is caused by its viscous behavior (the energy dissipation). By analyzing the lag in the material response, δ, one can determine the ratio between the loss and the storage modulus and by knowing the shear rate at which δ is measured, one can deduce G' and G'' using the following equations:
$$\tan\delta = \frac{G^{II}}{G^{I}}$$
$$\sigma = \sigma_0^{I}\sin(\omega t) + \sigma_0^{II}\cos(\omega t)$$
$$G^{I} = \frac{\sigma_0^{I}}{\gamma_0}$$
$$G^{II} = \frac{\sigma_0^{II}}{\gamma_0}$$

6. Thermo-responsive polymers

The chemical structure of a repeat unit of PNIPAM is



PNIPAM has a lower critical solution temperature (LCST). Hence it is swollen at T < LCST and collapsed at T > LCST.

At T < LCST: H-bonds between the NH group of PNIPAM and water can form and hence, PNIPAM is hydrated (surrounded by water molecules). The system maximizes entropy.
At T > LCST: The H-bonds become weaker relative to the thermal energy. At T > LCST, H-bonds are broken and the system maximizes the enthalpy by minimizing the contacts of water molecules with PNIPAM. Hence, PNIPAM collapses.