

2. Case II diffusion: The rate of penetrant diffusion is higher than the relaxation rate of polymer chains. This case is characterized by a mass solvent uptake that is proportional to the time, $Q \sim t$. All that results in a continuous renewable interface between the swollen hydrogel region and the internal not hydrated polymer network (glassy core). This interface moves continuously from the external region to the internal core as the solvent uptake proceeds till to the formation of a fully swollen hydrogel. Generally, more a hydrogel is crosslinked, lower its water uptake is. The absorption process in highly crosslinked hydrogels resembles that occurring for metal mesh. It works like a single diffusion process as the high crosslink density limits polymer chain movement.
3. Case III or anomalous diffusion: Both rates are comparable, $Q \sim t^a$. The exponent of the time dependence amounts between 0.5 and 1.

We must admit a lot of papers discussed this topic and other mathematical formulas were used too, but here we emphasized the different factors regulating the rate of the swelling process in a simple schematic way.

Mechanism of Dehydration

As in the swelling process, the de-swelling mechanism occurs through three different steps, the loss of free water, the loss of interstitial water and at last and only partially the loss of the bound water (Barbucci and Pasqui 2013; Okano 1998) (Fig. 21).

The de-swelling process provokes dehydration with a consequent shrinking of the hydrogel even if complete removal of water molecules doesn't ever occur. By heating

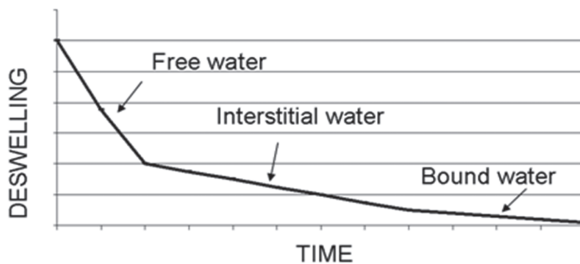


Fig. 21. Typical deswelling of hydrogel versus time graph.

or lyophilizing the hydrogel a further reduction of volume occurs for the further loss of the solvent, mainly from the interstitial and bound layers.

Free water evaporates first from the hydrogel, the interstitial water then begins to evaporate, and the hydrogel transforms into an intermediate state between that of a gel and a glass. When the water content is reduced to less than a boundary level, the hydrogel transforms into a glassy state, with a trace of bound water remaining in the dried polymer. The relative amount of the three types of water varies according