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Relationship between swelling and mechanical properties of cross-linked polymers mixed with sand

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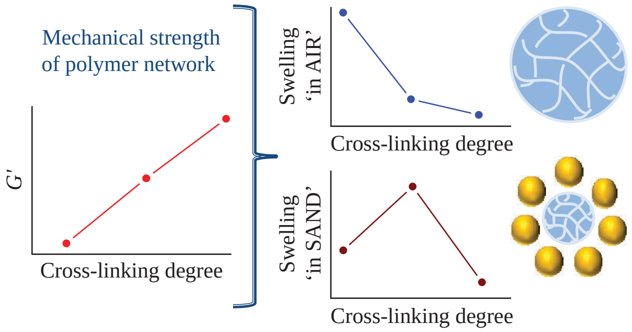
Cross-linked polymers consisting of acrylamide, sodium acrylate, starch fragments and a cross-linker were synthesized with the same content of carboxyl groups and three degrees of cross-linking *Q* of 0.04, 0.2 and 1 wt%. An increase in *Q* gradually reduces the swelling of polymer gels in water; when distributed in sand, polymer gels exhibit maximum swelling at *Q* = 0.2 wt%. It is shown that the behavior of polymer gels in sand is determined by the balance between the elasticity of swollen polymer gels and the resistance of sand particles.



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Weakly cross-linked hydrogels are soft materials consisting of a hydrophilic polymer network and an aqueous solution absorbed by the polymer matrix.[1,2] Due to the unique ability to hold a huge amount of water, hundreds of times greater than the weight of dry cross-linked polymers, hydrogels have found application in agriculture and crop production.[1–3] It has been shown that the superabsorbent capacity of weakly cross-linked network polymers is related not only to the nature of the (co)monomer units, but also to the degree of cross-linking.[4–6] In the non-swollen state, network subchains form compact structures (coils or globules), which, after swelling, straighten as much as possible, thereby significantly increasing the volume of the polymer network.[4]

Most of the works are devoted to the behavior of hydrogels in the free state without external mechanical influences;[5–7] in that case, the degree of swelling of the gel increases with a decrease in the content of the cross-linking agent. However, the question arises of gel swelling when a dry polymer is deposited in soil and forced to swell under mechanical resistance from soil particles.[8–11] This situation is typical for agriculture, when a dry cross-linked polymer is applied to the soil.[8–11] For this reason, the study of the swelling of hydrogel granules in a matrix formed by solid particles has become increasingly important.[12,13]

In this report, we discuss the correlation between the water swelling of granulated anionic cross-linked polymers (ACPs) before and after mixing with sand and the cross-linker content of the polymers. We also demonstrate that swelling is directly related to the mechanical properties of hydrogels.

ACPs were synthesized from acrylamide, sodium acrylate, starch fragments and *N*,*N*′-methylenebisacrylamide as a cross-linking agent according to the procedure described previously.[8] The mechanism of the process[14] involves the formation of radical sites along the polysaccharide chain, followed by graft polymerization of co-monomer/cross-linker mixtures. The quantitative yields of the copolymers[8] made it possible to draw a conclusion about the degree of cross-linking (*Q*) of the synthesized ACPs: the *Q* value was 0.04, 0.2 and 1 wt% for ACP-1, ACP-2 and ACP-3, respectively. The degree of cross-linking is a key parameter of the polymer gels studied in this work. The content of carboxyl groups in the ACPs, which is the same for all copolymers, was quantitatively determined by potentiometric titration[8] and amounted to $(6.4 \pm 0,1) \times 10^{-3}$ mol per 1 g of each ACP.

When added to 0.001 M phosphate buffer solution with pH 6.5, ACPs swell and form transparent hydrogels. The degree of swelling of ACPs (α), that is, the ratio of the weight of absorbed water to the weight of the initial dry polymer, depending on the value of *Q*, is shown in Figure 1 (bars labeled *1*) (for the quantification

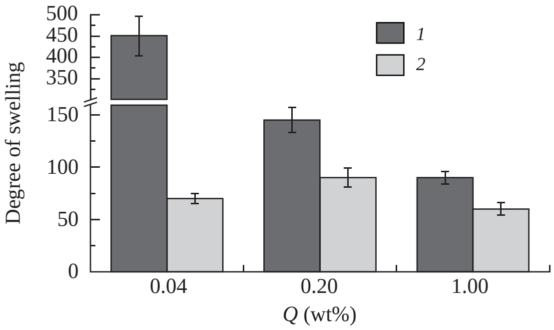

Figure 1 The degree of swelling (α or α_{lim}) of the copolymers in 0.001 M phosphate buffer depending on the degree of cross-linking of the copolymers in the case of (*1*) free absorption in the absence of sand or (*2*) limited absorption in the presence of sand.

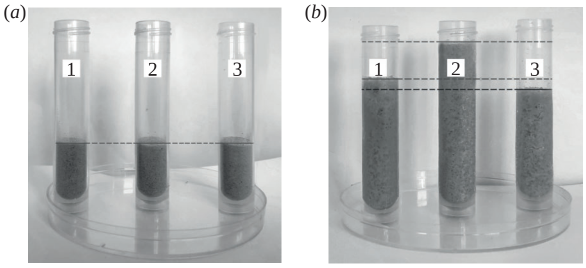

Figure 2 Images of sand mixed with network copolymers (*1*) ACP-1, (*2*) ACP-2 and (*3*) ACP-3, (*a*) before and (*b*) after swelling of the copolymers in 0.001 M phosphate buffer at pH 6.5.

protocol for Q, see Online Supplementary Materials). It is expected that in the absence of external mechanical forces, the swelling of the gel increases with decreasing Q. ACP-1 with the lowest $Q = 0.04$ wt% shows the highest value of $\alpha = 450 \pm 47$, for ACP-2 with an intermediate $Q = 0.2$ wt%, the value of α is 145 ± 12, and for ACP-3 with $Q = 1$ wt%, α is only 90 ± 6. This effect demonstrates the relationship between the swelling of the gel and the degree of its cross-linking, which correlates with published data.[5,6]

After that, dry polymers and sand were thoroughly mixed and the buffer solution was added. It was expected that in the absence of physicochemical interactions between the components, the polymers distributed in sand are able to absorb the same amount of water as in the case of free absorption in the absence of sand. In reality, the behavior of polymers in the limited pore space of sand was different. Primarily, the swelling did not reach the values typical for free swelling. The value of α_{lim} in the presence of sand decreased compared to the value of α in the absence of sand and amounted to 70 ± 5 for ACP-1, 90 ± 9 for ACP-2 and 69 ± 6 for ACP-3 (Figure 1, bars labeled *2*). The most remarkable thing in the histogram is the maximum at $Q = 0.2$ wt%, which was not observed during the swelling of polymers in the absence of sand. Most likely, the observed phenomenon reflects the mechanical resistance of the sand particles, which does not allow the hydrogel to absorb water beyond a certain amount.

Different mechanical properties of hydrogels with varying degrees of cross-linking could be observed even visually. In a related experiment, mixtures of these dry polymers with sand were placed in plastic tubes, where they formed columns of the same height [Figure 2(*a*)]. The addition of water to the mixtures caused the polymers to swell and increase the height of all three columns [Figure 2(*b*)]. The highest column was observed for ACP-2 according to the data presented in Figure 1 (bars labeled *2*).

It is known that the elasticity of swollen polymer networks reflects their ability to resist deformations caused by external forces, on the one hand, and restrict the straightening of polymer chains, on the other.[9] To quantify the elasticity of the network, rheological studies of the ultimately swollen hydrogels were carried out using a rotary rheometer (see Online Supplementary Materials). The values of the storage modulus G' and the loss modulus G'' depending on the angular frequency of shear vibrations are shown in Figure 3. For each sample, the frequency dependences of the G' and G'' values are parallel, and the G' values are always higher than the G'' values. These data indicate that all three networks with different degrees of cross-linking behave like viscoelastic bodies. The ACP-1 hydrogel with a minimum $Q = 0.04$ wt% showed a rather low storage modulus $G' = 25$ Pa (Figure 3, curve *1*). The increase in Q is accompanied by a sharp rise in the value of G' up to 6 kPa for ACP-2 with $Q = 0.2$ wt% and 11 kPa for ACP-3 with $Q = 1$ wt%. Since the storage modulus characterizes the elastic mechanical energy of the sample, these results reflect an increase in the elastic response of the polymer network to an external force with an increase in the degree of cross-linking, which is in good agreement with the theory.[9]

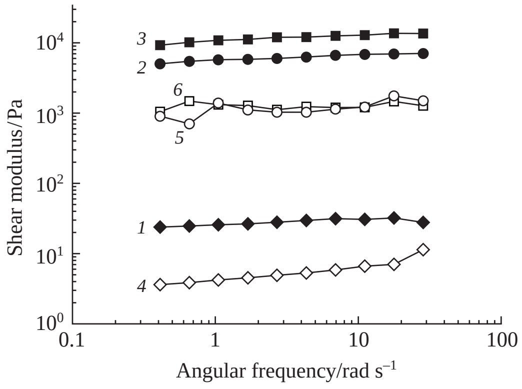

Figure 3 Dependences of (*1*)–(*3*) storage modulus G' and (*4*)–(*6*) loss modulus G'' on the angular frequency of shear oscillations for (*1*),(*4*) ACP-1, (*2*),(*5*) ACP-2 and (*3*),(*6*) ACP-3 hydrogels.

Comparison of data on swelling and rheology of the polymer gel for two cases, in the absence and presence of sand, allows us to draw the following conclusions. In the first case, swelling is determined only by the degree of cross-linking: the higher Q, the lower α. This is due to the fact that the length of polymer subchains in the network decreases with increasing Q. Also, an increase in Q stimulates a rise in the elastic modulus G', which reflects the higher resistance of polymer chains to straightening.

Mixing polymers with sand radically changes the situation. Now the dependence of α_{lim} on Q has a maximum at $Q = 0.2$ wt%. Obviously, under conditions of limited pore space, swelling is determined by the balance between the mechanical strength of the swollen polymer and the resistance from the sand particles. The ACP-2 and ACP-3 hydrogels have sufficient strength to push sand particles apart and fill the interpore space. However, in these cases, the pressure exerted by the sand particles is significant and restricts the spread of the hydrogel. As a result, the α values for both polymers mixed with sand decrease compared to those for polymers swollen in the absence of sand, while $\alpha_{\text{lim}} = 90$ for ACP-2 remains higher than $\alpha_{\text{lim}} = 69$ for ACP-3 (see Figure 1). The most dramatic situation is observed for the hydrogel obtained from the polymer with $Q = 0.04$ wt%; its mechanical strength is too low due to sparse cross-linking and cannot compete with mechanically strong sand. This leads to a catastrophic loss of swelling for ACP-1 in a polymer/sand mixture and the appearance of a maximum at $Q = 0.2$ wt% on the plot of α *vs.* Q (see Figure 1, bars labeled *2*).

In summary, in the absence of external forces, the cross-linked polymers swell in water according to the traditional scheme: swelling increases as the degree of cross-linking Q decreases. In a mixture with sand, polymer swelling is described by a bell-shaped ‘swelling *vs.* Q’ plot. This behavior reflects the combination of a falling ‘swelling *vs.* Q’ plot and an increasing ‘mechanical elasticity *vs.* Q’ plot, which eventually results in a maximum for $Q = 0.2$ wt%.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.01.025.

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