

Zhansaya Sadakbayeva: Microstructure, swelling and deformation behavior of methacrylate hydrogels with interpenetrating network structure

Synthetic polymer hydrogels are very promising materials for medicinal applications. Compact and porous hydrogels with chemical structure of interpenetrating networks are prepared and studied in presented work.

The thesis structure is classical. Theoretical part (Chapter 1) gives a look into IPN hydrogels formation, their chemical structure and microstructure, swelling and deformation behaviour of swollen gels, and applications in biomedicine. The chapter is the excellent overview about IPNs hydrogels with rich bibliography.

Chapter 2 introduces aims and the scope of the thesis. Sample preparation procedures and techniques used for structure study and mechanical properties evaluation are described in Chapter 3, Experimental part. The description of these is clear and concise.

Results and their discussion are summarised in Chapter 4, divided into 5 sections, briefly introduced as Scope (Chapter 2). The chapter structuring helps reader to orient himself in large amount of results and it also helps the author to focus discussion on results belonging to the same nature. However, not only experimental results are in the chapter. Theoretical background of swelling and elasticity of single network presented in chapter 1 (part 1.8) is extended to IPN in part 5.3.

Some additional information to that can be found in Chapter 6, Appendices. Chapter 5 "Conclusions" summarises all main results.

I have a few questions to applicant or topics for discussion:

- Terms *micro-* (< 2nm), *meso-* (2 – 50 nm) or *macrosize* (> 50 nm) are used for classification of porous hydrogels (p. 29) according to pore size. However, the size of all categories is in order of nm. What is reason for that? (It is not "compatible" with today's popular "nano" terminology.)
- Chapter 3.6.1, Tensile test (page 59).
 - How did you measure deformation of specimen central part?
 - What was reason for so low grip velocity of 10 $\mu\text{m/s}$? (If specimen deformation would proceed only in 8 mm long central part, for $\lambda = 3$ it requires grip displacement 16 mm \equiv 1600 s. Technical standards recommend time to break around 60 s.)
 - Mistakes in Equations 3.11 and 3.12. The first mistake (incorrect: $strain = 100 \times \frac{L - L_i}{L}$
 \rightarrow correct: $strain = 100 \times \frac{L - L_i}{L_i}$) one can consider as a typing error, but no the second one (Incorrect: $\sigma_{true} = (\lambda - 1) \sigma_{break} \rightarrow$ correct: $\sigma_{true} = \lambda \sigma_{break}$). From that reason true strength data S_b and the product $S_b Q_v$ values in Table 13 (p. 126) are not correct. (True strength is always higher than "engineering strength" due to cross-section decrease when specimen stretched.) Nevertheless the validity of discussion on p. 124 – 126 referring to these parameters remains.

- The crossover of G' and G'' [133] or the time at which G' starts to be higher than G'' [135] is used in many reports and also in this work as the criterion of gel point, e.g. in the Fig. 30 (p. 77). However, in the Fig. 31 (p. 78) $G' > G''$ is also at the beginning, not only at the end of network forming. It means none or two (or even number) crossovers. What is your explanation of that? The gel point is the first or the second cross?
- Why the graph in the Fig. 48 (p. 101) starts from 0? In the similar graph (Fig. 49, p. 102) it starts (more logically) from 1?
- Positive effect of crosslink density on modulus of elasticity is well known. Similarly, the increase of crosslink density (but up to certain level only) results in higher tensile strength. From that viewpoint, increased crosslink density is logical explanation of higher tensile strength of IPN (page 117). It is easy to imagine that for IPNs with higher crosslinker levels in network 2 creation. However, what is a reason for increased crosslink density of IPN of two loosely crosslinked networks (e.g. H0/0.2–H0.0, the example given on the same page) compare to single network H0/0.2? Could be additional entanglements resulting from interlocking of both networks responsible for the increase? Can you estimate that contribution?
- The lower capacity of homogeneous IPN hydrogels to absorb water is discussed (p. 119 + Fig. 55) due to assumed higher density of crosslinked chains in IPNs than single networks. Do you expect higher total crosslink density of IPN when compare e.g. H40/6 and H40/6–H0/0? What do you think about the effect of pre-stretched network 1 on degree of swelling (= water absorption)? Can you comment that in point of view thermodynamic background given in chap. 5.3.1?

Conclusion

The applicant obtained new experimental results and demonstrated good orientation in the field of preparation of polymer materials, their structure determination and relation with properties. Zhansaya Sadakbayeva proved her capability of scientific research work and writing research report, which fulfills all requirements for doctoral thesis. I recommend the thesis to defense and Ms. Zhansaya Sadakbayeva to be awarded with the Ph.D. degree.

In Prague, 16th March 2018

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