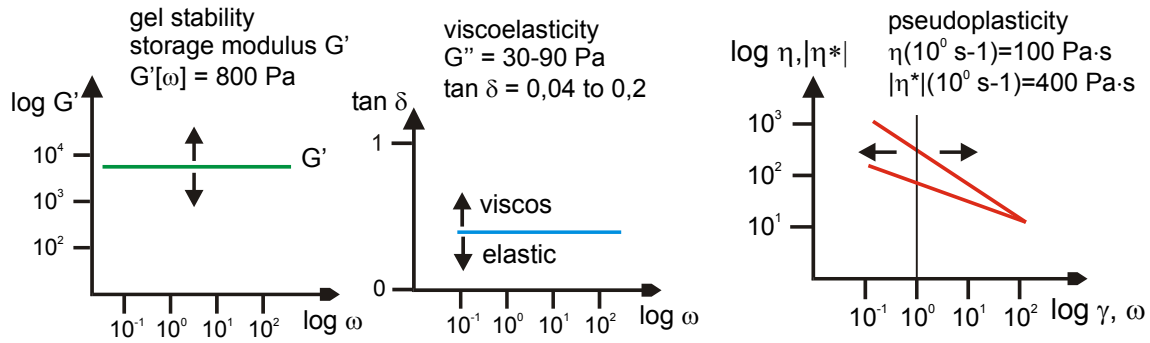


Summary

Gels based on chemically linked polymer networks which are water-swellaable, are called hydrogels. They are used in a wide range of foodstuffs and in technological and medical applications. For these different areas of use, it is necessary to modify the characteristic traits such as stability, swellability and elasticity. For example superabsorbers have an absorption capacity of over a 1000 times of their own solid content in salt-free solutions. Contact lenses on the other hand have only a very limited swellability, but show a high elasticity and stability. The characteristic traits can be specifically tuned through differences in the synthesis of the used polymers.

In the project "Ultrasonic gels based on starch" from the Fachagentur Nachwachsende Rohstoffe e.V. (FNR), hydrogels were synthesized with the specification that the ecological and toxicological problems of the conventional petrochemical ultrasonic gels were to be avoided. These hydrogels using starch and starch derivatives were synthesized in the workgroup of Prof. Dr. M. D. Lechner of the University of Osnabrück and by CHP Carbohydrate Pirna. These hydrogels were rheologically characterized and the ideal viscoelastic properties for the use as ultrasonic gels were adjusted. In the course of these tests, general insights into the synthesis and the flow behaviour of hydrogels based on starch were won and can be transferred to other areas of use.

In the beginning, the benchmarks for the ultrasonic gels were gained from examining the conventional petrochemical hydrogels. Thus the following benchmarks were determined at a frequency resp. shear velocity of 1 s^{-1} . For the gel stability a storage modulus of 800 Pa, for the viscoelastic properties a loss factor of $\tan \delta = 0,04$ to $0,2$, for the shear viscosity a value of $100 \text{ Pa}\times\text{s}$ and a oscillatory viscosity of $400 \text{ Pa}\times\text{s}$ were determined.



Rheological Benchmarks for the ultrasonic gels

At first hydrogels were synthesized through cross-linking using polyfunctional carboxylic acids (Malic-, Tartaric-, Citric-, Malonic-, Succinic-, Glutaric-, and Adipic Acid) from carboxymethyl starch (CMS; DS = 0,45). These esterified carboxymethyl starch hydrogels were then rheologically characterized using dynamic oscillatory measurements, where the storage and loss modules (G' , G'') and the complex oscillatory viscosity $|\eta^*|$ in dependance of the frequency ω were of particular interest. From measurements of the plateau region storage modulus G'_p , the network parameters molar mass between two entanglement points M_e (M_e ranging from 9.318 to 281.397 $\text{g}\cdot\text{mol}^{-1}$), cross-link density ν_e and the distance between two entanglement points ξ were calculated. Flow curves, which were recorded for the comparison between the complex oscillatory viscosity $|\eta^*|$ and the shear viscosity η using the Cox-Merz rule, showed a pseudo-plastic flow behaviour for all CMS-hydrogels.

In conclusion it can be seen that the different polyfunctional carbon acids have a strong influence on the sturdiness of the synthesized CMS-Hydrogels. The different cross-linking agents permit the modulation of a wide spectrum of different gel sturdiness and viscoelastic properties according to the requirements of the later application of the gel. Thus citric acid forms the strongest, while tartaric acid forms the weakest gels. Using carbon acids without functional groups, a maximum in gel sturdiness is found at a spacer length of two CH_2 -groups, otherwise no significant differences were found. The problem was that as expected the esterified gels showed a reduced long-term stability due to hydrolysis. With these products an on-site fabrication could be a possibility.

For this reason all further hydrogels were synthesized using an etherification. The majority of the starchbased gels were produced using Dichloroacetic acid (DCA) as a

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crosslinking agent and Monochloroacetic acid (MCA) as a substituent, to make the starch more hydrophilic. In order to tailor each hydrogel to its area of use, extensive knowledge of the synthesis is needed. Thus the basic synthesis was modified in the important details, so that the effect of the variations on the hydrogels could be studied.

The varied parameters were reaction time, reaction temperature, the amount of washing, the ratio of DCA to MCA on the reaction, incorporation of preservatives and the amount of starch and water in the reaction batch. Furthermore washed and unwashed samples of the gels with different starch content in the reaction were produced and characterized. These gels were characterized using turbidity measurements, swelling experiments and oscillatory measurements. From measurements of the plateau region storage modulus G'_p the network parameters molar mass between two entanglement points M_e , cross-link density ν_e and the distance between two entanglement points ξ were calculated for the samples.

The samples with a varied amount of starch in the reaction batch proved to have the best concurrence with the benchmarks. The DS values and the turbidity go up with a decreasing amount of starch and the free swelling capacity goes up with an increased amount of starch in the batch. Thus the variation of the amount of starch in the batch shows that the amount of crosslinks goes up with an increased amount of starch. The swellability is reduced and the concentration to form a stable hydrogel is increased. The gel 160501 in the concentration of 5 mass-% with an amount of 12,5% starch in the reaction shows the best results when compared to the benchmarks of gelling time, gel stability and viscoelastic and pseudoplastic behaviour. The long-term stability that was measured using temperature cycle tests and the gel 160501 showed a high durability. The ultrasonic examinations by a medical doctor and the data from the toxicological tests showed that this gel is suitable for the use as an ultrasonic gel.