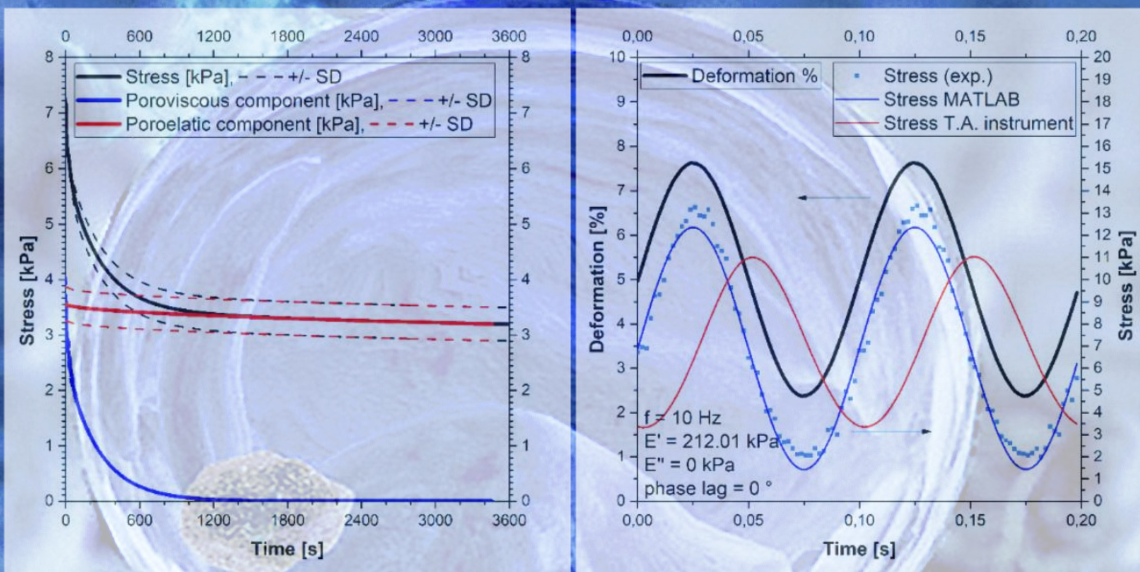
Characterization of poroviscoelasticity of hydrogels



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Characterization of poroviscoelasticity of hydrogels
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Department of Industrial Engineering

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Characterization of poroviscoelasticity of hydrogels

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Summary

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Abstract

Hydrogels are three-dimensional hydrated network formed by hydrophilic polymers. Hydrogels are used in different fields and their applicability requires an in-dept knowledge of their behavior and therefore a characterization of their poroviscoelasticity. Viscoelasticity is linked to the local rearrangement of the polymer chains maintaining a constant volume and it is essential in all the applications in which it is required a simple adaptability of the structure. Poroelasticity is essentially related to the transportation of small molecules or solvent, it is responsible both of the swelling and of the shrinking of the hydrogels and it is important for all the applications in which the transportation of specific molecules is the key factor.
In this thesis it is developed and used a methodology able to distinguish between the poroelastic and the viscoelastic effects.

The method, developed in a linear region both for stress-relaxation test and creep test, is based on the separation of the viscoelastic effect, linked to a variation in shear modulus, from the poroelastic effect, linked to a variation in Poisson's coefficient. In particular it was demonstrated that the variation of the Poisson's coefficient during the tests, can be described with a power law equation (which is in turn the solution of the diffusion equation) whose parameters can be safely derived from just two experimental points. Once the Poisson's coefficient variation is known, the generalized Maxwell's model or the generalized Kelvin-Voigt's model, respectively for the stress-relaxation test and for the creep test, can be used as models to evaluate the viscoelastic parameters of the hydrogels.

In the experimental part of this thesis, the used techniques to characterize the poroviscoelastic behavior of agarose hydrogels are the

dynamical mechanical analysis (DMA), the stress-relaxation tests and the creep tests.
From the DMA technique it has been possible to characterize only the viscoelastic behavior of hydrogels. In particular, in the analyzed range, the viscoelastic relaxation is not complete and therefore a part of the theoretically dissipable energy is still present in the gel and in particular it is still considered as stored energy for which it is incorporated in the values of the storage modulus.
With the stress-relaxation test it has been possible to characterize both the viscoelasticity and the poroelasticity of hydrogels in a frequency range wider than that of the DMA and realizing two weights (at the beginning and at the end of the test) the Poisson's coefficient has been obtained. With the used duration of the stress-relaxation test has been possible to explain all the viscous relaxation obtaining a complete description and separation of the lost and stored energy.
In the case of the creep test it has been also possible to characterize both the poroelastic and the viscoelastic behavior of hydrogels, but in this case the duration of the creep test it was not sufficient to describe all the viscous effect. Moreover, since with this technique the strain is not controlled, it should be considered the possibility to have a high strain, therefore overcoming the linear region.

In conclusion, analyzing the different techniques, it is possible to affirm that dynamic mechanical analysis has different disadvantages in terms of a small range of analysis (due to the inertia of the probe), determining an incomplete evaluation of the viscoelastic behavior, in terms of time consumed due to the presence of a dead time during the change from one specimen to another and in the end also in terms of the impossibility to describe the poroelastic effect. For completeness, it should be considered that since the rheometry is the equivalent shear dynamic technique, all the disadvantages described for the axial DMA are also the same that are present in rotational. Creep and stress-relaxation tests are theoretically both capable to overcome these limitations however, for the creep test, a further observation about the maintenance of the linear regime is required.
Considering these results, the stress-relaxation technique can be considered the best one to perform a complete poroviscoelastic characterization of hydrogels.

Riassunto

Gli idrogel sono strutture idratate e tridimensionali formate da polimeri idrofili. Gli idrogel sono utilizzati in diversi campi e la loro applicabilità richiede una conoscenza approfondita del loro comportamento e di conseguenza una loro caratterizzazione poroviscoelastica. La viscoelasticità è legata al riarrangiamento locale delle catene polimeriche che avviene mantenendo costante il volume. La viscoelasticità è essenziale in tutte quelle applicazioni in cui è richiesta una semplice adattabilità della struttura polimerica. La poroelasticità è correlata essenzialmente al trasporto di piccole molecole o di solvente, ed è responsabile sia dello swelling che dello shrinking degli idrogel. La poroelasticità risulta essere fondamentale per tutte le applicazioni in cui è richiesto il trasporto di molecole specifiche.
In questa tesi viene dapprima sviluppata e poi successivamente utilizzata una metodologia in grado di separare l'effetto poroelastico da quello viscoelastico.

Nella parte sperimentale di questo lavoro, per la caratterizzazione del comportamento poroviscoelastico degli idrogel di agarosio, sono state utilizzate le tecniche di caratterizzazione meccanica quali l'analisi meccanica dinamica (DMA), il test di stress-rilassamento e il test di creep.
Con la tecnica DMA è stato possibile caratterizzare solo il comportamento viscoelastico degli idrogel. In particolare, nell'intervallo analizzato, il rilassamento viscoelastico non è completo e quindi una parte dell'energia teoricamente dissipabile risulta ancora presente nel gel come energia immagazzinata e per tale motivo il suo contributo è considerato all'interno dello "storage modulus".
Con il test di stress-rilassamento è stato possibile caratterizzare sia la viscoelasticità e sia la poroelasticità degli idrogel all'interno di un intervallo di frequenza più ampio di quello del DMA. In particolare mediante due pesate (all'inizio e alla fine del test) è stato possibile valutare il coefficiente di Poisson. Il test di stress-rilassamento ha permesso di spiegare tutto il rilassamento viscoso ottenendo quindi una

descrizione ed una separazione completa dell'energia persa e di quella immagazzinata.
Anche nel caso del test di creep è stato possibile caratterizzare sia il comportamento poroelastico che quello viscoelastico degli idrogel, tuttavia in questo caso la durata del test non è stata sufficiente per descrivere l'esaurimento di tutto l'effetto viscoso. Inoltre, poiché il creep non permette di controllare la deformazione, è necessario considerare anche la possibilità di raggiungere deformazioni elevate e di superare quindi la zona lineare.

In conclusione, analizzando le diverse tecniche, è possibile affermare che l'analisi meccanica dinamica presenta diversi svantaggi. In particolare, a causa di un ristretto range di analisi (dovuto all'inerzia della sonda), la valutazione del comportamento viscoelastico risulta incompleta, relativamente invece al tempo impiegato si ha che l'analisi dinamica richiede dei tempi maggiori a causa dei tempi morti nel momento del passaggio da un campione all'altro ed infine un altro aspetto negativo è dovuto all' impossibilità di descrivere l'effetto poroelastico. Per completezza, è necessario considerare che tutti gli svantaggi descritti per l'analisi dinamica assiale, sono gli stessi presenti anche per l'analisi dinamica condotta in "shear" (reometria). I test di creep e di stress-rilassamento sono teoricamente entrambi in grado di superare questi limiti, tuttavia, per il test di creep, è necessaria un'ulteriore verifica del mantenimento del regime lineare. Considerando questi risultati, è possibile ritenere che la tecnica di stress-rilassamento rappresenta il metodo migliore per eseguire una completa caratterizzazione poroviscoelastica degli idrogel.

Bibliography

1. M. Bahram, N. Mohseni and M. Moghtader, An Introduction to Hydrogels and Some Recent Applications*, IntechOpen*, 2016.

2. E. M.Ahmed, Hydrogel: Preparation, characterization, and application: A review, *Journal of Advanced Research*, 2015, **6**, 105-121.

3. R. Singhal, A Review: Tailor-made Hydrogel Structures (Classifications and Synthesis Parameters), *Polymer-Plastics Technology and Engineering*, 2016, **55**,54-70.

4. D. Caccavo, S. Cascone, G. Lamberti, A.A. Barba, Hydrogels: experimental characterization and mathematical modelling of their mechanical and diffusive behavior, *Chem. Soc. Rev.*, 2018,**47**, 2357-2373.

5. J.S. Bergstrom, Mechanics of solid Polymers: Theory and Computational Modeling, *Elsevier Science*, 1st edition, 2015.

6. A.H.D.Cheng, Y.Abousleiman, J.C.Roegiers, Review of some poroelastic effects in rock mechanics, *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, 1993, **30**, 1119-1126.

7. H.J. Kümpel, Poroelasticity: parameters reviewed, *Geophysical Journal International*, 1991, **105**, 783–799.

8. W.Hong, X.Zhao, J.Zhou and Z.Suo, *J.Mech. Phys. Solids*, 2008, **56**, 1779-1793

9. N. Isobe, S. Kimura, M. Wada, S. Deguchi, Poroelasticity of cellulose hydrogel, *Journal of the Taiwan Institute of Chemical Engineers*, 2018, **92**, 118-122.

10. X. Zhao, N. Huebsch, D. J. Mooney and Z. Suo, Stress-relaxation behavior in gels with ionic and covalent cross-links, *Journal of Applied Physics,* **107**, 063509 (2010).

11. S. Hafeez, H. Ooi, F. Morgan, C. Mota, M. Dettin, Viscoelastic Oxidized Alginates with Reversible Imine Type Crosslinks: Self-Healing, Injectable, and Bioprintable Hydrogels, *Gels*, 2018, **4**, 85.

12. W. E. Rudzinski, A. M. Dave, U. H. Vaishnav, S. G. Kumbar, A. R. Kulkarni, T. M. Aminabhavi Hydrogels as controlled release devices in agriculture, *Journal Designed Monomers and Polymers*, 2012, **5**,39-65.

13. N. Sahiner et al., Fabrication and characterization of cross-linkable hydrogel particles based on hyaluronic acid: potential application in vocal fold regeneration, *Biomaterials Science Polymer*, 2008, **19**, 223-43.

14. H. Wang, S. C. Heilshorn, Adaptable Hydrogel Networks with Reversible Linkages for Tissue Engineering, *Advanced Materials*, 2015, **27**, 3717-3736.

15. https://www.thewellbio.com/how-does-vitrogel-works/in-vitro-3d-cell-models/

16. E. Caló, V. V.Khutoryanskiy, Biomedical applications of hydrogels: A review of patents and commercial products, *European Polymer Journal*, 2015, **65**, 252-267.

17. M. Gasik, A. Gantar, S. Novak, Viscoelastic behaviour of hydrogel-based composites for tissue engineering under mechanical load, *Biomed. Mater*, 2017. **12** 025004

18. G. Lamberti, D. Caccavo, M. Grassi, M. Abrami, Caratterizzazione di idrogel e criogel di agarosio, relazione in collaborazione tra UNISA e UNITS.

19. S. Cai, Y. Hu, X. Zhao, Z. Suo, Poroelasticity of a covalently cross-linked alginate hydrogel under compression, *Journal of Applied Physics*, **108**, 113514 (2010).

20. Y. Hu, X. Zhao, J. J. Vlassak, and Z. Suo, Using indentation to characterize the poroelasticity of gels, *Appl. Phys. Lett.*, **96**, 121904 (2010).

21. M. Galli , K. S. C. Comley, T. A.V. Shean and M. L. Oyen ,Viscoelastic and poroelastic mechanical characterization of hydrated gels, *Journal of Materials Research*, 2009, **24**, 973-979.

22. D. Caccavo, S. Cascone, S. Poto, G. Lamberti, and A.A. Barba, Mechanics and transport phenomena in agarose-based hydrogels studied by compression-relaxation tests, *Carbohydr. Polym*, 2017, **167**, 136-144.

23. Q.M. Wang, A.C. Mohan, M.L. Oyen, X.H. Zhao, Separating viscoelasticity and poroelasticity of gels with different length and time scales, *Acta Mechanica Sinica*, 2014, **30**, 20–27.

24. D. G. T. Strange, Separating poroviscoelastic deformation mechanisms in hydrogels, *Appl. Phys. Lett.*, **102**, 031913 (2013).

25. Determining frequency dependent moduli and complex viscosity data quickly and easily using creep testing, Technical Notes, Malvern Panalytical.

26. https://www.sigmaaldrich.com/technicaldocuments/articles/biology/agarose.html

27. D. Nordqvist, T.A. Vilgis, Rheological Study of the Gelation Process of Agarose-Based Solutions, *Food biophysics,* 2011, **6**, 450-460.

28. S. Poto, Analisi del comportamento poro-visco-elastico di idrogel a base di agarosio, tesi di laurea interna al gruppo di ricerca Transport Phenomena & Processes, 2016.

29. K. P. Menard, Dynamic mechanical analysis A practical introduction, *CRC Pres*s, 2nd edition, 2008.

30. P. Myler and L. M Wyatt, Mechanics of solids - Mechanical Engineer's Reference Book, *Edward H. Smith*, chapter 8th, Twelfth Edition, 1994.

31. M. S. Voss, X. Feng, Arma model selection using particle swarm optimization and aic criteria, *IFAC Proceedings Volumes*, 2002, **35**, 349-354.

32. S. A. Ashter, Thermoforming of Single and Multilayer Laminates, 1st Edition, Chapter 7, *William Andrew*, 2013.

33. P. L. Ritger and N. A. Peppas, A simple equation for description of solute release I. Fickian and non-fickian release from non-swellable devices in the form of slabs, spheres, cylinders or discs, *Journal of Controlled Release*, 1987, **5**, 23-36.

34. D. Caccavo, An overview on the mathematical modeling of hydrogels' behavior for drug delivery systems, *Int J Pharm*, 2019, **560**, 175-190.

35. R.S. Escarpini Filho, S.P.C. Marques, A Model for Homogenization of Linear Viscoelastic Periodic Composite Materials with Imperfect Interface, *Lat. Am. j. solids struct*., 2016, **13**, 2706-2735.

36. John D. Ferry, Viscoelastic Properties of Polymers, 3rd Edition, *John wiley & sons*, 1980.

37. S.W. Park and R.A. Schapery, Methods of interconversion between linear viscoelastic material functions Part I: a numerical method based on Prony series, *International Journal of Solids and Structures*, **36**, 1999.