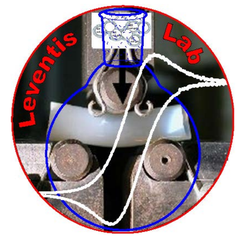
K-index as a Complex Nanomorphology Descriptor, Predictor and Correlator to Other Material Properties

Under NSF 1530603: SNM: Low-cost, Large-scale Nanomanufacturing of Inorganic, Polymeric and Composite Aerogels

N. Leventis, T. Taghvaee, P. Rewatkar, H. Majedi Far, S. Donthula and C. Sotiriou-Leventis

Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, 65409, U.S.A.

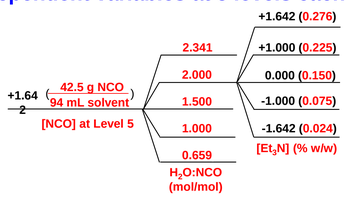


Introduction of the *K*-index

Nanomorphology is a qualitative property of nanostructured matter that is articulated after visual inspection of SEM images. For deterministic procedures that relate nanomorphology to synthetic conditions, it is necessary to express nano/micro-structure numerically. Selecting polyurea aerogels as a model system with demonstrated potential for rich nanomorphology, and guided by a statistical Design-of-Experiments method, we prepared a large array of materials (208) with identical chemical composition, but quite different nanostructures. From SEM imaging it was realized that our first pre-verbal impressions about nanostructure are related to openness and texture; the former is quantified by porosity (Π), and the latter is oftentimes related to hydrophobicity, which in turn is quantified by the contact angle (θ) of water droplets resting on the material. At that point all our polyurea aerogel samples were assigned a θ/Π ratio that is referred to herewith as their *K*-index, and it was noticed that based on their *K*-indexes all samples could be put in eight morphology groups ranging from caterpillar-like assemblies of nanoparticles, to thin nanofibers, to cocoon-like structures and to large bald microspheres. A first validation of the *K*-index as a morphology descriptor was based on samples compressed to different strains: the porosity decreased, but the water contact angle also decreased proportionally, and the *K*-index remained constant. In addition to being a morphology descriptor, the *K*-index is also a morphology predictor and a co-relator of morphology to other material properties. The predictive power of the *K*-index is demonstrated with new polyurea aerogels prepared in 20 new binary solvent mixtures. Subsequently, using response surface methodology, *K*-indexes and several other properties of polyurea aerogels were correlated to the monomer, water and catalyst concentrations and the three Hansen Solubility Parameters of the sol, thus enabling synthesis of materials with up to six prescribed properties at a time.

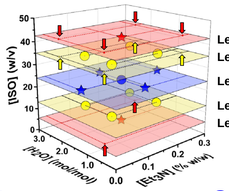
Synthesis of Polyurea Aerogels

- **Three independent variables at 5 levels each**



- **Formulations based on Design of Experiments (DoE)**

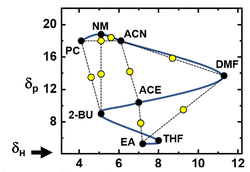
central composite rotatable design



enhanced with 10 additional runs

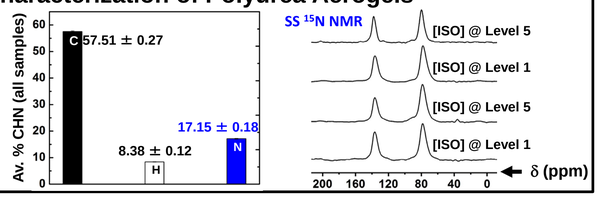
total number of runs = 26

- **Solvent selection based on Hansen Solubility Parameters**

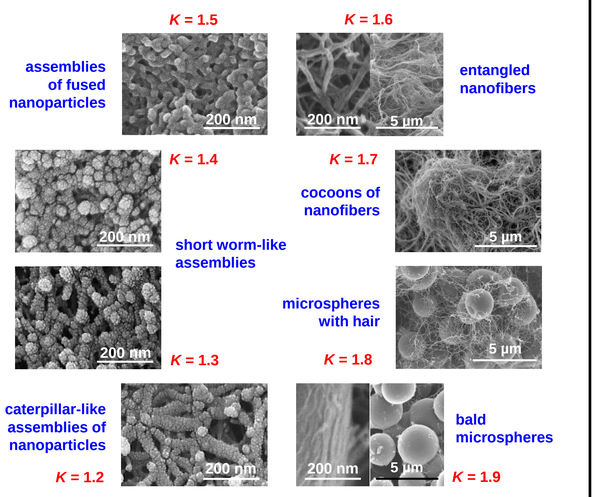


Yellow dots: position of mixed solvents

Characterization of Polyurea Aerogels



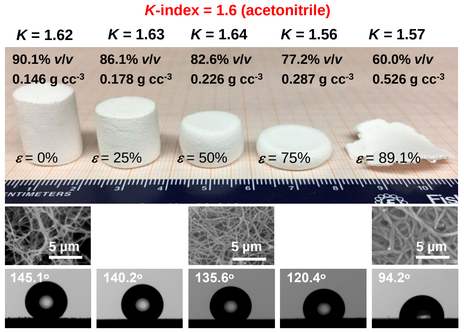
K-index as a Descriptor of Nanomorphology



➢ Validation of the *K*-index by Compression

The logic here is:

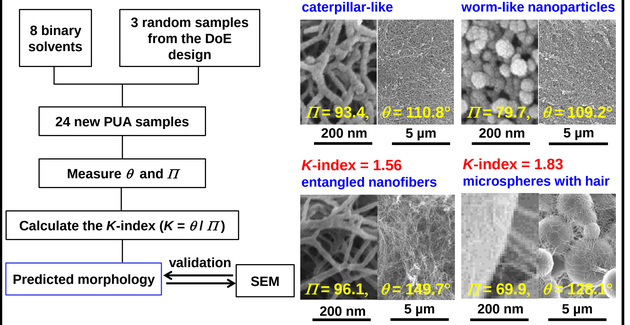
- By compressing monoliths at different strains (*E*), nanomorphology does not change, therefore the K-index should be retained.
- Porosity (Π) obviously decreases, thereby the water contact angle (θ) should follow spontaneously.



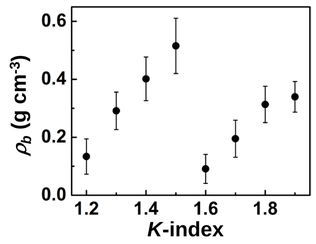
➢ Validation of the *K*-index using Binary Solvents

The logic here is:

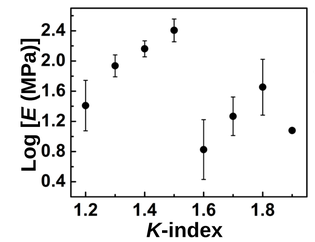
- Irrespective of how we arrive $\alpha\tau$ a *K*-index, the morphology should be one of the eight morphology groups above. And it *is*!



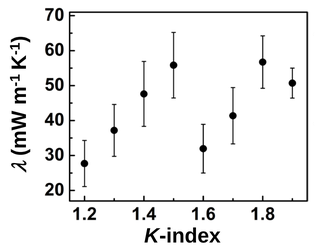
K-index as a Correlator of Material Properties



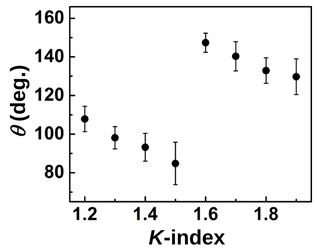
- The variation of the bulk density with nanomorphology is discontinuous.
- Most densities show up at two different morphologies.
- Lowest density samples were possible only with entangled fibers (*K* = 1.6).
- Highest density samples were possible only with fused nanoparticles (*K* = 1.5).
- Interestingly, beyond the discontinuity point, materials with *K* ≥ 1.6, were possible only in high-polarity CH_3CN, CH_3NO_2 and propylene carbonate.



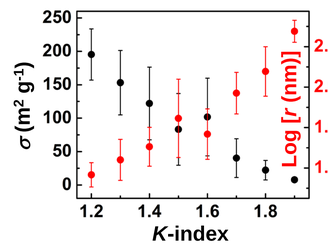
- The elastic modulus (*E*) depends on the bulk density, thereby, like density, it shows two independent branches with nanomorphology.



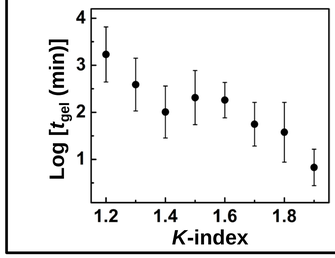
- Likewise, the thermal conductivity (λ) depends also on the bulk density, thereby, like density, it shows two independent branches with nanomorphology.
- Interestingly, the lowest thermal conductivity is displayed by polyurea aerogels consisting of caterpillar-like nanostructures.



- Hydrophobicity, quantified by the water contact angle (θ) of a water droplet on the material, shows also two branches with nanomorphology.
- The most hydrophobic samples were low-density and consisted of entangled fibers.
- The most hydrophilic samples were high-density and consisted of fused nanoparticles.

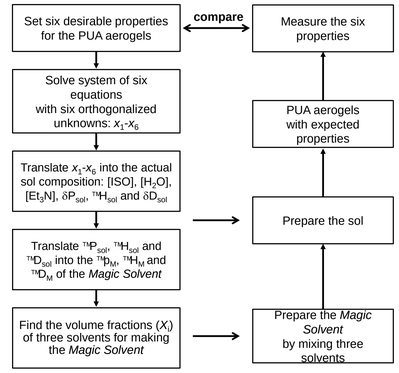


- Not all material properties were discontinuous with the nano-morphology, though.
- The BET surface area and The primary particle size were continuous albeit not monotonic in the drastic nanomorphology transition range 1.5 ≤ *K* ≤ 1.6, which coincides with the transition from less to more polar solvents.

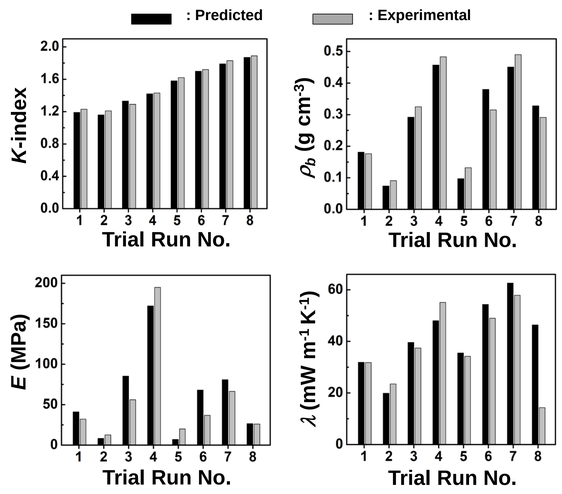


- The gelation time was also continuous, yet not monotonic in the transition range from less to more polar solvents.
- It is speculated that at 1.4 < *K* < 1.6 there is a change in the gelation mechanism.
- Based on the sample morphology it is speculated that when:
  - ➢ *K* ≤ 1.4 ⟶ **nucleation and growth;**
  - ➢ *K* ≥ 1.6 ⟶ **spinodal decomposition;**
  - ➢ 1.4 < *K* < 1.6 ⟶ **both mechanisms.**

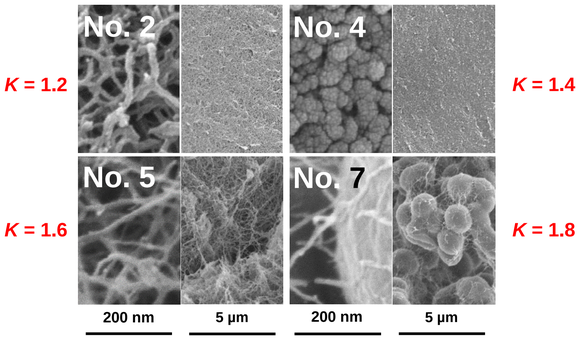
K-index as a Predictor of Nanomorphology



Experimental data match the predicted properties of eight Trial Runs



Nanomorphologies, in particular, match closely to those predicted from the *K*-index (refer to the *K*-index as a Descriptor, above)



Conclusion

- *K*-index **is defined** as the water contact angle (θ) / porosity(Π).
- *K*-index **describes** nanomorphology.
- *K*-index **correlates** material properties to nanomorphology.
- *K*-index **predictes** nanomorphology.