Peculiarity in Nonlinear Stress Relaxation of Near-Critical Gels under Stretching Deformations

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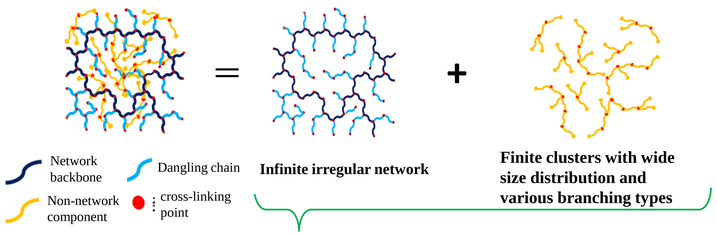
Introduction

Near-Critical Gel : Obtained slightly above the gel point



Hierarchical fractal structure ➡ **Remarkable viscoelasticity**

Almost no study on nonlinear viscoelasticity of (near) critical gels

Time-Strain Separability (TSS) in Nonlinear Viscoelasticity

$$\Delta\sigma(t,\gamma) = m(t)\cdot n(\gamma)$$

(Stress, Time, Strain; Time-term, Strain-term)

Verifying TSS for

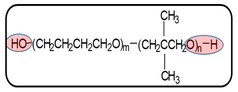
- **dual Cross-link PVA gels (Uniaxial and biaxial extension)**
  - T. Narita , K. Mayumi , G. Ducouret , and P. Hébraud ,*Macromolecules* 2013 , **46** , 4174
  - T. Kimura, K. Urayama, *ACS Macro Lett*, 2020, **9**, 1-6
- **Critical PVC gels (shear deformation)**
  - H. Watanabe, T. Sato , K. Osaki , Y. Aoki, L. li, M. Kakiuchi and M.-L. Yao, *Macromolecules* 1998, **31** , 4198-4204

Objective

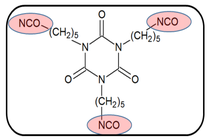
Assessing TSS for near-critical gels using various deformation modes

Materials : Two types of near-critical gel

PTHF gel : G055



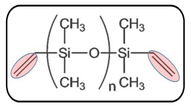
Poly[(tetrahydrofuran)-(neopentyl glycol)]



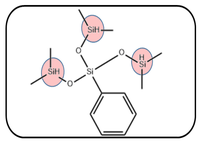
Isocyanuric acid tris (5-pentyl isocyanate)

r = 0.55 r (gel point) = 0.50 80°C, 6h

PDMS gel : Z064



Poly(dimethylsiloxane)



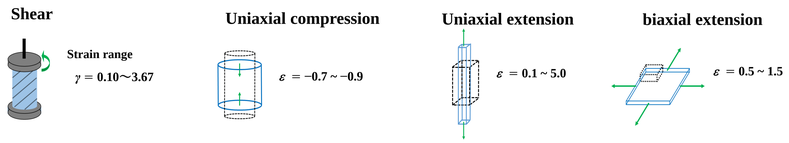
Phenyltris(dimethylsiloxy)silane

r = 0.64 r (gel point) = 0.60 25°C, 6h

$r = \frac{[B]}{[A]}$ [A]: Molar concentration of functional group in precursor chain; [B]: Molar concentration of functional group in crosslinking agent

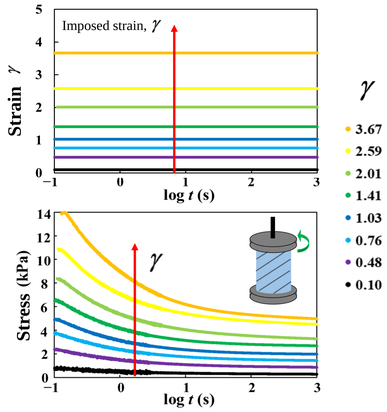
Stress relaxation test : measuring the time course of stress after step strain

Four types of deformation modes



Results

Stress relaxation in shear for G055

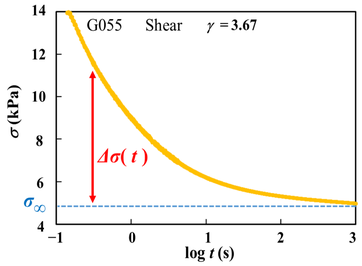


Stress decreases with time and reaches the equilibrium value σ_∞ (>0).

Evaluating the relaxation component

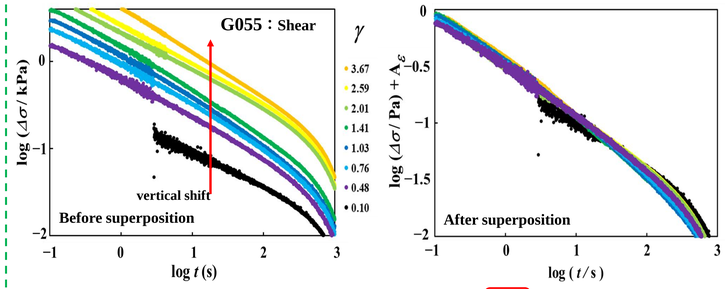
$$\Delta\sigma(t) = \sigma(t) - \sigma_\infty$$

σ_∞ :equilibrium stress



Assessing TSS

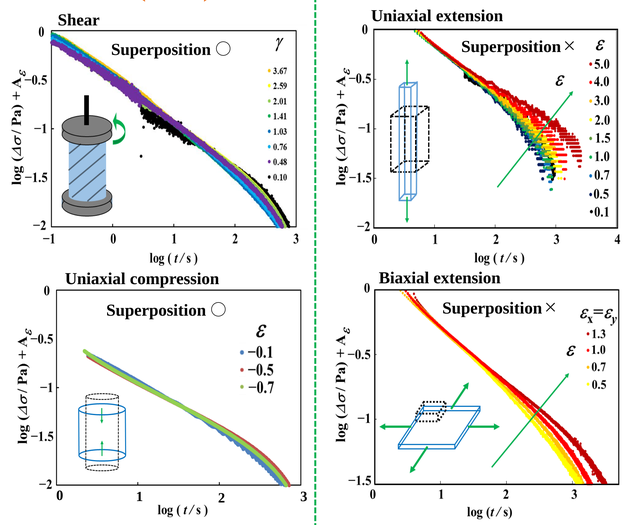
Superposition of the log $\Delta\sigma$ – log t curves by arbitral vertical shifts



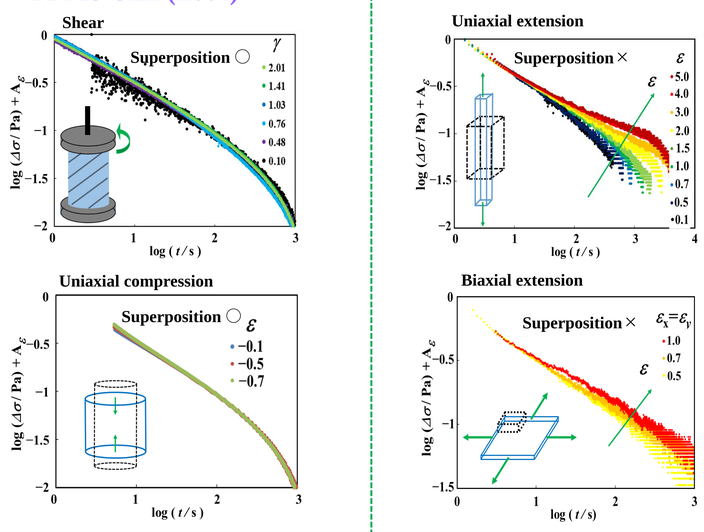
$m(t)$ **is independent of strain** $\Delta\sigma(t,\gamma) = m(t)\cdot n(\gamma)$

Successful superposition ➡ **Verifying TSS**

PTHF GEL (G055)



PDMS GEL (Z064)

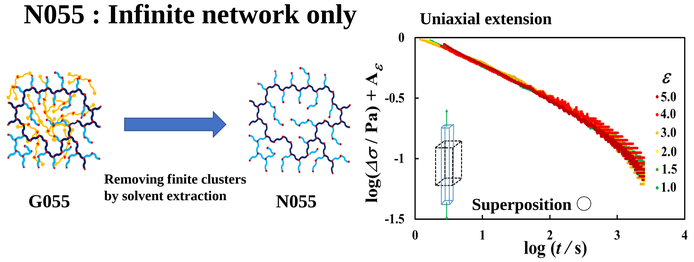


Shear and Compression : Verifying TSS

Uniaxial and Biaxial Extension : Failure of TSS ➡

- ・$m(t)$ depends on strain
- ・Stress relaxation becomes slower with increasing strain

N055 : Infinite network only



Discussion

○ Origin of TSS failure

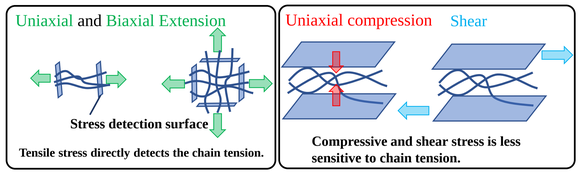
Near-critical gel consists of infinite irregular network and finite clusters with significantly different viscoelasticity.

➡ Possibility of strain-induced phase separation

Under investigation by small angle X-ray scattering measurement

○Origin of TSS failure specific to stretching deformation

Possible origin : Tensile stress is considerably sensitive to stretching of polymer chains than shear and compressive stresses.



Conclusions

Nonlinear stress relaxation behavior of near-critical gels significantly depends on the deformation mode.

- ・Relaxation time is independent of strain in shear and compression.
- ・Relaxation becomes slower with increasing strain in uniaxial and biaxial tension.