# On the Sensitivity of Alginate Rheology to Composition

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## Experimental

Alginic acid sodium salt from brown algae with low viscosity (4-12 cP for 1% in water at 25 °C) and PBS tablets were purchased from Sigma Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC-HCl) was purchased from Carl Roth. 3-Aminophenyl boronic acid monohydrate was purchased from TCI Europe. All chemicals were used as received without further purification.

*Synthesis of Alg-PBA*: Alginate-phenyl boronic acid (Alg-PBA) was prepared by following our previously reported procedure.[1] Briefly, sodium alginate (5 g, 25 mmol based on monomer unit) was dissolved in deionized water (500 mL) to which EDC-HCl (4.8 g, 25 mmol) and 3-aminophenylboronic acid (1.95 g, 12.5 mmol) were added. The mixture was stirred at room temperature (RT) for 24 h and then dialyzed against deionized water for 1 week, replacing water at least 7 times, and then lyophilized to obtain a white-yellowish powder.

*General procedure for sample preparation*: The required quantity of dry Alg-PBA was dissolved in 1 mL 0.1 M PBS buffer (pH =7.4). For example, for a 3 wt.% sample, we dissolved 30 mg of the dry Alg-PBA in 1 ml 0.1 M PBS buffer. To this, a specified quantity of 1 M NaOH was added and the solution was vigorously stirred. After preparation, samples were equilibrated at RT overnight.

***Instrumental Methods*:** We performed stretching experiments using the rectangular tension geometry in the RSA-III DMA for 3-75 Alg-PBA. As-prepared samples were cut using a surgical blade into rectangular shapes for tensile testing. They were then clamped vertically in the rectangular geometry and stretched. In contrast, 7-35 Alg-PBA thins rapidly on clamping in the rectangular fixture. Therefore, we prepared samples in the form of cylinders and performed stretching experiments using the 8 mm diameter stainless steel parallel plate geometry on the RSA-III DMA. The flat faces of cylindrical sample adhered strongly to the metal plates of the rheometer fixture during the stretching experiment. All measurements were repeated several times (each, at least 5 times) to confirm reproducibility. Shear flow experiments were carried out using a TA- ARES G2 strain controlled rheometer equipped with a normal force transducer. Different geometries (25 mm roughened parallel plate and 25 mm, 0.1 radian cone angle, cone and plate geometries) were used to probe the rheological response of the test fluids. Both steady shear and small amplitude oscillatory tests were performed. The frequency sweep measurements were performed on the gels in a frequency range of

0.1 to 100 rad/s with strain amplitude in the linear viscoelastic regime and for samples loaded initially with a normal force of 0.2 g. Samples were coated on the edges with silicone oil to prevent water evaporation during measurements. Frequency sweeps were performed from high frequency (100 rad/s) to low (0.1 rad/s). The steady shear experiments were performed within the strain rate range of 0.1 to 100 $s^{-1}$.All measurements were performed at room temperature (25°C).

**Table S1:** List of gels made with different compositions of alginate- PBA with NaOH.

| Alg-PBA | Volume of NaOH (1M) added (uL) | | | | |
|---|---|---|---|---|---|
| **(% w/v)** | 15 | 25 | 35 | 50 | 75 |
| 3 | L | $G^{a}$ | $G^{c,e}$ | G | G |
| 5 | L | $G^{a,e}$ | $G^{d,e}$ | $G^{c}$ | G |
| 7 | L | $G^{a}$ | $G^{a,c,e}$ | $G^{b,d,e}$ | G |
| 10 | | | $G^{a,c,e}$ | $G^{a,d,e}$ | |

L = liquid; G = gel, [a] very elastic [b] elastic [c] approximately, 1 cm bounce when gel drops from 20 cm height [d] approximately,7 cm bounce when gel drops from 20 cm height [e] shapeable

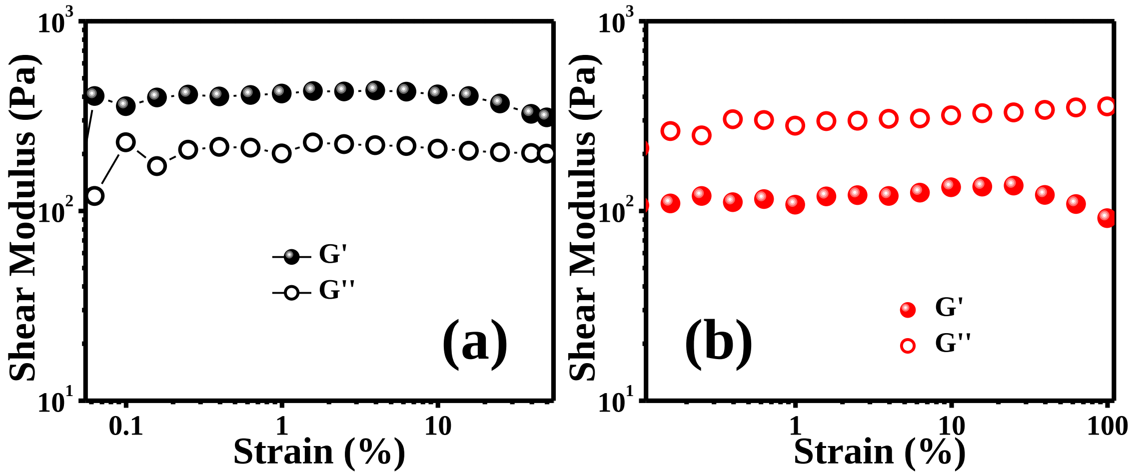


**Fig. S1**: Strain sweep experiment on **(a)** 3-75 and **(b)** 7-35. Experiments were performed at 1 rad/s.

**Table S2:** Crossover frequency, frequency shift and modulus shift factors calculated for different gel formulations.

| Sample name: (PBA- alginate wt.%- NaOH amount in µl) | Crossover frequency, $\omega_c$ (rad/s) | Crossover modulus, $G_c$ (Pa) | Shift parameters | |
|---|---|---|---|---|
| | | | Frequency shift | Modulus shift |
| 3-75 | 0.25 | 360 | 1 | 1 |
| 3-35 | 1 | 425 | 0.25 | 1.14 |
| 5-75 | 6 | 1100 | 0.0417 | 0.4 |
| 7-35 | 15 | 2550 | 0.0167 | 0.15 |

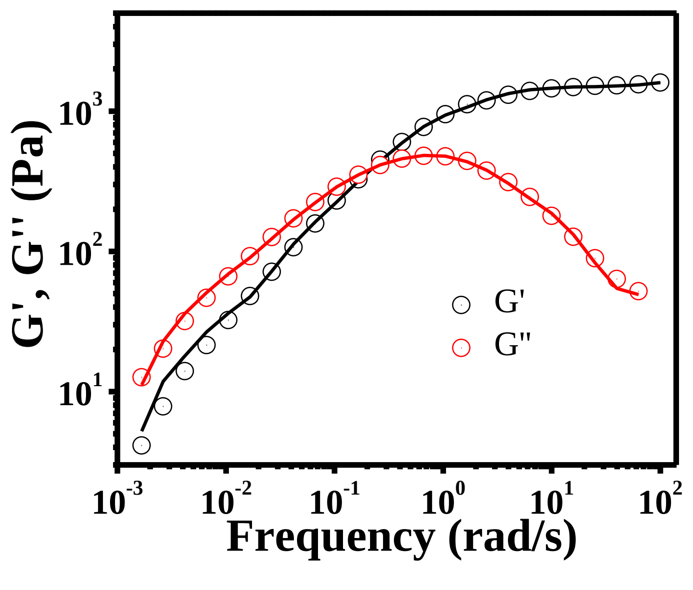


**Fig. S2**: Maxwell fit on the master curve. The solid line represents the fit.

**Table S3**: Parameters obtained by fitting discrete relaxation spectrum function to the shear rheology data.

| $G_k$ (Pa) | $\tau_k$ (s) |
|---|---|
| 5162 | 0.02 |
| 2603 | 0.08 |
| 775 | 0.36 |
| 598 | 3.1 |

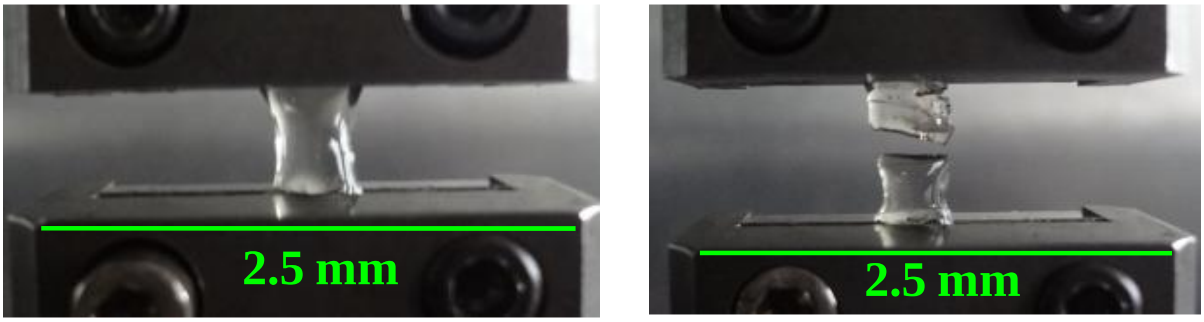


**Fig. S3:** Photographs of the 3-75 sample during tensile testing at 0.1 $s^{-1}$ Hencky strain rate.

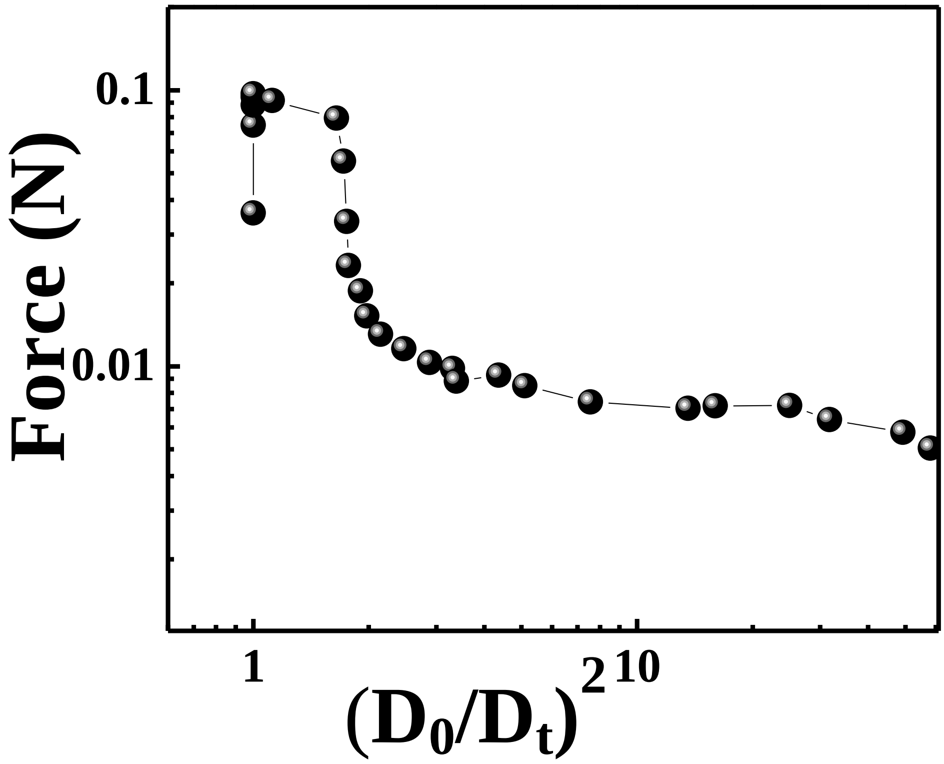


**Fig. S4**: Plot of normal force as a function of $\left({}^{D_0}/{}_{D_t}\right)^2$, where $D_0$ and $D_t$ are the diameters of cylindrical sample at time 0 and $t$. The plot corresponds to the stretching of 7-35 fluid with a Hencky strain rate of 0.1 $s^{-1}$.


1. A. Pettignano, S. Grijalvo, M. Haering, R. Eritja, N. Tanchoux, F. Quignard and D. D. Diaz, *ChemComm*, 2017, **53**, 3350-3353.