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**Prova orale del 8 maggio 2024  
Serie N. 1**

- Controllo umidità durante misurazioni con reometri commerciali
- Scelta dei parametri iniziali per misure di viscosità in campioni di gel di interesse biologico





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**Prova orale del 8 maggio 2024  
Informatica N. 1**

- Operazioni e funzioni statistiche in Excel
- Preparazione di un grafico con gnuplot



## Supporting Information for

### G-Quartet Hydrogels for Effective Cell Growth Applications

A. Rotaru, G. Pricope, T. N. Plank, L. Clima, E. L. Ursu, M. Pinteala, J. T. Davis and M. Barbolu

**Abstract:** Supramolecular hydrogels composed of natural components are of high interest in drug delivery and tissue engineering. In addition, formation of hydrogels with increased water content is crucial for cell growth and viability. Our strategy for making such functional hydrogels involves the use of G4-K<sup>+</sup> and G4-Ba<sup>2+</sup> quartets, made from the natural product guanosine and 0.5 equiv. of benzene-1,4-diboronic acid. The resulting guanosine-borate hydrogel can be further modified by selectively cross-linking gel fibers with Mg<sup>2+</sup> cations. The addition of Mg<sup>2+</sup>, as an external cross-linker, provided an impressive swelling of the resulting hydrogels, a desirable property for biocompatible materials that are optimal for cell growth and tissue engineering. The guanosine-borate hydrogels were characterized by NMR, CD, AFM, and rheology. These guanosine-borate hydrogels support cell growth and do not show visible signs of degradation.

#### Experimental section

##### 1. Hydrogel synthesis

**Synthesis protocol BDBA-K:** In a glass vial 0.05g, 0.2 mmol (1 eq) of guanosine (G 1) is mixed with 0.0146 g, 0.1 mmol (0.5 eq) of benzene-1,4-diboronic acid (BDBA 2). Distilled water (1.9 mL) is added, and the mixture is sonicated for a few minutes, until all the components are dispersed. The suspension is then heated in an oil bath preheated to 120°C until the solution becomes transparent. To avoid pressure in the vial upon heating a syringe needle in the plastic cap of the vial is used (Fig. S1). Then, 100 µL, 0.01 g, 0.2 mmol KOH (1 eq, stock solution of KOH: 0.66 g in 6.6 mL distilled water) is added and the mixture is heated and stirred for a few more minutes, and then left to cool down at room temperature. After cooling, a transparent and self-standing hydrogel is formed.

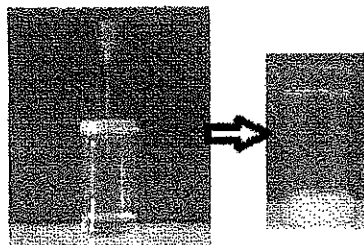


Figure S1: Vial with syringe needle in the plastic cap.

**Synthesis protocol BDBA-Ba:** In a vial, an amount of 0.05 g, 0.2 mmol (1 eq) of G 1 is mixed with 0.0146 g, 0.1 mmol (0.5 eq) of benzene-1,4-diboronic acid (BDBA 2). Distilled water (6.58 mL) is added, and the mixture is sonicated for a few minutes, until all the components are dispersed. The suspension is then heated on an oil bath preheated to 120°C until the solution becomes transparent. To avoid pressure in the vial upon heating a needle in the cap of the vial is used. Then, 1.42 mL containing 0.015 g, 0.1 mmol Ba(OH)<sub>2</sub>·H<sub>2</sub>O (0.5 eq, stock solution of Ba(OH)<sub>2</sub>·H<sub>2</sub>O: 0.31 g in 30 mL distilled water) is added and the mixture is heated and stirred for a few more minutes, and then left to cool down at room temperature. After cooling a transparent and self-standing gel is formed. Note that, with smaller amounts of water used, the gel is cloudy.

**Synthesis protocol BDBA-Mg:** In a vial, an amount of 0.05g, 0.2 mmol (1 eq) of G 1 is mixed with 0.0146 g, 0.1 mmol (0.5 eq) of benzene-1,4-diboronic acid (BDBA 2). Distilled water (1.9 mL) is added, and the mixture is sonicated for a few minutes, until all the components are dispersed. The suspension is then heated on an oil bath preheated to 120°C until the solution becomes transparent. To avoid pressure in the vial upon heating a needle in the cap of the vial is used. Then, 100 µL containing 0.01 g, 0.2 mmol, KOH (1 eq) is added and the mixture is heated and stirred for a few more minutes, and then left to cool down at room temperature. After cooling, the gel is diluted with 38 mL of distilled water in a NUNC tube (50 mL). The mixture is then

## 6. Rheology

Gels were made as described in the procedures above and allowed to sit at room temperature overnight before experiments were performed. Experiments were run on an AR2000 stress-controlled rheometer from TA Instruments in New Castle, DE at 20 °C with a 20 mm diameter parallel plate geometry. The gels were loaded onto the rheometer and allowed to equilibrate on the plate for 10 min before running the experiment. Frequency sweeps were performed at 0.2% strain (Fig. S7).

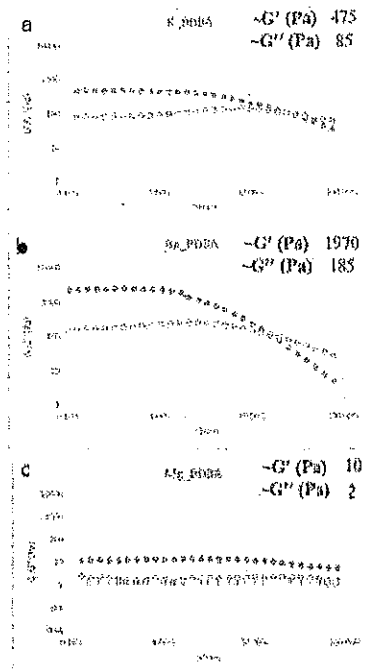


Figure S7: Rheological strain sweeps of the 3 gels show the storage modulus  $G'$  (●) and the loss modulus  $G''$  (○).

## 7. Atomic Force Microscopy (AFM)

The Ntegra Spectra Atomic Force Microscope (NT-MDT, Russia) operated in tapping mode under ambient conditions was used to image gels structures. Silicon cantilever tips (NSG 10, NT-MDT) with gold reflecting coating, a resonance frequency of 140–390 kHz, a force constant of 3.1–37.6 N m<sup>-1</sup> and a tip curvature radius of 10 nm were used. Sample preparation: a 10 mL aliquot of the gel solution was deposited on freshly cleaved mica substrates and dried in air at room temperature prior to imaging.

## 8. Scanning Electron Microscopy (SEM)

The freeze-dried BDBA-K hydrogel showed a sponge-like microstructure with pore diameters varying from 5 to 8 μm (Fig. S8).

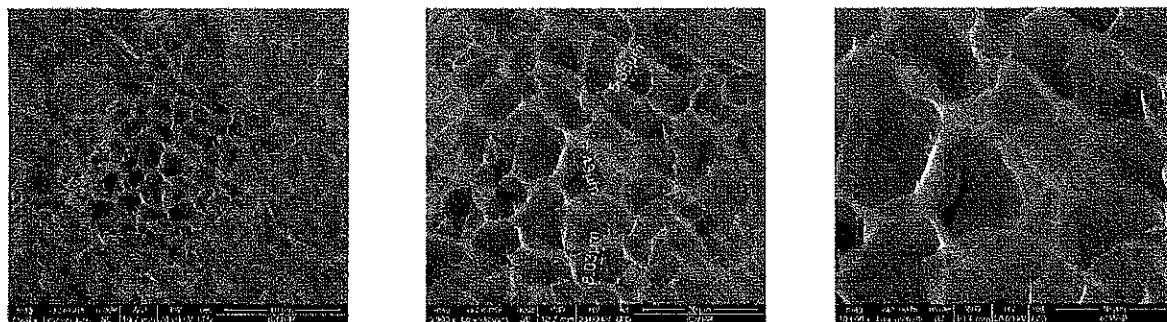


Figure S8: Examples of SEM images for freeze-dried BDBA-K hydrogel.



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**Prova orale del 8 maggio 2024  
Serie N. 2**

- Modalità sperimentali per misure di  $G'$  e  $G''$
- Software per misure sperimentali e parametri predefiniti





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**Prova orale del 8 maggio 2024  
Informatica N. 2**

- Funzionalità di PowerPoint per la preparazione di un poster
- Data fitting con gnuplot





## Describing flow behavior of polymer gel in fracture using rheology

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## ABSTRACT

In many successful conformance controls to reduce excessive water production, large volumes of gels were extruded through fractures during placement. The pressure gradient for gel extrusion depends strongly on fracture width and gel composition. Extrusion experiments directly measure gel properties in fractures, but they are both expensive and time-consuming. The rheology behavior of the gels showed a strong parallel to the results obtained from previous gel extrusion experiments. The previous researches showed two discrepancies and one similarity between the rheology estimation and extrusion experiment. The two discrepancies are: the pressure gradient required to extrude a gel through a fracture substantially greater than anticipated based on rheology measurements; different relationships of pressure gradient versus fracture width. The similarity is the relationships between pressure gradient versus flow rate and shear stress versus shear rate are fairly close. This paper examined these discrepancies and the similarity, in hopes of understand and ultimately substituting the rheology measurements for extrusion experiments. Extensive experiments established that wall slip and first normal stress difference were not responsible for the pressure gradient discrepancy. Steady shear and oscillatory shear data were collected with a rheometer using both smooth and rough parallel-plate geometries and employing various gap heights. Wall-slip effects were present with smooth plates but negligible with rough plates. To explain the discrepancy, we noted that the aperture for gel flow (for mobile gel wormholing through concentrated immobile gel within the fracture) was much narrower than the width of the fracture. Considering the shear-thinning properties of the gels, two models were developed combining power-law model and shell momentum balances. The first model explained the discrepancy of the relationships between pressure gradient versus fracture width. The second model correlated pressure gradient, shear stress, flow rate, and shear rate to bridge the gap between gel rheology in fractures versus in a rheometer and explained the similarity between the rheology measurement and extrusion experiment.

## 1. Introduction

Excess water production increasingly plagues oil and gas production worldwide. In naturally fractured reservoirs, large volumes of Cr(III)-acetate-HPAM gels have been successfully extruded into place to reduce channeling and excess water production (Sydansk and Moore, 1992; Borling, 1994; Hild and Wackowski, 1999; Lane and Sanders, 1995). During gel placement in fractures, the pressure gradient for gel extrusion depends strongly on fracture width and gel composition (Seright, 2003a, 2001, 1999a). Extrusion experiments directly measure gel properties in fractures, but they are both expensive (for core materials and casting) and time-consuming (two to three days per experiment, with one to two weeks of setup time). In contrast, a single rheology test can be performed at a fraction of the cost (negligible cost for gel materials) and can be completed within several minutes (after one to two days of setup time). Therefore, the objective of this research is to study whether rheology testing can be used as a more cost-effective and efficient

alternative for predicting gel behavior in fractures. The previous researches found two discrepancies and one similarity between the rheology measurement and extrusion experiment.

### 1.1. Discrepancy on pressure gradient required for gel extrusion through the fracture

Two apparent discrepancies are encountered when using rheometers to predict gel behavior in fractures. First, the pressure gradients observed during gel extrusion through the fractures were much greater (by more than 10 times) than those predicted by the simple force balance approach (Seright, 2003a, 2001, 1999a). When gel is extruded through a fracture, a minimum pressure gradient must be applied in order for the gel to flow, which suggests the gel material exhibits a yield stress (Seright, 1999a, 2001, 2003a, 2003b). The yield point is the end of a reversible elastic deformation and the beginning of an irreversible deformation, or visco-elastic/viscous flow. In the low deformation range, the material exhibits

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