Novel Nanobiocomposite Hydrogels Based on Gelatin/Chitosan and Functionalized Graphene

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Introduction

Hydrogels are highly hydrated three dimensional polymeric cross-linked networks that excel over other biomaterials to nearly mimic the native tissue microenvironment. However, limited mechanical stiffness and failure after cyclic loading significantly hinder their biomedical applications[1]. Despite recent progress in preparing stiff and tough hydrogels, it's still challenging to design a cell-compatible, highly porous and high modulus hydrogels in a congenial and sustainable approach.

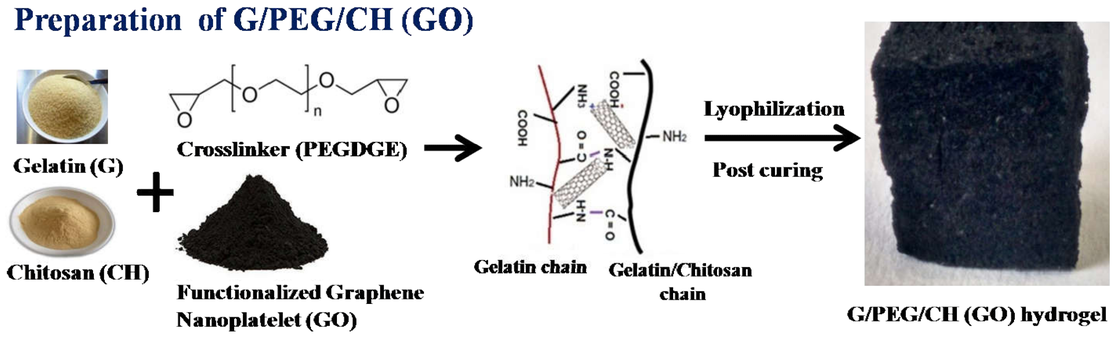
Objective

Developing a novel nanobiocomposite network hydrogels in combination of graphene nanoplatelet and gelatin/chitosan polymer matrix maintaining more mechanical modulus, stability and strength without sacrificing pore morphology and internal hydrogel architecture utilizing a simple, green and environment-friendly fabrication approach.

Experiments

Four different composite hydrogels namely G/PEG/CH, G/PEG/CH (GO-1), G/PEG/CH (GO-2) and G/PEG/CH (GO-3) were synthesized (**Table-1**) using a simple and easy synthetic method under aqueous condition without using any solvents, chemical reagents such as, catalysts, coupling agents and so on.

Preparation of G/PEG/CH (GO)



Results and Discussions

Thermogravimetric analysis (TGA) was used to evaluate the actual amount of graphene layers in the dry samples and the data are shown in Table 1.

TABLE 1. The composition, graphene content (%) in dry and wet conditions and mechanical both tensile and compressive properties of the composite hydrogels.

Sample Code	G* (%)	G** (%)	Tensile Properties			Compressive Properties	
			Initial Elastic Modulus (MPa)	Strength (MPa)	Strain at Max. Stress (%)	Initial Elastic Modulus (MPa)	Strength at 50% Strain (MPa)
G/PEG/CH	0	0	0.024 ± 0.12	0.010 ± 0.003	39 ± 11	0.037± 0.003	0.042 ± 0.01
G/PEG/CH (GO-1)	4.6	0.6	0.162 ± 0.01	0.027 ± 0.01	18 ± 4	0.073 ± 0.001	0.059 ± 0.02
G/PEG/CH (GO-2)	7.2	0.8	0.259 ± 0.07	0.046 ± 0.02	22 ± 6	0.079 ± 0.01	0.081 ± 0.01
G/PEG/CH (GO-3)	7.4	0.9	0.353 ± 0.06	0.053 ± 0.03	22 ± 8	0.057 ± 0.001	0.047 ± 0.01

G= Graphene nanoplatelet content in dry (*) and wet (**) wet sample.

Swelling Experiment

Water uptake of hydrogel composites is in the range of 650-750 %. The graphene layers do not remarkably modify the swelling ability of hydrogels, which is high for all the samples. It could be observed that the water absorption slightly increases with the nanoplatelets content. Such a high water absorption appears suitable for tissue engineering applications.

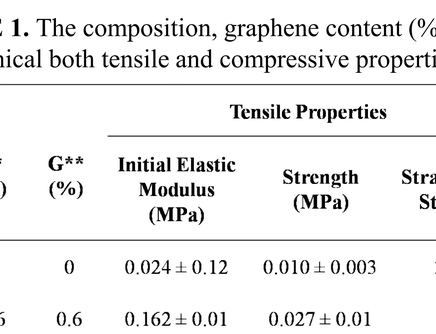


Fig 1. Water uptake of the hydrogels as a function of soaking time in water at 37 °C.

Tensile Test

The addition of graphene nanoplatelet even at lower concentration relative to polymer resulted in more than 10-fold increase of tensile stiffness.

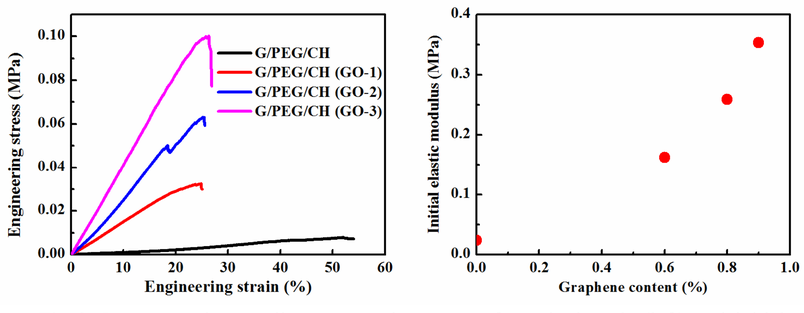


Fig 2. Representative tensile stress-strain curves of wet hydrogels (left) and initial elastic modulus as a function of graphene content in the wet samples (right).

Results and Discussions Continue…….

Cyclic Compression Test

Cyclic compressive tests up to 80% of strain were done on wet cubic specimens to test their fatigue resistance and reversible behaviour.

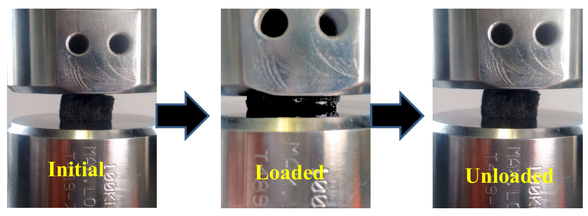


Fig 3. Images of nanocomposite gels undergoing compression testing.

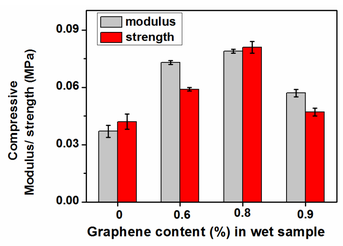


Fig 4. Profile of initial elastic modulus/strength as a function of graphene content in wet sample.

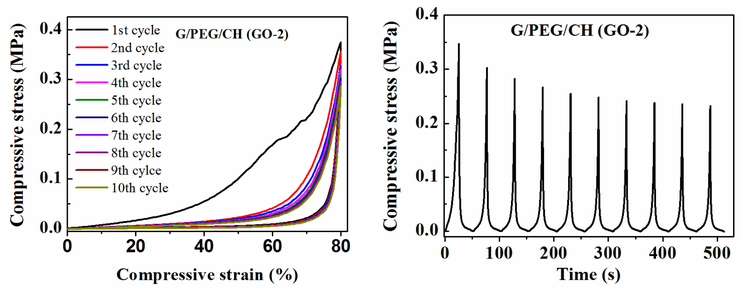


Fig 5. Cyclic compressive loading-unloading curves of representative G/PEG/CH (GO-2) nanocomposite without waiting time with 80% strain upto 10 cycles (left), and stress-time curves for the corresponding 10 cycles (right).

❖ During the first cycles, the nanocomposites show a Mullins effect, with the reduction of stiffness and stress at every cycle. After few cycles the material behavior is stabilized (**Figures 5 and 6**) and the hydrogel is able to sustain a compressive strain of 80% with full strain recovery without macrofracture demonstrating excellent elasticity and good mechanical stability.

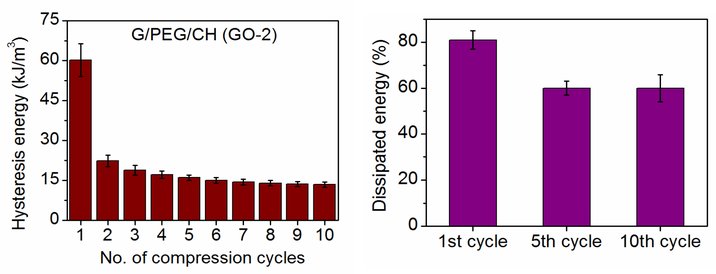


Fig 6. The hysteresis energies of the representative G/PEG/CH (GO-2) nanocomposite with increasing cycle numbers (left) and the percentage dissipated energy of the 1st , 5th and 10th cycles of the gels subjected to 80% strain.

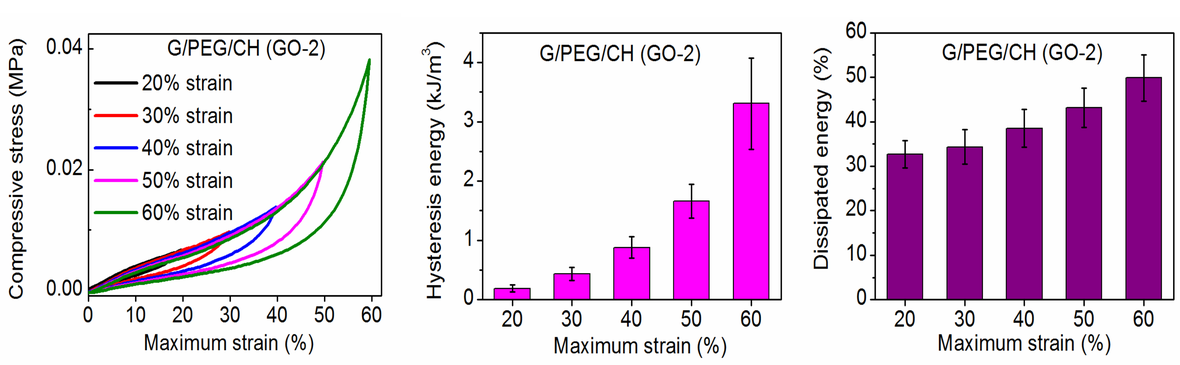


Fig 7. The hysteresis loops of G/PEG/CH (GO-2) nanocomposite at different maximum strains (left), the hysteresis energies of the representative nanocomposite with increasing maximum strains (middle) and the percentage dissipated energy of the corresponding maximum strains (right).

The exponentially increasing hysteresis energies of nanocomposite with increasing maximum strains (**Figures7**) shows strong fatigue resistance of the gels.

Pore Morphology

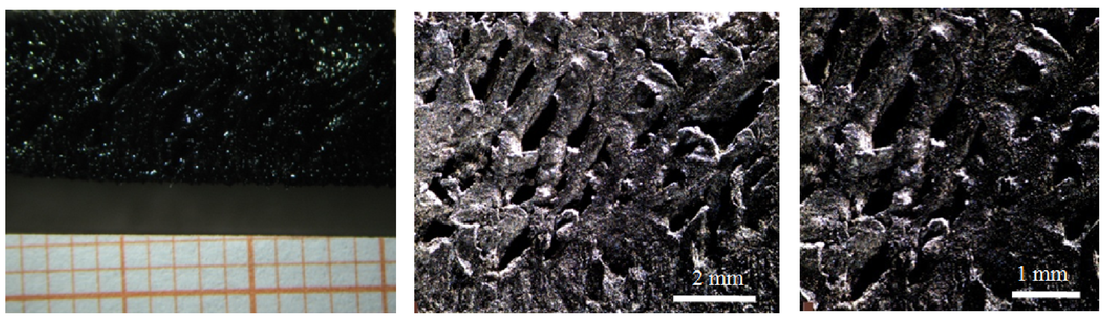


Fig 8. Optical images of the nanocomposite gel showing the macroporous networks of well-connected pores.

Conclusions

Graphene nanoplatelets were added to hydrogels based on gelatin and chitosan at congenial environment. High water uptake was maintained and significant increase of mechanical properties, stiffness and strength, was obtained along with strong fatigue resistance. Overall, these results demonstrate a green and facile approach to modulate morphological, mechanical and electrical properties of the gelatin/chitosan based hydrogels for numerous biomedical applications.

References

1. Manish K. Jaiswal et al., ACS Nano, 2016, 10, 246-256.

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