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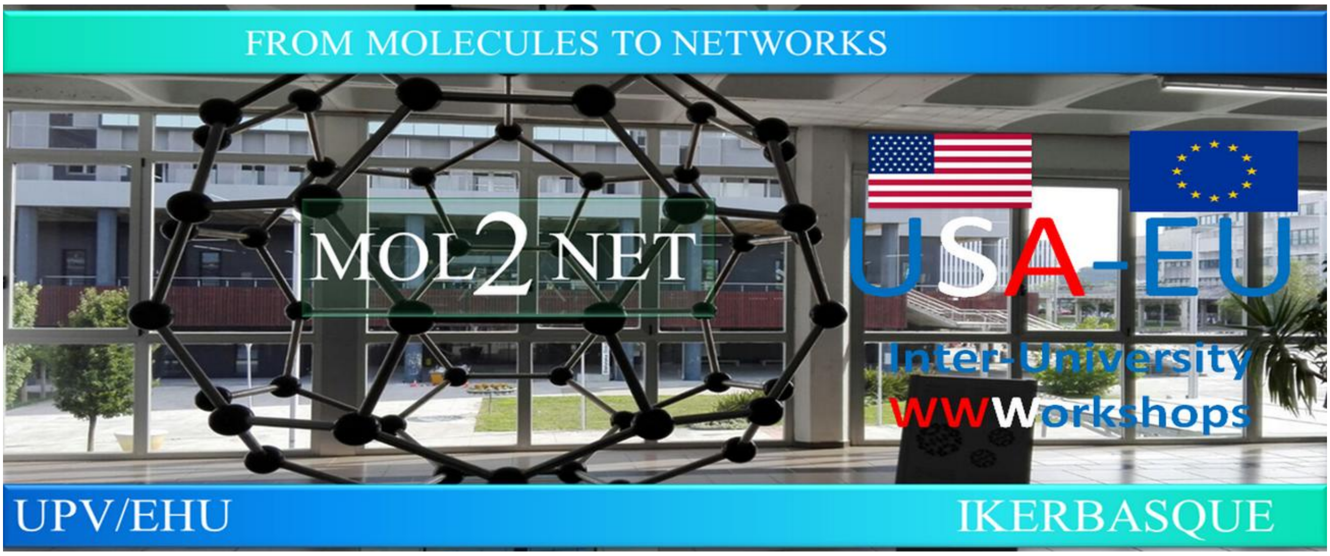

Rheological properties of bioinspired hybrid hydrogels

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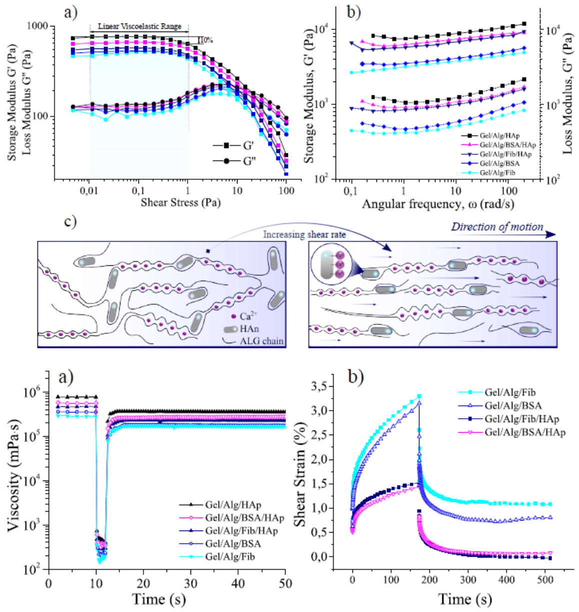
Graphical Abstract



Abstract

Hydrogels can display a wide variety of chemical and physical properties that enable them as nanostructured scaffolds for tissue engineering. Yet, single-component hydrogels have inherent limitations. To enhance and reinforce the versatility of the single component, different multi-component hydrogels have been designed and characterized. The influence of the nanoscascale of the systems on their macroscopic response was assessed, demonstrating that with a proper composition, multifunctional hybrid hydrogels can be optimally designed and successfully developed.

Discussion

The relationships between the viscoelastic properties of the films and the frequency are often found analyzing the results of the Frequency Sweep Measurements. At the specific temperature of 25 ºC the films present a gel-like behaviour because the storage modulus is bigger than the loss modulus [1]. This condition is constant for all the samples throughout the frequency domain studied. It can also be concluded that loss and storage moduli are dependent of the frequency, indisputable fact that has already been investigated in previous works [2]. Plots of Figure 1 are equivalent to the results achieved measuring soft glassy materials with a gel structure [3]. Needless to say, the modulus of every of the three samples presents firm nanoparticle concentration dependence. Both the loss and also the storage modulus are higher within the samples where the HAp has more concentration. This evidence was previously reported in several studies. [4] [5]. Additionally, it has been previously demonstrated that the Ca atoms present on the Hap interact with the oxygen sites of alginate [6] [7]. The CaOH site of HAp surface form bonds with the COO^- group of alginate. On the opposite hand, the HPO_4^{2-} groups don't interact with the biopolymer, especially the phosphate-hydroxyl active group [8]. Still, and gathering the knowledge, it's safe to assure that the alginate is successfully grafted on the HAp surface, ordering the nanostructure of the films. This reinforces the idea that the rheological behaviour of the material corresponds to a glass material, as it has been previously inferred from the dependence of the moduli with the frequency. The particle bonding to the polymer network has an instantaneous effect on the toughness, but it is not the unique factor, because it has been proved the content of nanorods is crucial also to the microstructures and thus the strength of the films [9].

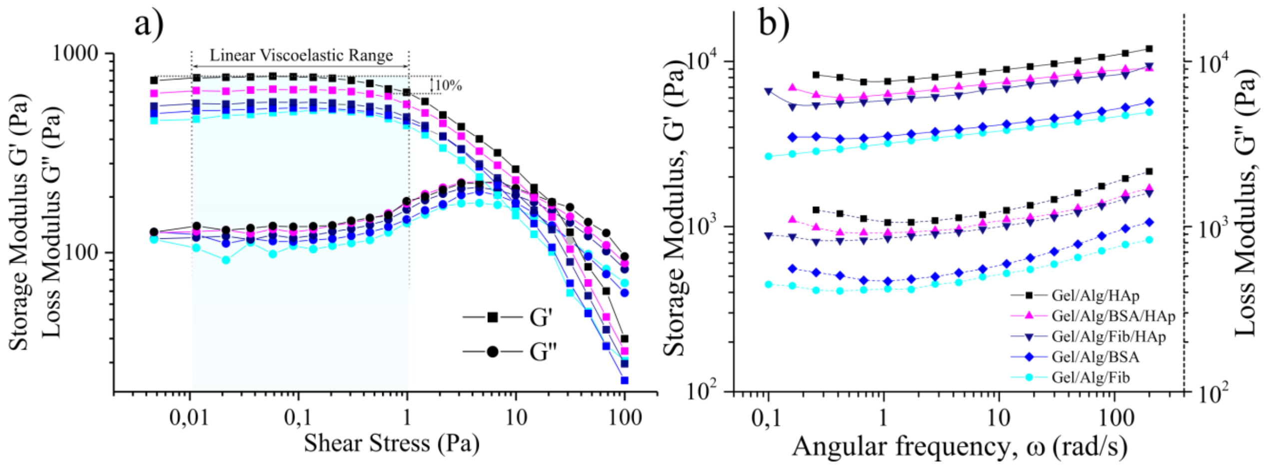


Figure 1. a) Linear Viscoelastic Range. b) Oscillatory frequency sweep.

Thixotropy is a non-Newtonian feature of certain fluids, in which the apparent viscosity decreases while a steady shear is applied; and it rises or falls when the shear rate is modified abruptly. In an identical way, while the shear is modified circularly, it causes the appearance of hysteresis loops, that are related to the energy loss [10]. The hysteresis area is very helpful for the evaluation of the degree of thixotropy [11]. Figure 1 shows the outcomes for the 3ITT exams at 25 ºC. The behaviour is similar for the five samples: in the first interval, viscosity values stay steady and within the third step the material shows a sensible thixotropic recuperation, 80%. It is typically assumed that the inner structure suffers modifications with the formation of aggregates with different crosslinking degree. When the shear is sufficient, the network is destroyed, turning the entanglements into monomers [12], however, when the implemented shear is paused, the network gradually rebuilds, meaning that the rate of disentanglement and the re-entanglement is slightly distinct, and therefore the thixotropic behaviour emerges.

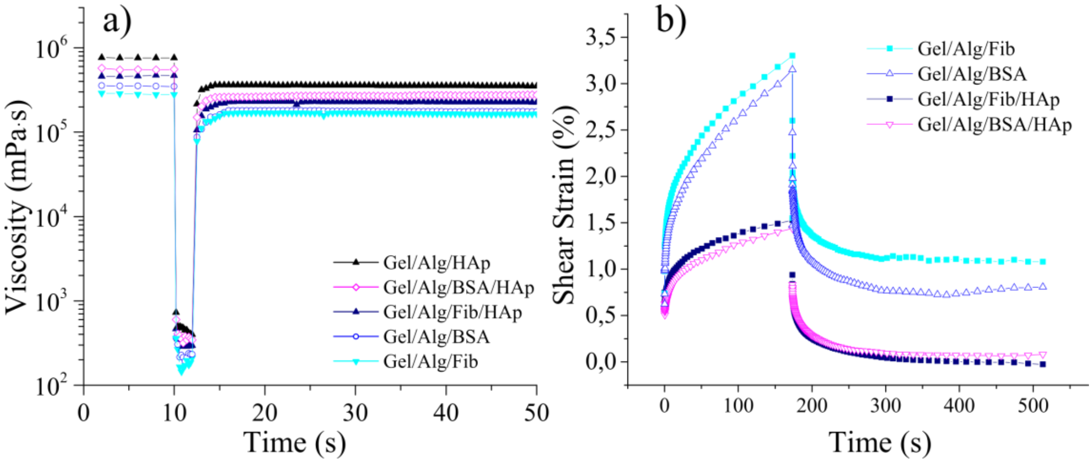


Figure 2. a) 3ITT test. b) Creep-recovery curves of the four studied samples.

Results acquired from the creep exams are depicted in Figure 2. Typically, creep curves follow a standard behaviour that may be separated in sections. Within the load phase, without delay after the beginning of the test, the deformation is solely elastic, resulting in a jump-like reaction and represents the immediate compliance. After that, a delayed viscoelastic reaction can be found and is related to the viscoelastic compliance. The values of compliance $J= \gamma/\sigma$, as a function of time are depicted in Figure 2 b). The time interval studied for all of the exams is: 0 to 173 s. The corresponding recuperation is studied for the interval $173 \leq t \leq 513$ s. Burger model was chosen to fit J=f(t) in the interval $0 \leq t \leq 173$ s. resulting in values of $r^2 \geq 0.98$. Calculated G_0, G_1, η_{zero} and η_1 parameters are shown in the following table:

Table 1. Values of the Burger model parameters.

	G_0 x 10^{-3} (Pa)	**η0 x 10^{-4}(Pa · s)**	**G_1 x 10^{-3}(Pa)**	**η_1 x 10^{-4} (Pa · s)**	**r^2**
Alg/Gel/BSA	5,62 ± 0,21	53,95 ± 2,22	6,52 ± 0,34	3,32 ± 0,49	0,986
Alg/Gel/Fib	4,64 ± 0,19	56,99 ± 2,81	5,97 ± 0,35	2,86 ± 0,47	0,980
Alg/Gel/BSA/Hap	9,29 ± 0,11	165,94 ± 5,32	12,21 ± 0,29	12,45 ± 6,95	0,997
Alg/Gel/Fib/Hap	7,75 ± 0,10	169,31 ± 8,17	12,01 ±0,40	10,51 ± 8,27	0,992

G_0 is lower for the gels without HAp. Furthermore, values of η_0, G_1 and η_1 are from two to three times lower to that found for the HAp-loaded samples. This fact and is in well accordance with the before verified assumption that the addition of the bioceramic reinforces the hydrogels network, contributing to strengthen them. On the other hand, differences found for the samples with BSA or Fib also prove previous results, telling that BSA-loaded samples have a better rheological performance due to the larger flexibility of this protein.

Conclusions

Rheological evaluation illustrates that the response of the studied gels is the typical found in soft glass materials. Creep analysis confirmed that the addition of nanorods to the inner network of the hydrogels reinforces their structure, strengthening them. It has also been proved that the addition of BSA causes an upgrading in the rheological behaviour. Ultimately, it has been demonstrated that the morphological and mechanical properties of this type of hydrogels can be effortlessly modified by means of including numerous additives, and consequently, offering better performances to tissue engineering applications.

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