MAGBIOMAT

Marie Curie Action Project 235673

“Study of magnetic responsive biopolymer based materials”

Summary of the main results

Introduction

The Marie Curie Action MAGBIOMAT aimed to elaborate and to characterize the structural and mechanical properties of new nanostructured magneto-responsive biopolymer-based materials.

To achieve these goals functionalized magnetic nanoparticles were synthesized and introduced in aqueous alginate sodium networks. The mechanical properties of these magnetic sensitive nanocomposites materials were then investigated by a new magnetorheological cell built up especially for the project.

Magnetorheological cell

The development of a specific device allowed the measurements of mechanical properties under continuous magnetic field in order to determine structure and dynamical properties at various external conditions as well as kinetics of structure transformation of such systems controlled by applied magnetic field. This device (Figure 1) consists of a mechanical part and a magnetic part. The former is a cone and plate geometry made on non-magnetic material. The latter is composed of two coils which are placed on both sides of the cone-plan geometry mounted on the rheometer with the bottom plate placed in the upper part of the lower coil. This Helmholtz configuration allows creating a homogeneous magnetic field perpendicular to the shear. An electric current of variable intensity between 0 and 25 A induces between the coils a magnetic field strength between 0 and 40.2 mT.

The temperature of the sample introduced on the bottom plate was controlled during rheological measurements by a first water circulation from a thermostatic bath.

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Figure 1: Magnetic cell

The high intensity flowing through the coils causes a large increase in temperature due to the Joule effect. In order to overcome this problem, the cooling of coils was achieved by a second water circulation with a set of pipes and flowmeters.

Every part of the magnetic cell (except the upper cone cell with long axis) has been developed in collaboration between MSC and PECSA laboratories.

The calibration curve between the applied current intensity and the magnetic field strength created by the coils was first determined.

Steady shear viscosity measurements of non magnetic standard oils was also carried out in the absence and presence of applied magnetic field in order to verify that the viscosity does not change with the application of the magnetic field. An example is given on Figure 2:

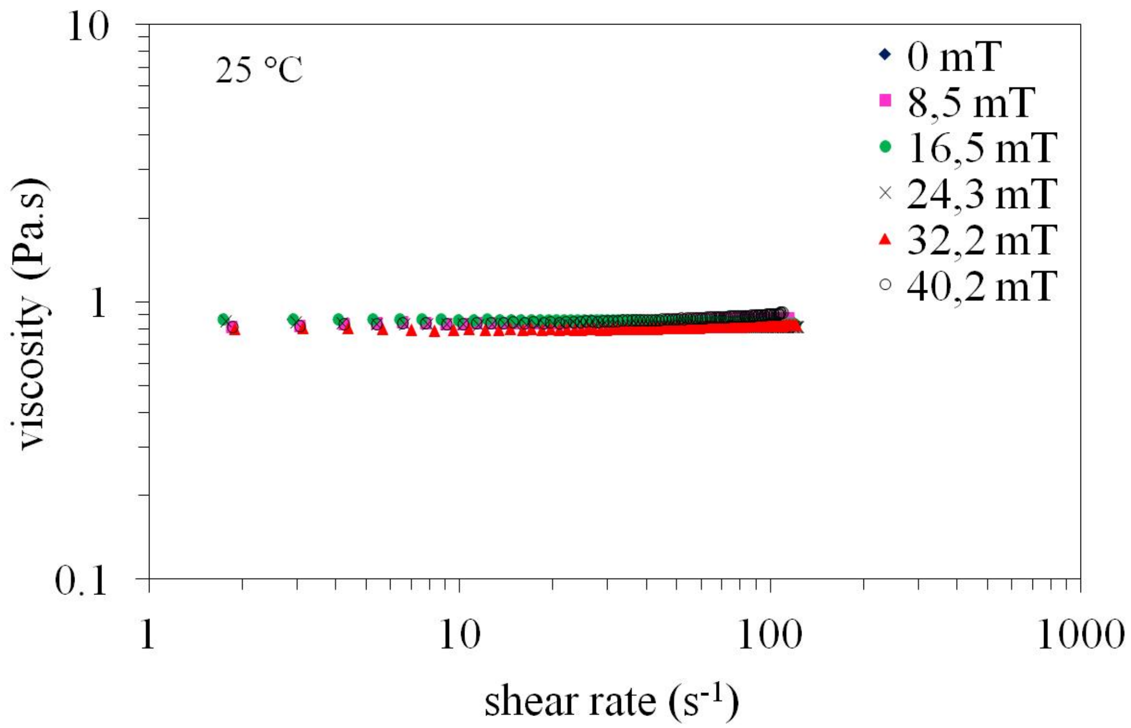

Figure 2: Viscosity as a function of the shear rate for the viscosity standard at different magnetic field strength

Characterization of ferrofluids

The magnetic nanoparticles were synthesized using a co-precipitation method. In order to obtain stable ferrofluids, citrate ions were adsorbed on the surface of the particles, by dispersion of sodium citrate in the solution.

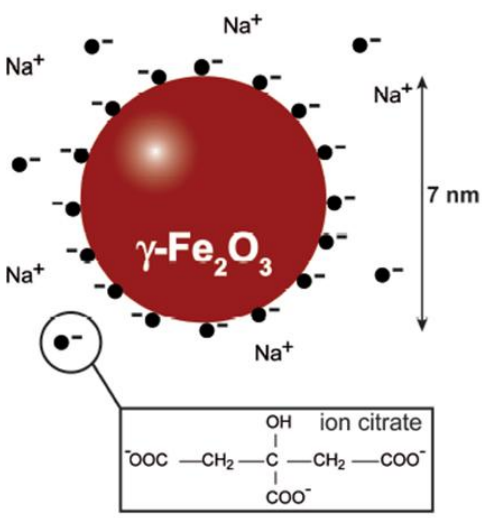

Figure 3: Maghemite nanoparticles functionalized by citrate ions

The citrated ferrofluids was characterized to obtain the volume fraction, the iron, sodium and citrate content, the particles isotropy, the ionic strength, the charge surface density, and the particle size and shape. The magnetic characterization was also carried out, and the magnetic properties were determined by means of the magnetization curves (Figure 4). In particular the magnetic susceptibility χ and the saturation magnetization m_s were computed from the linear part of the curve in the low magnetic field range and the constant value at high magnetic field values respectively.

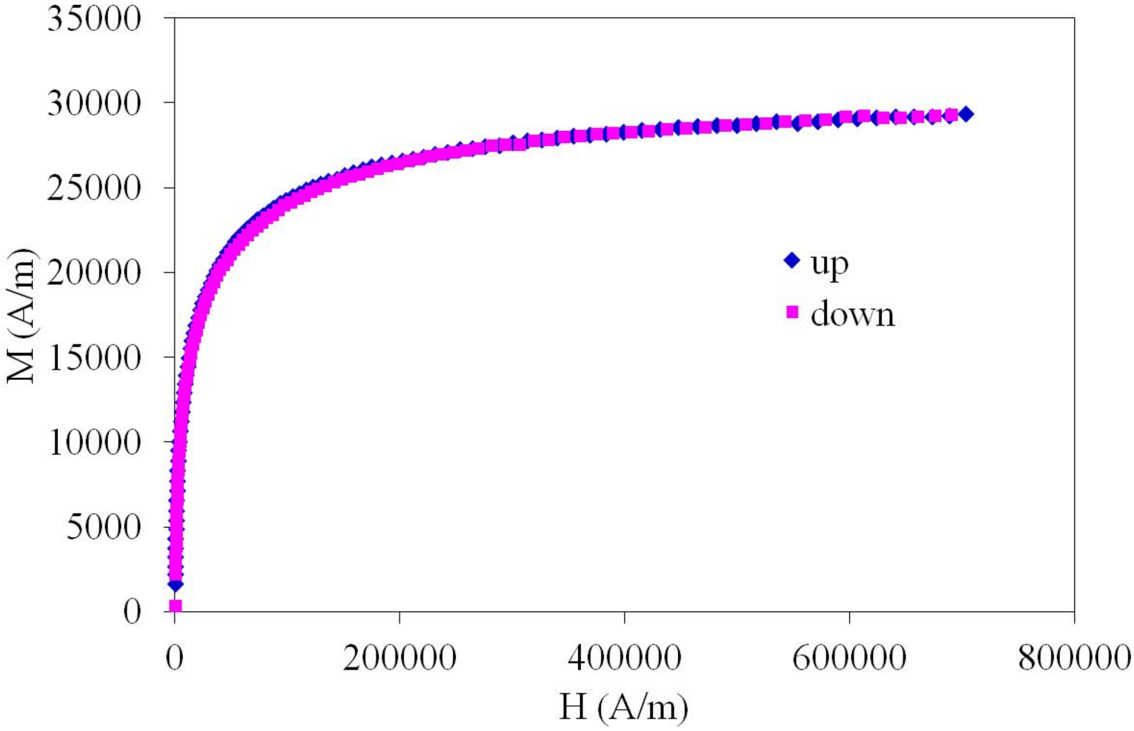

Figure 4: Ferrofluid (maghemite particles stabilized by citrate ions) magnetization curve. Volume fraction ϕ = 9,5%, magnetic permeability χ = 0,925, saturation magnetization m_s= 325342 A.m^{-1}

To study the rheological behaviour and the effect of an applied magnetic field in the mechanical properties of the ferrofluids, steady-state shear flow measurements at different values of the magnetic field strength was performed at constant temperature (θ = 25.0 ± 0.1 °C). The samples were subjected to a shear rate ramp between 20 and 500 s^{-1} and the corresponding shear stress and viscosity was recorded as a function of the shear rate (Figure 5).

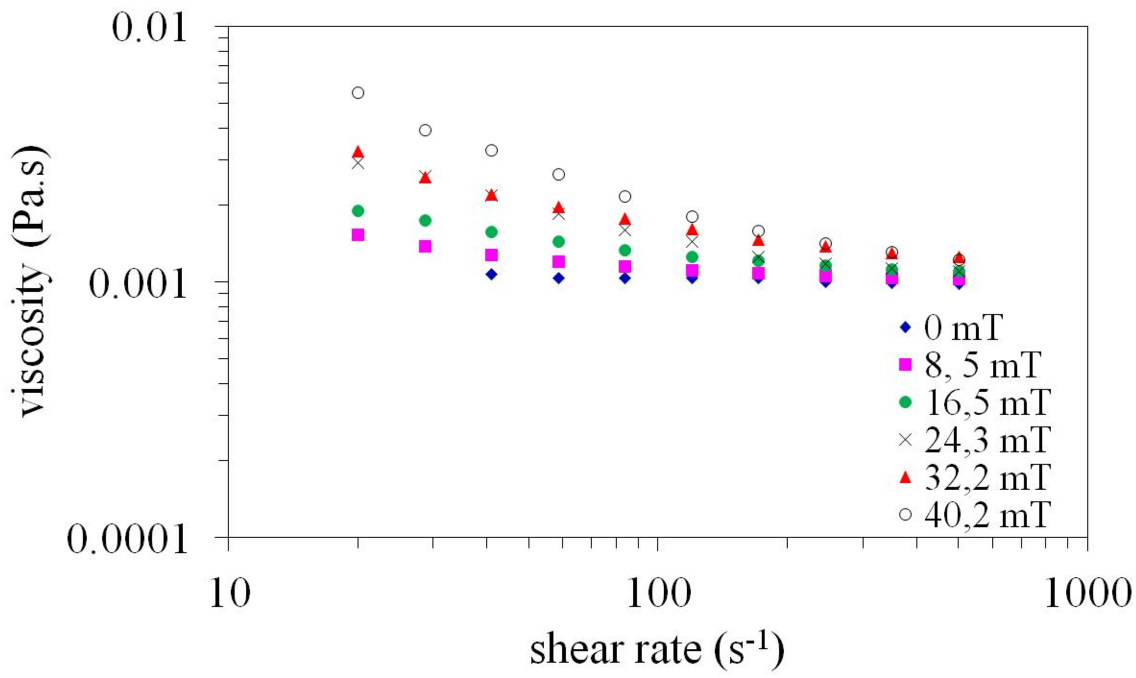

Figure 5: Viscosity as a function of the shear rate at different values of the magnetic field strength for a ferrofluid with ϕ = 3.47%

In the absence of the applied magnetic field, the behaviour is the typical one corresponding to a Newtonian fluid and the viscosity is constant within the studied range of shear rate. However, when the magnetic field is applied, a weak increase of the viscosity at low shear rate is observed. This behaviour could be explained by the under field deformation of microscopic droplets of magnetic liquid.

Alginate and ferrofluid solutions

The protocol of preparation of alginate and ferrofluid solutions was optimized and homogeneous solutions with different concentrations of alginate and volume fractions of ferrofluid were prepared. A volume of ferrofluid was added to an alginate solution and the mixture was stirred by means of a mechanical stirrer. The speed of stirring, the time and the temperature were carefully controlled.

The steady shear flow measurements of the prepared alginate and ferrofluid solutions were performed at various magnetic field strengths. In this case, the shear rate ramp was varied between 0.01 and 2000 s^{-1}.

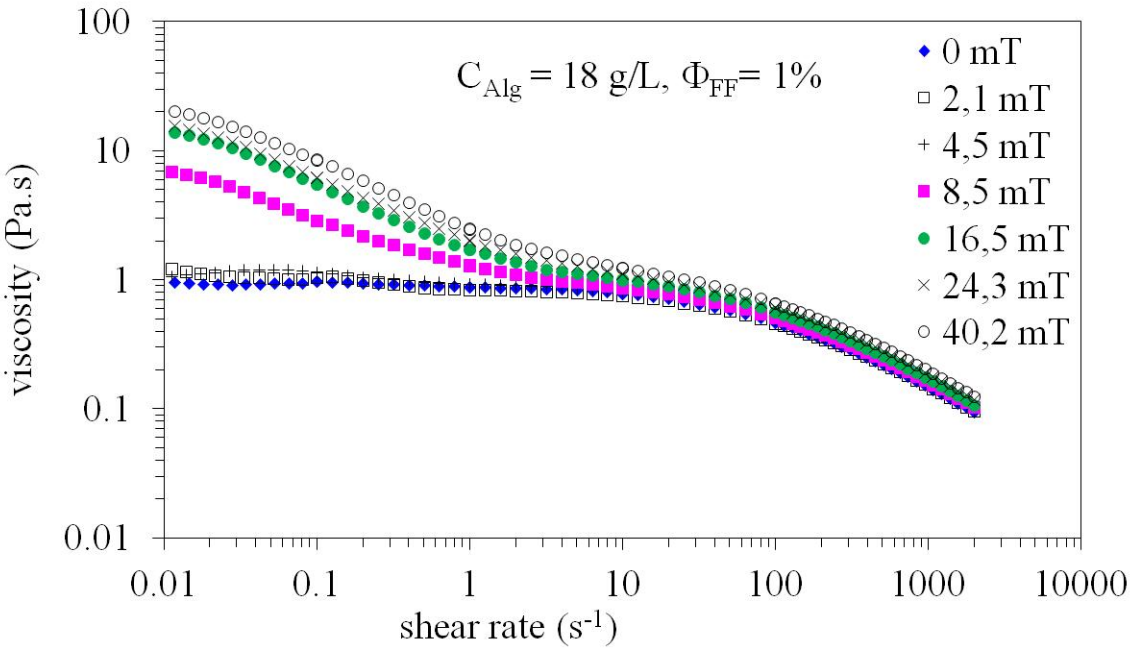

Figure 6: Viscosity as a function of shear rate at different values of the external magnetic field for an alginate and ferrofluid solution. C_{alg} = 18 g/L; ϕ_{FF} = 1%

The behaviour of the solution in the absence of an applied magnetic field is the typical one corresponding to a solution of entangled polymers. The first part of the curve shows Newtonian behaviour; the shear stress is too weak to modify the chains conformation and the viscosity remains constant. The second one corresponds to a decrease of the viscosity; the shear stress is more important and it can induce disentanglement of the polymer chains.

When the magnetic field is applied, the viscosity at low shear rate increases as the magnetic field strength increases. As in the case of ferrofluids, it means that magnetic field induced structures are formed as observed by optical microscopy (see below) with the increase of the magnetic field.

The analysis of these curves together with the magnetic parameters obtained from the magnetization curves provided the ratio between the viscous and magnetic forces, giving information about the structures formed in the solutions by the magnetic field and the breaking of these structures by the shear.

To study the viscoelastic behaviour, oscillatory measurements were performed. An oscillatory strain either at constant frequency and variable amplitude, or at variable frequency and constant amplitude was applied, and the storage modulus, *G'*, and the loss modulus, G'', were measured. The storage modulus, *G'*, is the real part of the complex rigidity modulus, G^*, that relates the sinusoidal stress and the sinusoidal strain, both in their complex form. *G'* is proportional to the storage power per volume unity in the suspension during a quarter of cycle. The complex part, *G''*, of the rigidity modulus is called loss modulus and it is proportional to the dissipated power by viscous friction.

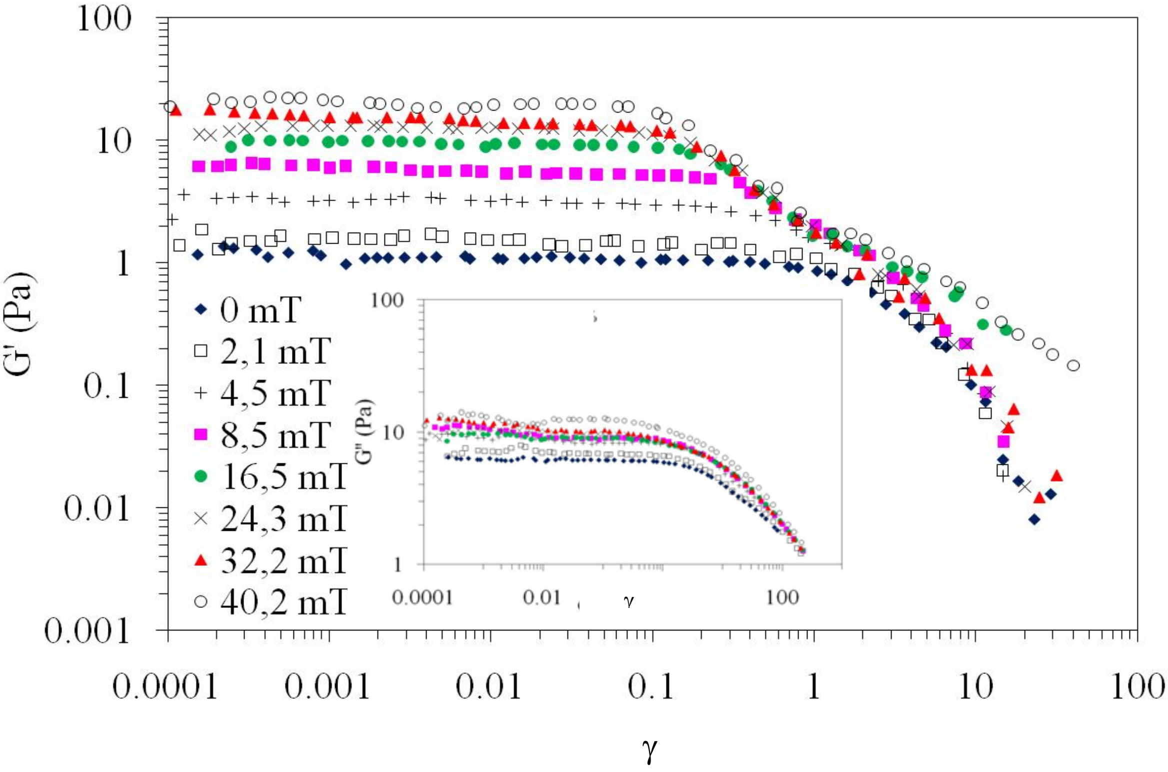

Figure 7: G' and G'' as a function of the strain amplitude at different external magnetic field for an alginate and ferrofluid solution. f = 1 Hz; C_{alg} = 18 g/L; ϕ_{FF} = 1%

It is clearly observed (Figure 7) that G' and G'' increase with the increase of the magnetic field in the linear viscoelastic region (part of the curve where G' and G'' are constant with the variation of the amplitude of the strain). The values of G' and G'' in the linear viscoelastic region have been plotted as a function of the external magnetic field (Figure 8).

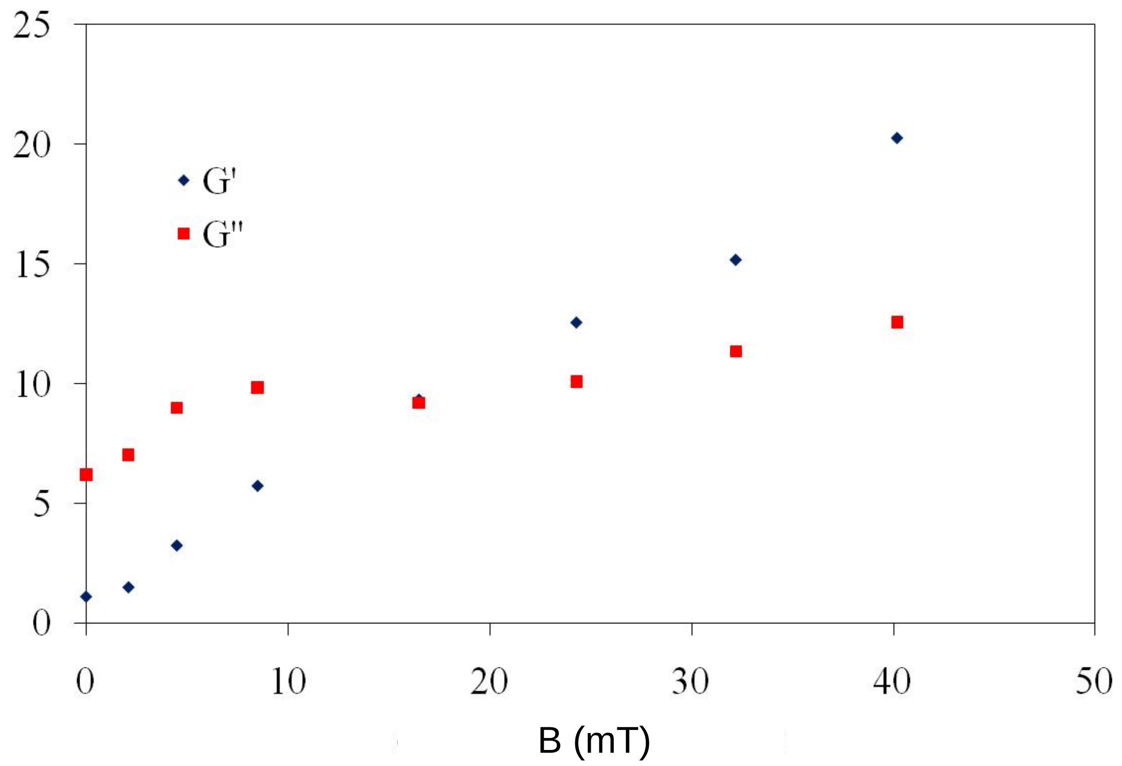

Figure 8: G' and G'' in the linear viscoelastic region (obtained from Figure 7) as a function of the external magnetic field

In the absence of applied magnetic field, G' is lower than G'', but as the magnetic field strength increases, the increase of G' is more important than the increase of G'' and G' becomes higher than G''. There is a change from a viscous state to an elastic state with the increase of the magnetic field strength.

A similar behaviour was observed in the oscillatory measurements at constant strain and variable frequency.

From the obtained results both in flow and oscillatory measurements, a magneto-viscous effect in the magnetic field-responsive nanocomposite biopolymer solutions was highlighted by an increase of both the shear viscosity at low shear rate and the linear viscoelastic modules when the external magnetic field is increased. This effect suggests the existence of magnetic field induced structures.

To study these structures that can be formed by the applied magnetic field, microscopic observations were carried out, using a microscopy slide which allows the application of a magnetic field during the observations. Two moving magnets were placed in slots, creating a magnetic field from 4 to 30 mT in the same range as for rheological measurements. In this way, microscopic observations of the alginate and ferrofluid solutions were performed in the absence of external magnetic field and when magnetic fields of different strengths are applied (Figure 9).

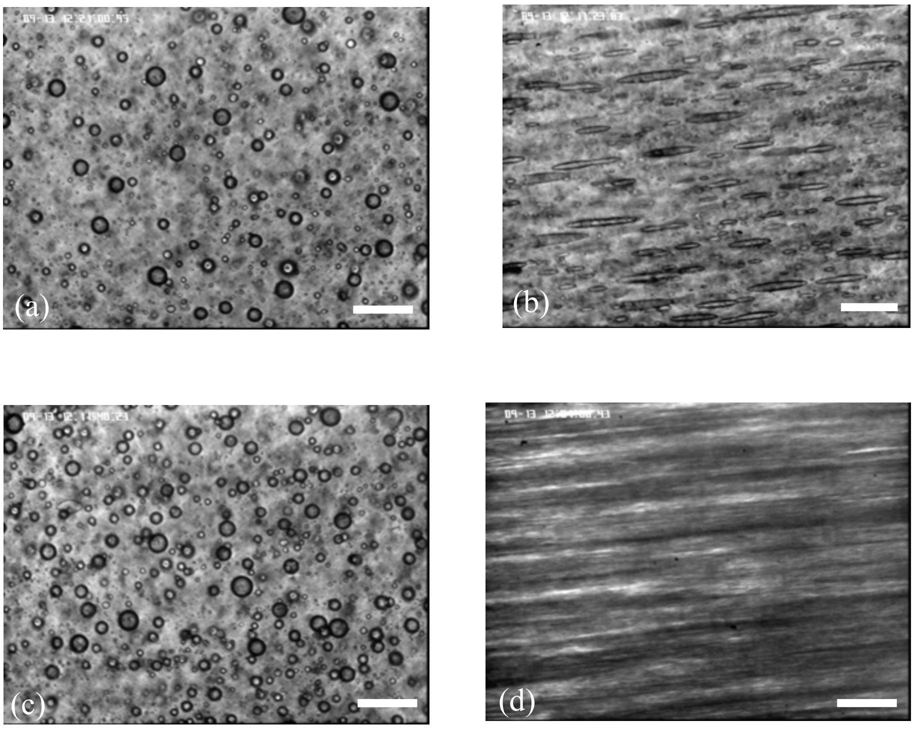

Figure 9: Microscopic observations of an alginate and ferrofluid solution. C_{alg} = 18 g/L; ϕ_{FF} = 1%. Bar length 100 μm (a) Initial state (t = 0) without magnetic field (b) final state B = 4 mT (c) initial state (t = 0) without magnetic field (d) final state B = 30 mT.

In the absence of applied magnetic field, spherical droplets of demixtion (regions with higher concentration of magnetic nanoparticles) are observed. These droplets are reversibly deformed under weak applied field magnetic. As the magnetic field increases the deformed droplets become to interact, inducing the formation of chain-like structures.

Alginate gel and ferrogels

Alginate sodium aqueous solution can form a gel by electrostatic interactions between divalent ions, such as Ca^{2+}, and carboxylate groups (COO^-) of polymer chains. There are several methods for gelation of alginate solution by adding calcium ions. We used the internal gelling method using EGTA-Ca as Ca source: EGTA-Ca was added and then calcium ions are released by slow acidification of the solution with Glucono delta-Lactone (GDL). This way, the release of calcium was controlled and the obtained gel was homogeneous. When preparing a ferrogel, the ferrofluid was added before starting the gelation process.

The gelation process was studied by shear oscillatory measurements at constant strain γ and constant frequency f without magnetic field and applying magnetic field for different concentrations of alginate and volume fractions of ferrofluid.

The gelation time t_g was first estimated by the crossover of both moduli as function of time (Figure 10).

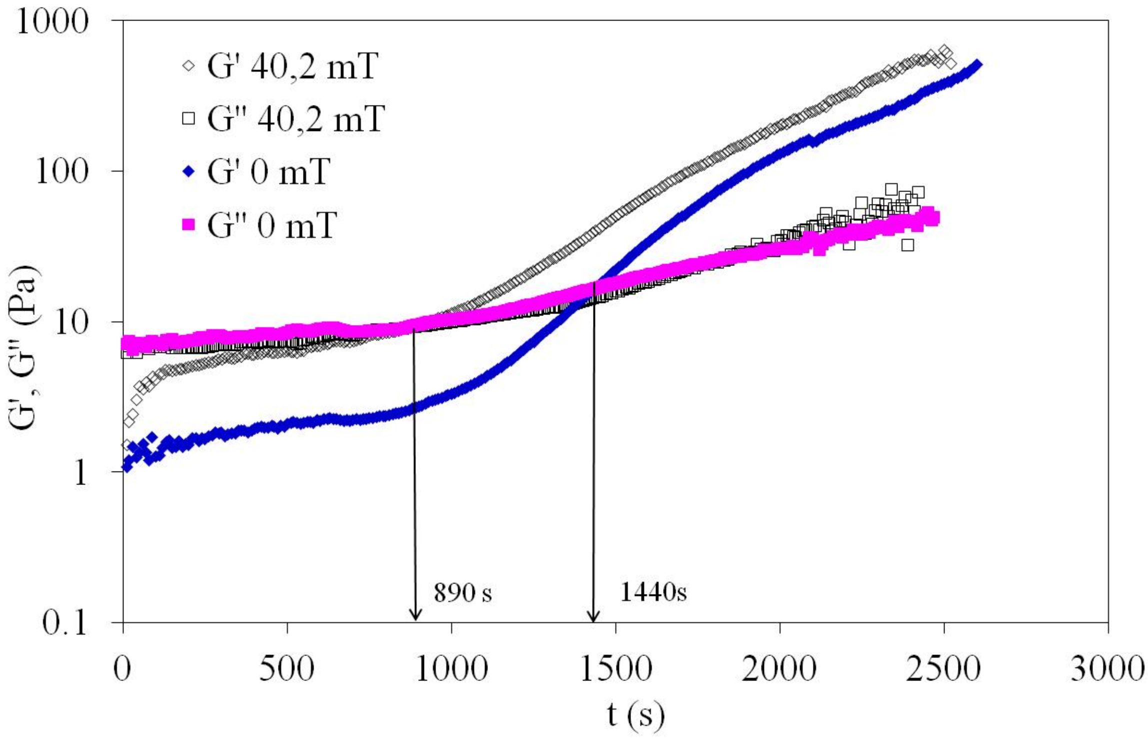

Figure 10: Determination of the gelation time for a ferrogel. Time dependence of G' and G''. C_{alg} = 18 g/L; ϕ_{FF} = 0.5%; f = 1 Hz; γ = 0.01; $[Ca^{2+}]/[Na^{+}]$ = 0.5

In the absence of the external magnetic field, the gelation time does not change significantly with the addition of the ferrofluid to the biopolymer network. However, when the magnetic field is applied, the increase of G' is faster and the gelation time is lower. This behaviour could be explained by enhance of the alginate network formation by the orientation of the demixion droplets.

If the volume fraction of the magnetic nanoparticles in the ferrogel is increased, the observed behaviour is similar. In the absence of the external magnetic field, the addition of the ferrofluid does not change significantly the gelation time. Nevertheless, the application of the applied magnetic field speeds up the gelation process and, for example, in the case of C_{alg} = 18 g/L and ϕ_{FF} =1%, the gelation is almost immediate.

Conclusion

This project was concerned with a first study of rheological properties under magnetic field of new nanocomposite biopolymers based on concentrated aqueous solutions of sodium alginate and functionalized magnetic nanoparticles of maghemite.

This study required the development of a magneto-rheological cell which allowed to perform temperature controlled flow and oscillatory shear measurements with the application of an external continuous magnetic field over the sample. A magneto-viscous effect in the magnetic field-responsive nanocomposite biopolymer network was highlighted by an increase of both the viscosity at low shear rate and the linear viscoelastic moduli when the external magnetic field is increased. Our results offered new perspectives of applications for these nanocomposites bio-based polymer networks.