

Probing the linear and nonlinear rheology of thermokinematically-trapped gels

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Many highly-structured gels commonly used in food-stuffs, bioengineering, and a wide variety of industrial applications (e.g., inks, paints and crude oils) display memory of the protocol used to achieve gelation [1–3]. As a result, their viscometric behavior, under both small and large deformations, is a function of the structural network established during gel formation, e.g. level of applied deformation and temperature history. Such systems therefore show what we refer to as *thermokinematic memory* [4]. Being able to characterize the evolution in material properties during gelation is of great importance and practical interest, although time-resolved rheometry may not always be practically feasible with available experimental techniques when the data acquisition time is greater than the characteristic timescale of mutation within the material [5].

In this paper, we consider a model thermo-reversible gel composed of a mixture of mineral oil and paraffin wax. Such a mixture is Newtonian above a critical temperature, established by the liquidus temperature at a given paraffin concentration (commonly referred to as the wax appearance temperature T_{wa}), while showing viscoelasticity as well as plastic yielding behavior below T_{wa} . The transition from a Newtonian fluid to a plastically-deformable gel, (also known as an elasto-visco-plastic (EVP) material), is due to the appearance of a loosely aggregated and percolated network of paraffin crystals with platelet-like shape (see Fig. 1 top), which interact via hydrodynamic as well as van der Waals forces. The importance of the underlying microstructure and its relationship with the resulting elasto-visco-plastic behavior observed below T_{wa} can be understood and quantified in terms of the microstructural morphology acquired during gelation as a function of both thermal and shear history [4].

Here, we present a detailed investigation of the effects that both temperature and deformation have on the linear and non-linear viscoelastic behavior measured during gelation (see Fig. 1). Using a novel experimental technique that we have developed to improve the temporal resolution of linear viscoelastic measurements, we study the evolution of the gel's complex modulus as a function of both cooling rate and shear rate. The protocol presented and developed for this particular material can be applied to study many different gel-like materials that show similar thermokinematic memory, and can be more generally adapted to investigate any time-evolving gel whose properties are changing due to either a controllable or a naturally occurring process (e.g., tunable external temperature, reaction-limited pH conditions). Finally, we present a theoretical framework that can be used to consistently describe the constitutive behavior of thermokinematic

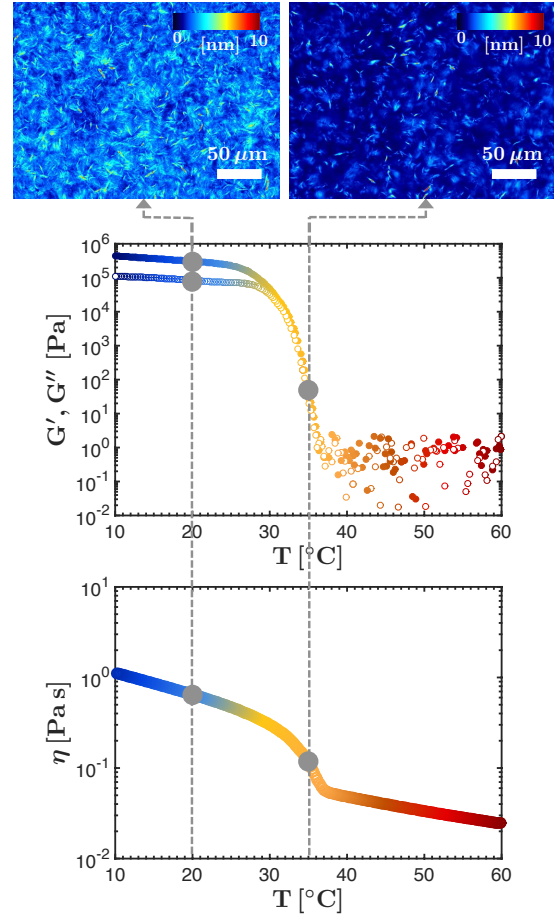


FIG. 1. From bottom to top: viscosity evolution as a function of temperature at constant cooling rate $\dot{T} = -1^\circ\text{C}/\text{min}$ and constant shear rate $\dot{\gamma} = 50\text{s}^{-1}$; evolution of viscoelastic moduli during gelation at the same constant cooling rate $\dot{T} = -1^\circ\text{C}/\text{min}$, $\omega = 1\text{rad/s}$ and $\gamma_0 = 0.1\%$; birefringence images of the gel microstructure under zero-shear conditions at different temperatures.

gels by directly accounting for both thermal and shear effects on the microstructural morphology.

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