Yield Stress Value Determinations of a Physical Gel

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ABSTRACT

Pluronic F127 solutions form gels in water with high elastic moduli. Pluronic gels can, however, only withstand small deformations and stresses. Different steady shear and oscillatory methods traditionally used to determine yield stress values are compared. The results show that the yield stresses values of these gels depend on test type and measurement time, and no absolute yield stress value can be determined for these physical gels.

INTRODUCTION

Block copolymers of ethylene oxide (E) and propylene oxide (P) in the form of $E_nP_mE_n$ copolymers, called Pluronics or Poloxamers are low toxicity compounds which are FDA approved for medical applications and used for delayed drug release. Copolymers are dissolved as single molecules, unimers, in water at low temperatures but form micelles, with a core of P-chains and a mantle of E-chains, at higher temperatures.[1,2] At higher concentrations and temperatures some Pluronic solutions form thermo-reversible physical gels. These gels consist of liquid crystals of packed either spherical or rod-like micelles.[1,2] In this paper we have investigated rheological properties of Pluronic F127, also known as Poloxamer 407, which has a composition $E_{99}P_{69}E_{99}$. This copolymer forms both bcc and fcc liquid crystals[3] and has been used in many pharmaceutical applications.[4]

To prevent flow in blood vessels and other materials the gels must have a yield stress, σ_y. At low applied stresses materials deform elastically, and flow only occurs when the applied stress, σ, exceeds the yield stress

$$\sigma > \sigma_y \qquad (1)$$

The existence of a yield stress has been much debated since Barnes and Walters[5] concluded that no liquids exhibit a yield stress. Improved instrumentation enabled them to perform measurements on several systems at lower shear rates and they observed Newtonian flow at low shear rates and thus no yield stress. Nonetheless yield stresses are very important in many technical applications. Paints need a yield stress to maintain stability of pigments in suspensions and to prevent flow or sagging of paints on a wall. In many other structured liquids sufficient yield stresses ensure stability of suspensions.[6] In the food industry yield stresses are important in e.g. yoghurt and jams.[7]

In a previous publication[8] we demonstrated that another Pluronic P104 forms gels, and we demonstrated that both the storage modulus and the yield stress, determined from steady shear stress ramps, depend linearly on concentration. Both steady shear stress ramps and oscillatory stress ramp techniques can be used to determine yield stress values.[9] In this study we have investigated rheological properties of Pluronic F127 gels and compared different techniques which are used to determine yield stresses. Yield stresses can be determined by applying increasing steady shear stresses to gels in order to determine at which stress flow occurs. Alternatively yield stresses can be determined from oscillatory experiments by applying increasing stress amplitudes. It will be shown that absolute yield stress values cannot be determined since they depend on which technique is used and the time involved in the determinations.

MATERIALS AND METHODS

Pluronic F127 was purchased from BASF and used as received. F127 was dissolved in Millipore water overnight under gentle shaking at 5 °C. Concentrations are given as w/w%.

The gelation of F127 solutions with concentrations between 15 and 30 wt% was monitored by small amplitude oscillatory deformations at 1 Hz using a Bohlin VOR rheometer with a C14 couette cell. Solutions were measured between 10 and 50 °C at a heating rate of 1°C/4min. In oscillatory experiments the storage modulus, G', and the loss modulus, G", were determined at an angular frequency, ω, and strain amplitude, γ_0, from the time dependence of the stress

$$\sigma(t)=\gamma_0(G'\sin\omega t + G''\cos\omega t) \qquad (2)$$

Yield stress values in steady shear were determined by use of a Haake RS100 instrument with a Z20 couette measuring cell. Degassed F127 solutions were loaded into the cell at 10 °C. The temperature was then increased to 37 °C, and after 20 min of thermal equilibration a steady stress ramp from 1 to 440 Pa was applied in either 100, 300 or 1000 s tests.

Yield stress values were also obtained from oscillatory measurements at 1 Hz with increasing stress amplitudes from 1 to 440 Pa.

RESULTS

F127 solutions behave like fairly low viscosity Newtonian liquids at 10 °C, as observed for P104.[8] When solutions are heated gels with G' >> G" are formed at temperatures which decrease with increasing concentration.[3] For the present study a concentration of F127 with a gelation temperature just above room temperature was ideal. 20 wt% solutions form gels above 21 °C and this concentration was used for all measurements. Solutions in the rheometer cell were heated to 37 °C and allowed to thermally equilibrate.

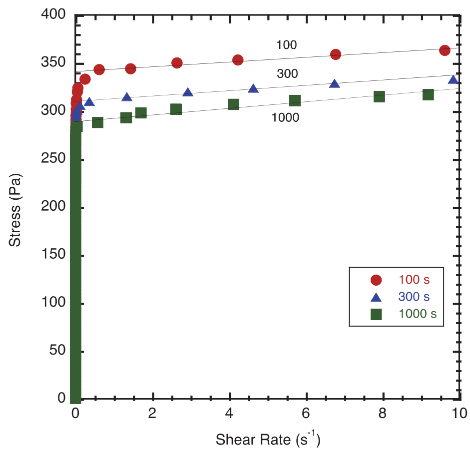

Figure 1. Steady shear stress ramps on 20 wt% F127 at 37 °C. Stress ramps from 0 to 440 Pa in 100 s (circles); 300 s (triangles); 1000 s (squares).

The result obtained when stress ramps to 440 Pa are applied is shown in Fig. 1 as stress against shear rate. The figure shows that the shear rate is virtually zero at small stresses and the data follow the simple Bingham liquid model

$$\sigma = \sigma_y + \eta_b \dot{\gamma} \quad (3)$$

quite well, where η_b is the Bingham viscosity. The yield stress, determined as the intercept at zero shear rate, is seen to depend on ramp rates. Lower yield stress is observed when the maximal stress of 440 Pa is reached in 1000 s.

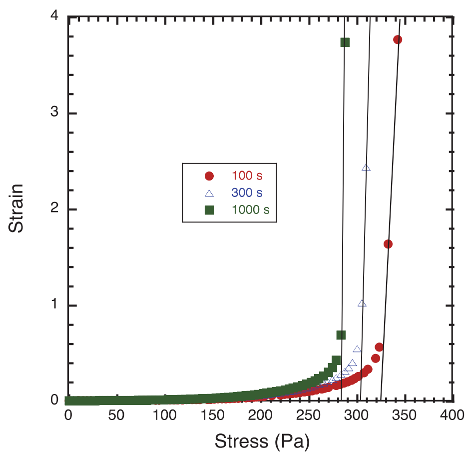

Figure 2. Steady shear stress ramps on 20 wt% F127 at 37 °C. Stress ramps from 0 to 440 Pa in 100 s (circles); 300 s (triangles); 1000 s (squares).

The same experimental data can also be plotted as strain versus stress, as shown in Fig. 2. The three tests exhibit a linear strain dependence on stress at low stresses, onset of non-linear behavior, followed by flow at the highest stresses. Another estimate of a yield stress is obtained by linear extrapolation of strains between 1 and 4. It is seen that these yield stresses also depend on the stress ramp rates, and that the values are dependent on which strain range is used for the extrapolation.

Oscillatory stress sweep at 1 Hz is shown in Fig. 3. G' and G" are only strictly defined in the linear viscoelastic range, where they are independent of stress amplitude (see Eq. 2). The figure shows that G' and G" are constant up to at most a stress amplitude of 100 Pa, and that the value of G' at small stresses is 18 kPa. At larger stress amplitudes G' decreases and G" has a maximum, and at the highest stress amplitudes G" dominates. The yield stress is often determined from the G'-G" cross-over stress which occurs at 240 Pa in Fig. 3.

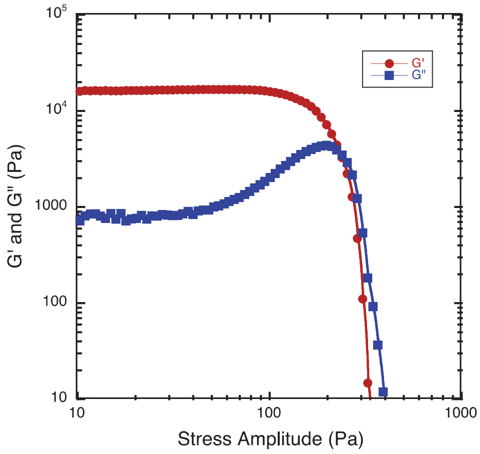

Figure 3. Stress amplitude sweep at 1 Hz on 20 wt% F127 at 37 °C. Apparent storage modulus (circles); apparent loss modulus (squares).

The same oscillatory data in Fig. 3 can also be plotted as strain amplitude against stress amplitude, as shown in Fig. 4. At low stresses on the log-log plot the linear range is seen with a slope of unity. At intermediate amplitudes strain softening is seen, followed by large strain increase during flow. The intercept of the linear regions can be taken as an estimate of the yield stress.[8] The value of 250 Pa is close to the value of 240 Pa determined in Fig. 3. Repeated stress amplitude sweeps on the same solution gave identical moduli and curves. This oscillatory test is therefore non-destructive and the gels are self-healing even after large strain amplitudes.

DISCUSSION

20 wt% F127 solutions form gels at 37 °C with moduli of 18 kPa. However, these

gels can only withstand small stresses or deformations. Figs. 3 and 4 show that non-linear behavior is seen at strains above 0.3% and stresses above 100 Pa. Yield stresses can be determined in several ways from both steady shear and oscillatory measurements. However, values depend on the technique and analysis used. Time scale is also important as shown in Fig. 1, where yield stress values vary between 280 and 340 Pa depending on ramp rate and time of measurement. F127 forms physical gels without any covalent crosslinks between micelles and are therefore expected to be liquids. Whether they exhibit a yield stress is therefore questionable,[5] but inverted tube tests over two months in an oven at 37 °C showed no signs of flow, so from a practical point of view they exhibit a yield stress.

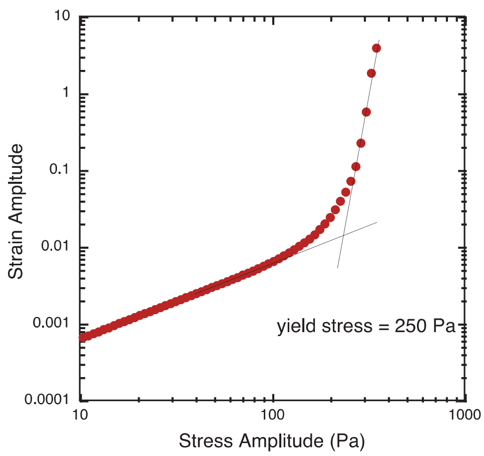

Figure 4. Stress amplitude sweep at 1 Hz on 20 wt% F127 at 37 °C. Apparent strain amplitude is plotted against stress amplitude.

ACKNOWLEDGMENTS

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