Journal of Non-Newtonian Fluid Mechanics 206 (2014) 40–56

Contents lists available at ScienceDirect

Journal of Non-Newtonian Fluid Mechanics

journal homepage: http://www.elsevier.com/locate/jnnfm

Large amplitude oscillatory shear of supramolecular materials

Alan Ranjit Jacob [a,1], Abhijit P. Deshpande [a,*], Laurent Bouteiller [b]

[a] Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, India
[b] Institut Parisien de Chimie Moleculaire (IPCM), UMR 8232, Chimie des Polymeres, Universite Paris 6-CNRS, 3, rue Galilee, Ivry sur Seine 94200, France

ARTICLE INFO

Article history:
Received 8 March 2013
Received in revised form 24 February 2014
Accepted 1 March 2014
Available online 12 March 2014

Keywords:
Large amplitude oscillatory shear
Supramolecular polymer
Giesekus model
Transient network model
Secondary loops in Lissajous plots

ABSTRACT

Large amplitude oscillatory shear [LAOS] helps to investigate non-linear rheology and the dynamic behaviour of materials when subjected to large deformations. Qualitative characterization of non-linear rheology can be easily done but quantification and physical interpretation of non-linear rheological characteristics is one of the most challenging aspects. In this work, LAOS tests are done on different materials generally known as 'living polymers', with similar linear response, in order to study their non-linear response using both quantitative and qualitative analysis. The effect of living polymer networks on LAOS was examined using different concentrations of 2,4 bis(2-ethyl hexyl ureido)toluene [EHUT] gels. Cetyl trimethyl ammonium bromide [CTAB] wormlike micellar solution is prepared to compare and contrast with EHUT gels since both these materials show similar linear viscoelastic response. Elastic loading/unloading and plastic deformations are identified as important processes that lead to the distinguishing behaviour for different materials. An equivalence is observed for Lissajous plots in the concentration frequency plane for EHUT. Giesekus model and Upper Convected Maxwell model coupled with transient network model [TNM], two well established models, are solved numerically for comparison with the experimental results. A modification of the Giesekus model to incorporate the network breakage/reformation as a linear function of strain amplitude, and nonlinear function of strain rate within an oscillation period is suggested. The proposed model is able to capture the competition between reptation, network breakage and reforming during LAOS. Moreover, the modified model suggests that the secondary loops during LAOS for EHUT gel occur soon after yielding due to competition between the network breaking and reforming at high shear rates and reptation at low shear rates within a cycle.

1. Introduction

Supramolecular assembly of molecules is being increasingly used to obtain material systems with controlled properties. These assemblies can be from small molecules as well as from polymers [1–3], and are promising for diverse applications. Supramolecular polymer gels are assembled as networks of one-dimensional objects formed from interactions among small molecules. In a supramolecular polymer, repetitive arrangement of monomeric units is brought about by highly directional and reversible secondary interactions [4,5]. These secondary interactions can be hydrogen bonds, metal-coordination bonds, π–π interactions, van der Waals forces and dispersion forces. Unlike the covalently bonded polymers, the supramolecular polymers break and reform, and are also called *living polymers*. In general, the dynamic characteristics of networks and their role in rheological behaviour are studied for varied applications. The network formation in supramolecular polymer gels and their behaviour under different conditions have also been of wide interest. Therefore, rheology of supramolecular polymer gels is important not only for studying the deformation behaviour, but also to probe the network structure.

2,4 bis(2-ethyl hexyl ureido)toluene [EHUT], an organic gelator, has been shown to form tubular equilibrium aggregates in solvents such as dodecane [6]. The molecular structure of the EHUT monomer and the tubular aggregate are shown in Fig. 1 [7,8]. The hydrogen bonding between the amide groups and oxygen, represented by the dotted lines, is responsible for the aggregation. The tubular structures shown in the figure form entanglements/meshes which entrap the dodecane solvent [6,8]. It is also known that EHUT does not form these tubular structures in bulky solvents [9]. EHUT has been investigated for applications such as drag reducing agent and hardener for asphalt [10–12]. Supramolecular polymers, such as EHUT gels, have been characterized using rheological techniques like steady shear and dynamic oscillatory shear tests [6,13–15]. The linear viscoelastic response of the gels was shown to be similar to the Maxwell model. EHUT gels are similar to wormlike micelles

* Corresponding author. Tel.: +91 44 22574169; fax: +91 44 22574152.
E-mail address: abhijit@iitm.ac.in (A.P. Deshpande).
[1] Current Address: FORTH-IESL, 71110 Heraklion, Crete, Greece.

http://dx.doi.org/10.1016/j.jnnfm.2014.03.001
0377-0257/

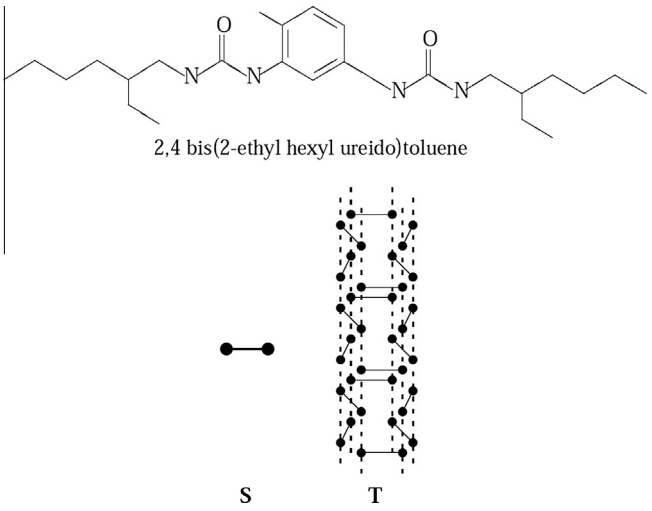

Fig. 1. The molecular structure and the predicted microstructural thick filament structure (T) formed from each of the mono-meric units (S) where both of the systems are thermodynamically stable [7,8] The amide group is represented as a filled circle and the dotted lines represent the hydrogen bonds.

as they tend to undergo scission and recombination. Static and dynamic properties of the wormlike micellar systems have been exhaustively studied [16,17]. The similarities of EHUT and wormlike micellar systems are in linear rheology as well as non-linear rheology. At high shear rates, a non-monotonic rise of the stress with respect to shear rate has been observed. This behaviour and associated shear banding have been reported for both micellar solutions and EHUT [18,19].

While small amplitude oscillatory shear [SAOS] is used to probe the linear response of complex fluids, the non-linear behaviour of complex fluids can be investigated using large amplitude oscillatory shear [LAOS]. Large volume of research is going on to develop frameworks to quantify non-linear behaviour of materials and model such non-linear behaviour. LAOS has been investigated for many materials like entangled polymer systems, suspensions, emulsions, polymer blends, block copolymer melts and gels [20]. Fourier transform is one of the oldest techniques for analysis of LAOS data but it is difficult to provide physical interpretations of material behaviour with this method [21,22]. Lissajous plots is one of the methods to qualitatively analyse LAOS behaviour [23–26]. One of the quantitative methods to analyse LAOS data was using G'_L and G'_M, derived from Chebyshev polynomials and can provide physical insights to viscoelastic material behaviour at LAOS [20,24]. Recently, analysis of data from strain, strain rate and stress space has been used to define new material functions to describe the physical processes during LAOS [27–30]. The appearances of the secondary loops in the Lissajous plots are due to specific changes in the microstructure of the material investigated [31] and have been investigated using constitutive models such as the Giesekus model.

In the present work 'living polymers' based on EHUT and CTAB, which have similar linear rheological response are shown to be exhibit rich variety of LAOS response, due to different microstructural processes occuring during a cycle. An extensive characterisation of the non-linear rheological response of EHUT using LAOS is performed in order to gain insights into the development of 'secondary loops' appearing in the Lisajous plots. A concentration frequency equivalence is explored with the Lissajous plots. A microstructural hypothesis is offered with the help of these non-linear experiments, which is further reinforced by modelling the EHUT response during LAOS with modifications to the Giesekus model. The results provide a platform and future directions for the understanding of non-linear rheology of 'living polymers'.

1.1. Material models relevant for LAOS

Many models have been used to examine the LAOS response, which include upper convected Maxwell, Giesekus [20,31], transient network model (TNM) [32], Leonov [33], molecular stress function (MSF) [34], corotational Maxwell [35] and Doi Edwards model [36]. A single relaxation mode as well as the relaxation spectrum has been used.

The Giesekus model is written for polymer and solvent contributions to overall stress ($\boldsymbol{\tau}_p + \boldsymbol{\tau}_s = \boldsymbol{\tau}$, respectively) [20,23,37–40].

$$\lambda_1 \overset{\nabla}{\boldsymbol{\tau}}_p + \left(1 + \frac{\alpha\lambda_1}{\eta_p}\boldsymbol{\tau}_p\right)\boldsymbol{\tau}_p = 2\eta_p \mathbf{D}, \tag{1}$$

where $\mathbf{D}$ is the strain rate or stretching tensor, λ_1 is the characteristic relaxation time, η_p is the viscosity coefficient, α is the non-linear parameter or mobility factor, and $\overset{\nabla}{\boldsymbol{\tau}}_p$ is the upper convected derivative. The solvent contribution to stress tensor is

$$\boldsymbol{\tau}_s = 2\eta_s \mathbf{D}. \tag{2}$$

This non-linear model has been used for LAOS extensively. The Giesekus model material functions for SAOS are given by,

$$G' = \eta_o \omega^2 \left(\frac{\lambda_1 - \lambda_2}{1 + \lambda_1^2\omega^2}\right), \tag{3}$$

$$G'' = \eta_o \omega \left(\frac{1 + \lambda_1\lambda_2\omega^2}{1 + \lambda_1^2\omega^2}\right). \tag{4}$$

where $\eta_0 = \left(\eta_s + \eta_p\right)$ and $\lambda_2 = \lambda_1\left(\eta_s/\eta_p\right)$ is the retardation time [41]. Giesekus model reduces to the TNM model, when $\alpha = 0$ in Eq. (1),

$$\boldsymbol{\tau} + \lambda_1 \overset{\nabla}{\boldsymbol{\tau}} = 2\eta_0 \mathbf{D}. \tag{5}$$

The SAOS Maxwell model material functions are given by substituting $\lambda_2 = 0$ in Eqs. (3) and (4). The TNM model has been used to study LAOS, for example the start up flows in Couette geometry [42].

In order to capture the variation in the *dynamic networks*, formation and breakage of *network points or bonds* is hypothesized. A structural parameter quantifies the status of the network. This variation in networks is captured by writing an evolution equation for the structural parameter. Such a model was used for LAOS, along with the TNM model [32],

$$\frac{dx}{dt} = \frac{f_1}{\lambda_1}(1 - x) - f_2 x[II_{\mathbf{D}}]^{(1/2)}. \tag{6}$$

where x is the structural parameter. In this equation, f_1 represents the rate of creation of network points, while f_2 includes the breakage of these network points and the effect of shearing is included by $\dot{\gamma}$, ($= II_{\mathbf{D}}$, second invariant of $\mathbf{D}$). $x = 0$ implies that the network has completely broken down and $x = 1$ implies the network in the undeformed state. Such an evolution equation is combined with TNM by assuming the parameters of TNM to be functions of x,

$$\lambda_1 = \lambda_1^o x^{1.4}. \tag{7}$$

where λ_1^o is the relaxation time, when no shear is applied or the relaxation time of undeformed network. Hence the structural parameter which is governed by the breaking and reforming of the bonds when coupled with TNM model, is able to capture the temporary nature of networks in the non-linear regime [32].

Another important aspect in the non-linear modelling of material systems, during LAOS, is the effect of yielding of materials. Models incorporating yield stress and yield strain have also been used to analyze LAOS response [43]. Rigorous and generalized models incorporating the effect of maximum applied strain, on