Ink-Jet Printing of Polymer Solutions in the Semi-Dilute Regime

Desheng Xu, Veronica Sanchez-Romaguera, Silvia Barbosa, Will Travis, Jos S. de Wit*†*, Paul Swan*† *and Stephen G. Yeates*,

Organic Materials Innovation Centre, School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom

(†) Eastman Chemical Company, European Technical Centre, Knowsley Industrial Park, Kirkby, Liverpool, United Kingdom, L33 7UF

Abstract

The influence of polymer concentration on going from the dilute through the overlap into the concentrated regime during drop on demand inkjet printing is investigated for a range of cellulose ester (CE) polymers from visual examination of ligament stretching as a function of applied wave form. The physical behaviour of the fluids in drop formation is indicative of the dominance of viscoelastic effects within the timescale of the process, in preventing ligament breakup at the pinch point compared with a glycerol / water / iso-propanol blend Newtonian fluid of similar viscosity. When formulated at the overlap concentration all polymers showed qualitatively similar behaviour with respect to time and length of ligament at rupture irrespective of polymer molecular weight. Beyond the overlap concentration the ligament rupture times continue to increase with increasing elasticity of the solutions but the ligament rupture lengths decrease rapidly. In this regime coil overlap and entanglement effects become increasingly important, dramatically increasing the elastic nature of the ligament. It is proposed that in the case of weakly associating polymers such as cellulose esters, the effective relaxation time is further increased due to the possibility that on chain extension intramolecular H-bonds are broken and may reform in the extended form as intermolecular associations. These intermolecular associations act as physical crosslinks, thereby creating a transient gel structure. Because these associations are transient in nature, this gel structure is capable of having a finite large viscosity. Once the strain is removed the gel will decay as the chains return to the more thermodynamically stable coil state.

Introduction

Ink-jet printing has developed as an important technology for the defined spatial deposition of polymer solutions in applications as diverse as graphics, textiles, digital electronics and displays(1-6). For many emerging opportunities the necessity to increase the concentration of polymer in the deposited fluid is of growing importance in order to maximise either material throughput and/or functionality. However the addition of polymer to an ink-jet ink has a strong impact on the nature of the drop generation and ejection process (7-13).

The influence of added polymer on drop formation and filament break-up has been studied as a function of both concentration, typically in the dilute regime up to the overlap concentration, c*, molecular weight and architecture. Four different regimes have been observed in inkjet drop generation behaviour as a combined function of concentration and molecular weight. The first regime occurs at either very low concentrations and/or molecular weight, where a long tail is formed that simultaneously breaks up along its axis to form several satellite droplets. This regime can often be a highly chaotic and irreproducible in nature, leading to poor print quality. The second regime occurs upon increasing concentration or molecular weight when only a few satellites appear at the tails end. Raising concentration or molecular weight further yields a single droplet without a tail, regime 3. This regime provides optimum print quality. Finally at high concentration or molecular weight the polymer solution becomes highly visco-elastic and the droplet does not detach and returns into the nozzle, regime 4. The concentration and molecular weight range over which the four regimes are identified is highly dependant upon the nature of the polymer, its molecular weight, architecture and the nature of the solvent.

It has been proposed that drop break-up behaviour is in part related to the strain hardening resulting from the presence of polymer at high strain rate (8-10, 12). This extension occurs at a strain rate which has been described by the Zimm, non-free-draining relaxation time (14). When the strain is removed, the extended macromolecule returns to the more thermodynamically stable coil state. It does this slowly because the extended chain experiences the full viscous drag of the solvent, and so behaves as a Rouse free-draining coil. Although the importance of the coil-stretch transition is noted it does not fully describe all situations and the existence of additional mechanisms have been eluded to. (8,9)

To date, for non rigid rod like polymers, studies on the effect of polymer concentration and molecular weight have been limited to simple homopolymer such as polyacrylamide(7), polyethylene oxide(9-13,15), and polystyrene(16) where the effect of variable backbone solvation is absent. In this paper we consider the influence of a series of cellulose esters (CE) polymers, which have a helical coil structure in solution and are considered weakly rod-like polymers(17), on the drop ejection process in drop on demand (DOD) printing. The influence of both polymer molecular weight and concentrations through the dilute and semi dilute regimes are considered and the possibility of longer lived relaxation mechanisms proposed. CE polymers are of interest because of their excellent solubility in a range of solvents allowing formulation to a high concentration whilst maintaining a comparatively low viscosity. In coatings and inks they confer a number of useful performance benefits including reduced drying time, good flow and levelling as well as being a good pigment dispersion medium.

Experimental Section

Materials

All solvents were obtained from Sigma Aldrich UK and were used as received. A range of compositionally equivalent cellulose ester (CE) polymers where supplied by Eastman Chemicals Ltd. and are summarized in Table 1.

The solubility characteristic of the CE polymers was determined by preparing 1 wt.-% solutions in a range of common solvents at 25°C and visually assessing solubility after 1 hour and after 24 hours. These where then classified as either soluble, partially soluble, gel or insoluble. Utilizing standard Teas notation (18) Ternary plots for each polymer were generated to identify parameter space where the polymers were most soluble. It is acknowledged that the construction of the Teas graph is based on the hypothetical assumption that all materials have the same Hildebrand value. Whilst this is not the case the approach it is an accurate and useful tool by which solubility data can be obtained. γ-butyrolactone was identified as a good solvent having suitable physical properties for ink-jet printing (boiling point = 204°C, surface tension = 40.4 mN/m; viscosity = 1.7 cP at 25°C) and was used in all further work. Details of the γ-butyrolactone solutions used are tabulated in Table 1.

Table 1. Physical properties of CE test fluids in γ-butyrolactone at 25°C.

CE	M_n (kDa)	[η] (dl/g)	c*	λz (μs)
1	10.5	0.247	4.04	0.53
2	30.7	0.631	1.58	3.43
3	46.5	1.153	0.86	12.9

Subsequent solutions of CE in γ-butyrolactone were prepared by gentle agitation and allowed to stand for 24 hours before use. Samples for inkjet printing were filtered through a glass microfibre filter (diameter 47 mm, 0.26 mm thick, 1.2 μm retention and filtration speed of 100/100 ml), after which there was no change in either solution viscosity (+/- 0.1 cP at 25°C) or determined polymer molecular weight and distribution.

Intrinsic viscosities, [η], in γ-butyrolactone were determined using an Anton Parr AMVn automated micro-viscometer which is based on the rolling/falling ball principle (DIN 53015 and ISO 12058). Using a 1.8mm diameter capillary at 25 +/- 0.5 °C at an angle of 70° times were determined as the average of 4 determinations (+/- 0.05 s). Solution viscosities, capillary range 2 – 70 cP, in γ-butyrolactone were similarly determined as the average of 4 determinations (+/- 0.2 cP). In order to determine c* we have used as a first approximation the classification of Flory (18) for flexible polymers solutions, where

$$c^* = 1/[\eta] \qquad (1)$$

and we define the reduced concentration as [η].c or c/c* (19).

Instrumentation

Ink-jet printing was carried out using a MicroJet ™ drop-on-demand dispensing device for room-temperature operation (Microfab, MJ-AB-01). The drop generator, developed for fluids with low shear viscosities in the range 0.5 – 20 cP and surface tensions in the range 20 – 70 mN/m, consists of a 50μm inside diameter glass nozzle with piezoelectric actuator sleeve driven by an external power supply. In all our experiments a bipolar waveform, with a 3 μs rise time, 40 μs duration and 3μs decay followed by a 3μs echo and 3μs rise, was employed with an external drive frequency of 4000Hz was used. Pulses ranging from 30 to 60V were employed. To prevent nozzle plate wetting and to create reproducible printing conditions, the glass capillary was regularly cleaned with a 20 wt.-% solution of potassium hydroxide in demineralized water and rigorously flushed with γ-butyrolactone.

A Visionjet™ optical stage was used to stroboscopically visualize the drop formation process, by varying the time delay between the signals to the piezo actuator and the strobe. Images of a droplet were taken at various time intervals and analyzed using Image Expert™ Software to extract distance traveled as a function of time.

All results are the average of at least three runs under each experimental condition. The size of the nozzle (defined) in each image is used as a reference. The typical variation in drop diameter and distance traveled under each condition is ≈ 10%.

Results and Discussion

Newtonian Fluid

For reference the behaviour of a Newtonian fluid was evaluated under the drop-on-demand conditions used in this study. The Newtonian case serves as an important inelastic baseline with which to compare the elastic effects of the polymers. Glycerol / water / isopropanol at 35/60/5 %v/v was used having a viscosity of 4.8 cP and a static surface tension of 36.0 mN/m. Figure 1 shows the photo sequence for the fluid at 40, 50 and 60 V applied voltage as a function of time, *t*.

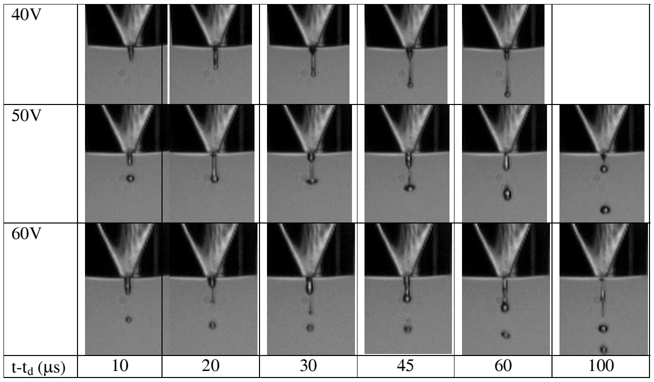

Figure 1. Photo sequence of formation of a Newtonian droplet consisting of glycerol/water/isopropanol with an applied voltage of 40, 50 and 60 V.

Results are shown where the data have been shifted by t_d, the delay between the initial voltage rise and the appearance of an outwardly moving meniscus. From the photo sequences we determine the distance traveled L by the primary droplet (the distance between the under-side of the primary droplet and the nozzle plate) as a function of time, shown in Figure 2. Qualitatively at low applied voltage (40 V) we observe rapid conical necking to form a large primary droplet and a long thin ligament tail. Pinch off occurs close to the nozzle after 60 μs with subsequent droplet and ligament coalescing into a single drop after 105 μs. Increasing the applied voltage leads to instability in the ejected ligament with multiple pinch-off events as shown for both 50 V and 60 V. This fluid exhibits many of the features previously reported for low-viscosity Newtonian fluids and is typical of the previously discussed regime 1 (1).

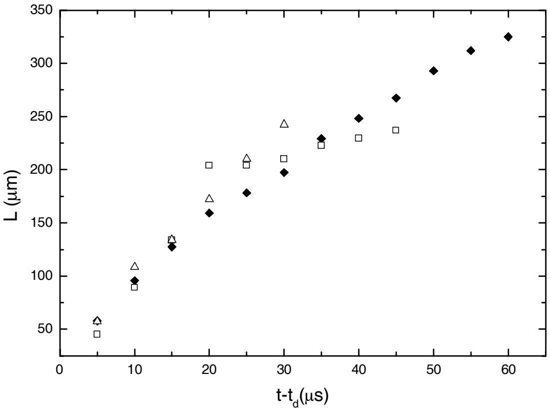

Figure 2. Distance travelled, L, as a function of time, t – t_d, to first break-off for the Newtonian Fluid at (◆) 40V, (□), 50V and (Δ) 60.

Effect of Polymer Concentration.

The effect of polymer concentration at constant molecular weight was evaluated over the reduced concentration range 0.5 – 3.8 for CE2 (Mn = 30.7 kDa). All fluids had surface tension and viscosity lying within the operational window of the MicroFab printhead. Figure 3 shows drop shape at pinch off for a 50 V applied voltage as a function of concentration expressed as the reduced concentration.

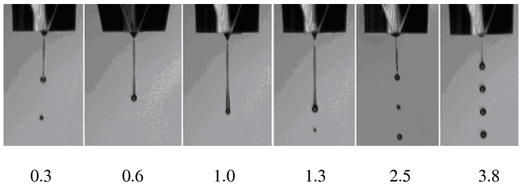

Figure 3. Drop profile at pinch off as a function of increasing c/c* for CE2 at an applied voltage of 50V.

The different stages of the drop ejection process are clearly visible (i.e. drop development, elongation and break-up). The delay time between the initial voltage rise and the appearance of an outwardly moving meniscus was 33 +/- 3μs for all fluids. Although the pulse employed and the overall timescale of drop ejection is the same as that shown for the Newtonian Fluid in Figure 1, the drop formation process is qualitatively different. All fluids show pinch-off near to the nozzle plate with a primary droplet attached by a thin ligament to a secondary and smaller droplet. At reduced concentrations up to 2.5 these then split into a primary and a smaller satellite droplet which did not coalesce within 1 mm of the nozzle plate. At a reduced concentration of 3.8 the primary droplet and ligament coalesce immediately after pinch-off with no satellite droplet formation. Qualitatively it is observed that the radius of the ligament increases up to up to a reduced concentration of 1 and decreases at higher concentrations.

From the obtained photo sequences we determine the distance traveled L by the primary droplet as a function of time shown in Figure 4, for an applied voltage of 50 V.

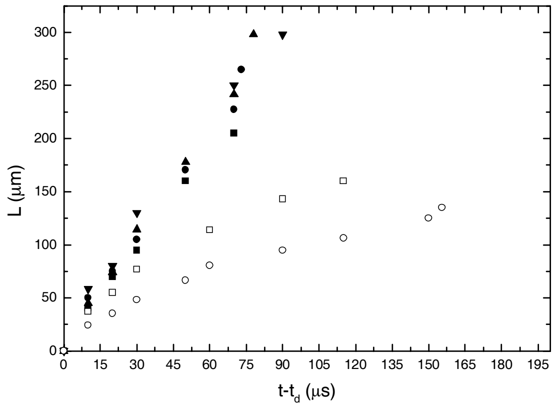

Figure 4. Distance travelled, L, for CE2 as a function of time, t, at 50V applied voltage for c/c*: (■) 0.32, (●) 0.63, (▲) 1.0, (▼) 1.28, (□) 2.52 and (○) 3.84.

From the L-t data we can identify two distinct regimes (9). At short times, t-t_d < 20 μs, the stretching is determined by the interplay of inertia and surface tension and therefore independent of polymer concentration and molecular weight. At long times, the traveled distance increases linearly with time and the velocity becomes constant, implying friction force on the droplet can be ignored and the ligament properties are determined by the rheological properties of the fluid. Similar behaviour has been reported for PEO in glycerol water (9) and polystyrene in acetophenone (8). For reduced concentrations up and close to 1 the L-t data are found to collapse to a single curve. However for reduced concentrations > 1 the slope of the curve becomes much shallower and is highly dependant upon concentration. Additionally it is observed that the ligament rupture time, t_{rup}, defined as the time from the first initial movement of the external meniscus and ligament break-off and rupture, appears to be independent of the applied voltage, Figure 5, as observed previously (8, 9). However it should be noted at 30 V and 40 V applied voltage it was not possible to eject fluids having a reduced concentration > 1.28, whilst at 60 V applied voltage only fluids having a reduced concentration in the range 2.5 – 3.8 were ejected. For all concentrations the ligament length at rupture L_{rup}, defined as the time from the first initial movement of the external meniscus and ligament break off and rupture, increases linearly with the applied voltage.

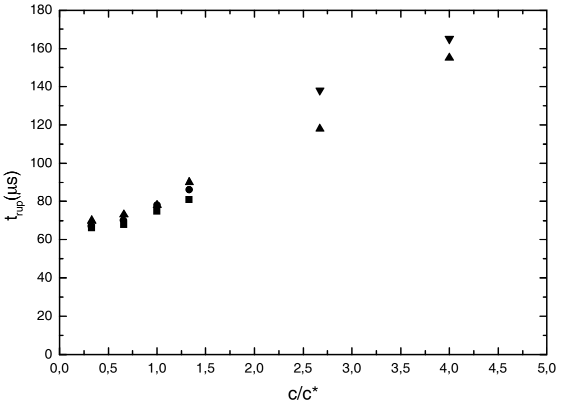

Figure 5. Ligament rupture time, t-t$_d$, for CE2 as a function of reduced concentration, c/c*, at: (■) 30 V, (●) 40 V, (▲) 50 V and (▼) 60 V applied voltage.

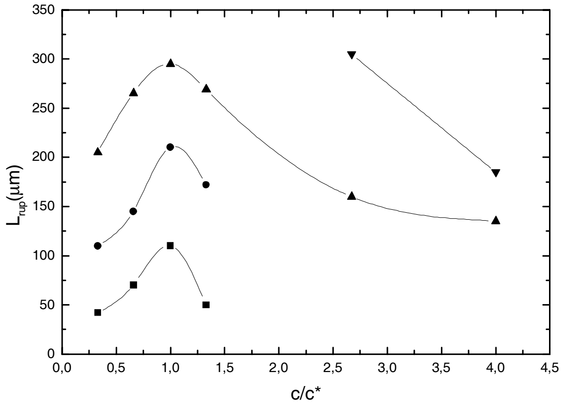

Figure 6. Ligament length at rupture, L$_{rup}$, for CE2 as a function of reduced concentration, c/c*, at: (■) 30 V, (●) 40 V, (▲) 50 V and (▼) 60 V applied voltage.

In Figure 6 we show the influence of reduced concentration and applied voltage on the ligament length at rupture L_{rup} and observe that it has a maximum at around the overlap concentration decreasing rapidly at higher concentrations. For all applied voltage we observe a decrease in ligament velocity at break off on going from a reduced concentration of 1 to 3.8. For an applied voltage of 50 V we observe a decrease in velocity from 2.25 m/s to 0.7 m/s. Therefore dependant upon polymer concentration and drive voltage the CE2 fluids show behaviour spanning regimes 2, 3 and 4 as the viscoelastic behaviour of the fluid changes.

Under conditions of sufficiently high strain rate linear polymers in solution show increasing elastic behaviour due to the polymer coil-stretch transition which occurs at a critical Weissenberg-number $We_{crit} = \varepsilon_{crit}.\tau_1 = 0.5$ where τ_1 denotes the longest polymer chain relaxation time and ε_{crit} the critical elongation rate$^{(20,21)}$. The rate of elongation (ε) has been calculated either from the rate of decrease in filament radius $^{(10)}$ or increase of the ligament length $^{(8)}$. Inspection of the images in Figure 4 shows that the thickness of the filament varies strongly along the length, indicating local variations in the elongation rate. However the experimental method used in this study makes accurate determination of filament radius difficult especially at long times. Therefore we determine the time averaged rate of elongation from the rate of increase in ligament length as described by de-Gans $^{(8)}$:

$$< \varepsilon >= \frac{1}{(t_2 - t_1)} \ln\left(\frac{L(t_2)}{L(t_1)}\right) \qquad (2)$$

where L is the ligament length at time t. To determine the Weissenberg-number the rate of elongation was multiplied by the longest relaxation time of the polymer chain which is given by the Zimm non-free-draining relaxation time (λz), approximated by $^{(14)}$:

$$\lambda z = \frac{[\eta] M_w \eta_s}{RT} \qquad (3)$$

where $[\eta]$ is the intrinsic viscosity of the fluid, η_s the viscosity of the solvent, T the temperature and M_w the weight average molecular weight. Calculated values are given in Table 2. To stretch the polymer in solution, *We* should exceed the critical value of 0.5, for a period exceeding $1/<\varepsilon>$. For CE2 over the range of applied voltages evaluated it was found that time averaged value of $1/<\varepsilon>$ is approximately 5 µs and the *We* exceeds the critical value of 0.5 for approximately 10 µs. From consideration of the extension rate within the ligament we have the situation where the time interval during which *We* exceeds W_{ecrit} is negligibly small and extension of the polymer molecules in this region is unlikely.

The physical behaviour of the fluids in drop formation however convinces us of the dominance of viscoelastic effects within the timescale of the process, in preventing ligament breakup at the pinch point compared with a Newtonian fluid of similar viscosity. Cooper-White $^{(9)}$ have argued that the only location in which extension rates can be sufficiently high to initiate extension of the polymer chain is at the pinch regions which had previously been eluded to $^{(22,23)}$. Therefore up to the overlap concentration the behaviour of the fluids are consistent with increasing viscoelastic behaviour of the fluid through polymer chain extension most probably at the pinch point and not within the ligament. In this regime 2 ligament rupture length and rupture time increase with increasing elasticity of the solutions $^{(8,9)}$. Beyond the overlap the ligament rupture times continue to increase with increasing elasticity of the solutions but the ligament rupture lengths decrease rapidly. In this regime the polymer chains in the extended state will become entangled after some time due to shear, turbulence and Brownian motion and as a consequence the effective relaxation time will be significantly longer than that calculated by the Zimm model. This dramatically increases the elastic nature of the ligament and resistance to forward inertia. In the case of CE polymers we have the case where at rest the polymer chains are in the random coil state, and have a number of transient intramolecular associations through H-bonding. The possibility therefore exists that on chain extension these intramolecular H-bonds are broken and may reform in the extended form as intermolecular associations. These intermolecular associations act as physical crosslinks, thereby creating a transient gel structure. Because these associations are transient in nature, this gel structure is capable of having a finite if large viscosity (24). Once the strain is switched off, the gel will decay as the chains return to the more thermodynamically stable coil state.

Effect of Molecular weight at $c/c^* = 1$.

To ascertain the effect of molecular weight all three polymers were ink-jetted at/or near the overlap concentration, $c/c^* = 1$, with fluid viscosities lying in the range 3.6 – 4.7 cP. It is important to note that whilst viscosity and surface tension are similar for all three fluids the polymer concentration is different varying from 4 g/dl for CE1 to 0.86 g/dl for CE3. Figure 7 shows the photo sequence for the four polymers at 50 V applied voltage as a function of time, $t\text{-}t_d$. The delay time between the initial voltage rise and the appearance of an outwardly moving meniscus was in the range 33 +/- 3μs for all four fluids.

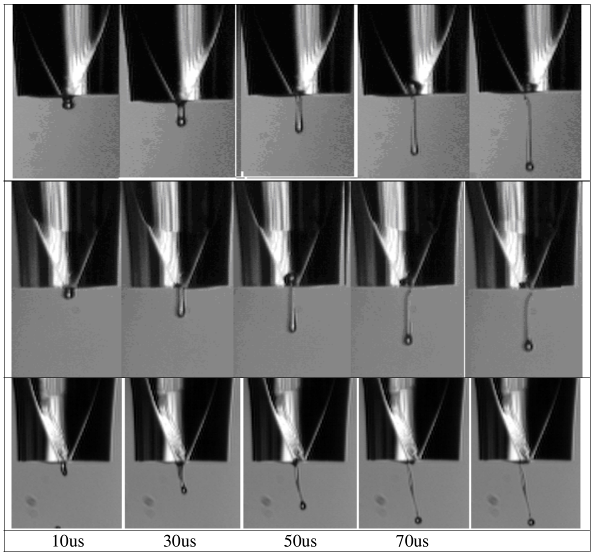

Figure 7. Photo sequence, top to bottom of (a) CE1; (b) CE2; (c) CE3 in γ-butyrolactone at 25^0C at $c/c^* = 1$ with an applied voltage of 50 V.

All three fluids showed qualitatively similar behaviour with drop break-off near to the nozzle plate with a primary droplet attached by a thin ligament to a secondary and smaller droplet. During flight these then split into a primary droplet and smaller satellite droplet which did not coalesce within 1 mm of the nozzle plate. For the range of molecular weights investigated the rupture time t_{rup} was found to be essentially independent of molecular weight, 70 – 78 μs and applied voltage over the range 30-50 V. For all CE's the L-t data collapsed to a single curve as previously reported (8,9) with the ligament length at rupture, L_{rup}, being weakly positively dependent on molecular weight. At short times, $t\text{-}t_d < 20$ μs, the stretching is determined by the interplay of inertia and surface tension and therefore independent of polymer concentration and molecular weight. At long times, the traveled distance increases linearly with time and the velocity becomes constant, implying friction force on the droplet can be ignored and the ligament properties being determined by the rheological properties of the fluid. Over the molecular weight range considered the droplet velocity at rupture was found to be essentially independent of molecular weight but increasing with applied voltage.

Conclusions.

We have studied filament formation during drop on demand inkjet printing of solutions of some industrially relevant cellulose esters. When formulated at the overlap concentration all polymers showed qualitatively similar behaviour with respect to time and length of ligament at rupture irrespective of polymer molecular weight. The distance travelled by the primary droplet, as a function of time, and droplet velocity was found to depend only on the applied voltage. The physical behaviour of the fluids in drop formation is due to the dominance of viscoelastic effects within the timescale of the process, in preventing ligament breakup at the pinch point compared with a Newtonian fluid of similar viscosity. From consideration of the extension rate within the ligament we have the situation where the time interval during which We exceeds W_{ecrit} is negligibly small for all polymers with polymer chain extension most likely occurring within the pinch region.

The effect of polymer concentration expressed in terms of reduced concentration was considered. Up to the overlap concentration the behaviour of the fluids are consistent with increasing elastic behaviour of the fluid through polymer chain extension. This is consistent with previous studies. Beyond the overlap concentration the ligament rupture times continue to increase with increasing elasticity of the solutions but the ligament rupture lengths decrease rapidly. In this regime the polymer chains become entangled in the extended state, and as a consequence the effective relaxation time will be significantly longer than that calculated by the Zimm model and so dramatically increasing the elastic nature of the ligament and resistance to forward inertia. In the case of weakly associating polymer such as cellulose esters, the effective relaxation time at all concentrations maybe further increased due to the possibility that on chain extension intramolecular H-bonds are broken and may reform in the extended form as intermolecular associations. These intermolecular associations act as physical crosslink's, thereby creating a transient gel structure. Because these associations are transient in nature, this gel structure is capable of having a finite but large viscosity. Once the strain is switched off the gel will decay as the chains return to the more thermodynamically stable coil state.

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Author Biography

Professor Yeates has over 20 years industrial experience working for ICI, Zeneca and Avecia Ltd in the area of specialty polymer chemistry. During that time he held a number of senior technical positions developing and implementing research strategy. Over the last 7 years in industry he developed a particular interest in organic semiconductors and inkjet printing for both industrial and SOHO applications. In November 2004 he was appointed to the full time academic position as Professor of Polymer Chemistry, a Organic Materials Innovation Centre (OMIC) at the University of Manchester.