

José A. Lopes da Silva
João A. P. Coutinho

Dynamic rheological analysis of the gelation behaviour of waxy crude oils

Received: 12 January 2004
Accepted: 23 February 2004
Published online: 6 April 2004
© Springer-Verlag 2004

This paper was presented at the first Annual European Rheology Conference (AERC) held in Guimarães, Portugal, September 11–13, 2003.

J. A. L. da Silva (✉)
Department of Chemistry,
University of Aveiro,
3810-193 Aveiro, Portugal
E-mail: jsilva@dq.ua.pt

J. A. P. Coutinho
CICECO, Department of Chemistry,
University of Aveiro,
3810-193 Aveiro, Portugal

Abstract In this work we have characterised the viscoelastic behaviour of paraffin crystals in three different complex crude oils, close to the gelation threshold and after curing the gels under quiescent isothermal conditions, by means of oscillatory shear measurements. An increase in gelation temperature is observed with increasing oil's molecular weight. The interactions between wax crystals and the formation of the space-filling network of interlocking wax crystals are thus facilitated by the presence of paraffins with higher molecular weight. The apparent gelation time, obtained from isothermal curing experiments, decreases as the curing temperature was decreased, and it is highly temperature-dependent. The presence and the importance of the ageing of the wax were established under isothermal conditions. It must result from a coarsening of the crystallites presents in the oil and it is, more important, close to the gel point where its full development is very slow taking several days to occur. After ageing the gels, the connective domains or junction zones linking the crystal arrays fail when

relatively small strains are applied to the system and the mechanical spectra of the gels reveal an imperfect elastic network, typical rheological characteristics of a particle gel. Despite the compositional differences among the samples, the similarity of their mechanical behaviour is quite remarkable indicating that in all cases the gel-like organisation of the waxy material results from the formation of identical structures in the different oils, which is related not only to the wax content but also to the presence of other material that may reduce the crystallinity of the structure.

The low fractal dimensionality obtained indicates elongated substructures. These results, together with the very high elastic modulus obtained at low volume fractions of crystallised material, are indicative of network structures with high degree of porosity: a lattice of wax crystals with large spaces among them filled by the oil and non-precipitated material.

Keywords Waxy crude oils · Viscoelastic behaviour · Gelation · Fractal aggregates

Introduction

Waxy crude oils, which contain significant proportions of heavy paraffin compounds, are known to produce a

gel-like structure when the crude oils are cooled below their pour point. Wax precipitation and deposition occurring due to oil cooling during production, transportation, and storage of crudes cause detrimental

effects in several aspects of crude oil processing. The rheological behaviour of waxy oils is thus considered to be of crucial importance in the design of a pipeline, fuel-cracking units, and for remediation purposes.

The presence of wax crystals imparts particular rheological behaviour to the oil, including yield stress, shear thinning behaviour and time dependency under steady shear flow, and the formation of strong thermo-reversible gels, a behaviour that is highly dependent on the shear and thermal histories of the sample (Wardhaugh and Boger 1991; Ronningsen 1992; Singh et al. 1999; Chang et al. 2000).

The gelation mechanism is close related to the crystallization of paraffins. The network of interacting paraffin crystals shows complex morphology and is due to the flocculation of orthorhombic wax crystallites, creating a highly porous and rigid structure full of entrapped oil (Dirand et al. 1998; Singh et al. 1999). The characteristics of these physical gels are known to undergo a change with time, becoming harder, richer in heavier paraffins and with lower amounts of entrapped oil (Creek et al. 1999; Singh et al. 2001; Cordoba and Schall 2001; Wu et al. 2002). The mechanism of ageing has been explained by a diffusion transport within the porous structure of the gel driven by temperature-composition gradients (Singh et al. 2000). This transport would be responsible for the increase in paraffin content of the gelled structure and for its further hardening. Although this mechanism is highly plausible it was also shown that it is not the only mechanism responsible for the ageing of wax deposits. Previous work from our group (Coutinho et al. 2003) showed that in the absence of temperature-composition gradients the hardening of the wax deposits is related to Ostwald ripening of the paraffin crystals, a mechanism by which the large crystals grow at the expenses of the melting of smaller crystals of higher energy.

The properties of the waxy-gels formed under quiescent conditions have practical significance especially in the case of restart processes after the shutdown of processing and transportation units. In this study we have investigated further details of the temperature effect on the crystallization-induced gelation of complex crude oil mixtures by small-deformation oscillatory rheometry. Particular attention was given to the kinetics of the gel formation and curing under quiescent isothermal conditions, and to the gel structure and viscoelasticity using fractal analysis.

Experimental

Three crude oils obtained directly from oil companies, with different origins and wax's composition, were used in this study. Their main characteristics are shown in Table 1. The asphaltene content in all the crudes is

Table 1 Properties of the crude oils

Sample	Oil type ^a	Wax content (wt%)		M_w	PP (°C)	WAT (°C)
		Total wax ^b	Saturates ^c			
A	Gas condensate	6.8	6.8	176	15	45
B	Microcrystalline oil	33	23	216	35	57
C	Heavy Paraffinic oil	35	21	286	40	73

^aAccording to oil supplier

^bTotal wax (acetone precipitation)

^cSaturates (after removal of polar material)

M_w —Oil average molecular weight

PP —Pour point (ASTM D-5853)

WAT —Wax appearance temperature (CPM)

negligible. The rheological behaviour is thus free of the effects of the asphaltenes on the gelation of waxy crudes, as reported by Venkatesan et al. (2003).

The cloud point of the crude oils, or the wax appearance temperature (WAT), was measured by cross-polarised microscopy. Pour points were determined accordingly to the ASTM method (D-5853). The total wax content was measured by following a modified UOP standard method 46 as proposed by Musser and Kilpatrick (1998). The waxes are precipitated by a mixture of acetone and petroleum ether (3:1 v/v), cooled at -20 °C and then filtered. The solid obtained is the total wax content. The saturated waxes are separated from the aromatics and polar material such as resins by chromatography on a 50-cm silica gel column with *n*-heptane. Both oils B and C present about 1/3 of precipitated solids other than saturated waxes. X-ray diffraction analysis of the waxes and oils below the pour point temperatures was performed as previously described (Coutinho et al. 2003). Small-deformation oscillatory measurements were performed using a controlled stress rheometer (AR1000, TA Instruments), with the temperature controlled to within ± 0.1 °C (Peltier device), fitted with a parallel plate measuring system (4 cm diameter, roughened surface, 1 mm gap). Each crude oil was initially heated up to a temperature 15 °C above its cloud point, for 1 h, to erase any previous thermal history or any possible waxy structure. The sample was loaded into the rheometer plate, pre-set at the same temperature. The temperature (0.2 °C/min) and time sweep experiments were performed at a frequency of 5 rad/s. For the isothermal time sweep tests, the sample was quickly quenched (6 °C/min) "in situ", from the pre-treatment temperature to the desired temperature of curing. Mechanical spectra of the cured waxy gels (frequency sweep experiments) were obtained in the frequency range 0.05–50 rad/s. All measurements were performed at a low strain of 5×10^{-4} .

For the sake of simplicity the precipitation curves for each oil (mass fraction of solids vs temperature) used in

this study were obtained not directly from measurements (e.g. DSC) but from a thermodynamic model by Coutinho and Daridon (2001). This model uses only as input the composition of the fluids obtained by high-temperature gas-chromatography. It has been shown (Coutinho and Daridon 2001) to be a reliable and accurate model to describe the fraction of solids for partially crystallized crudes and it has in the last few years become a standard procedure for this purpose. The model uses the Flory-free volume model to describe the non-ideality of the fluid phases and the predictive UNIQUAC model for the non-ideality of the solid phase. A more detailed description of the model can be found elsewhere (Coutinho and Daridon 2001; Coutinho et al. 2001; Daridon et al. 2001).

Results and discussion

Temperature dependence of the G' – G'' cross-over time

The effect of temperature on gel formation was first investigated by constant rate cooling of the crude oil samples pre-heated well above the cloud point. Figure 1 shows the changes on viscoelastic moduli in the vicinity of the gelation temperature. A sharp increase in the viscoelastic moduli is observed when the temperature reaches a certain value, characteristic of each oil sample, below the cloud point but well above the pour point.

It is now well accepted that the G' – G'' cross-over is not a universal property of the gel point; it might be close to, but not identical with, the sol-gel transition time. An unambiguous rheological criterion to define the gel point is related to the power law relaxation occurring

at the sol-gel transition (Winter and Chambon 1986; Winter 1987). Accordingly to this criterion, the G' and G'' dependence on oscillatory frequency should scale as a power law with a singular exponent, dependent on the specific nature of the network (te Nijenhuis and Winter 1989; Lin et al. 1991; Scanlan and Winter 1991; Lopes da Silva et al. 1996). However, the G' – G'' cross-over criterion is still used and considered satisfactory in many studies, especially for some fast aggregation processes, where the incipient but quick development of structure precludes meaningful results from being obtained for the frequency dependence of the viscoelastic moduli before and at the gel point, due to experimental limitations.

In this work we used the point at which G' (elastic response) became greater than G'' (viscous response) to define the characteristic time and temperature associated with the sol-gel transition. Accordingly to this criterion, the observed gelation temperatures were 32.8 °C, 41.5 °C and 50.4 °C, for oil samples A, B and C, respectively. An increase in gelation temperature is observed with increasing oil's molecular weight. The gelation temperature depends also on the concentration profile and the presence of non-wax components, but the paraffin's molecular weight is likely playing the more important role on the interactions between wax crystals and the formation of the space-filling network of interlocking wax crystals.

The pour point temperature is widely used as the industrial standard to define the gel temperature of crude oils. Not unexpectedly, the temperatures obtained by the more fundamental criterion monitored by mechanical spectroscopy were higher than the experimental pour points (see Table 1). The differences may be attributed to the different thermal history and cooling rates used in both methods, but more likely to what is being measured by the two different approaches. The visual ASTM criterion used to determine the pour point corresponds to the point where no flow occurs, thus requiring the network to be self-supporting, whereas the instrumental criterion of the onset of gelation ($G' = G''$) corresponds to the initial development of an infinite network, which would occur at a much lower degree of cross-linking.

The effect of temperature on gelation time was investigated by isothermal curing under quiescent conditions at different temperatures. The initial period of isothermal gelation is plotted in Fig. 2, for a short temperature range (5–6 °C). Taking the cross-over point as an apparent gelation time, we can observe that this characteristic time decreases as the curing temperature was decreased, and it is highly temperature-dependent. For lower curing temperatures the apparent gel point (the G' – G'' cross-over point) could not be estimated because it was shorter than the time elapsed before the beginning of the cure experiment: The $G' = G''$ singularity was already achieved during the cooling step, and

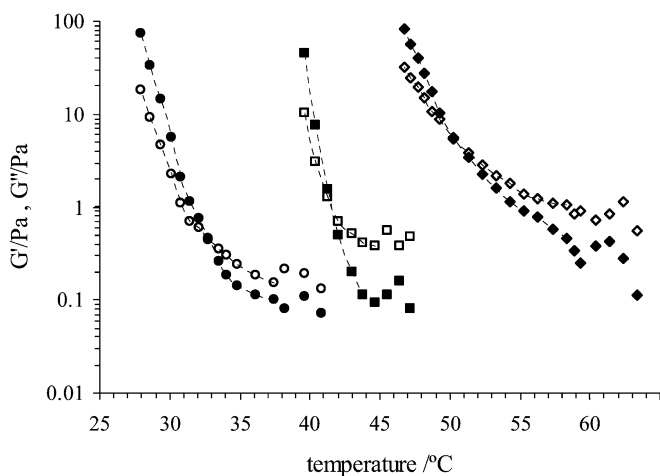


Fig. 1 Changes on the viscoelastic moduli (G' —filled symbols, G'' —open symbols) as a function of temperature (cooling rate 0.2 °C/min, $\omega=5$ rad/s), close to the gelation threshold: circles—oil A; squares—oil B; diamonds—oil C

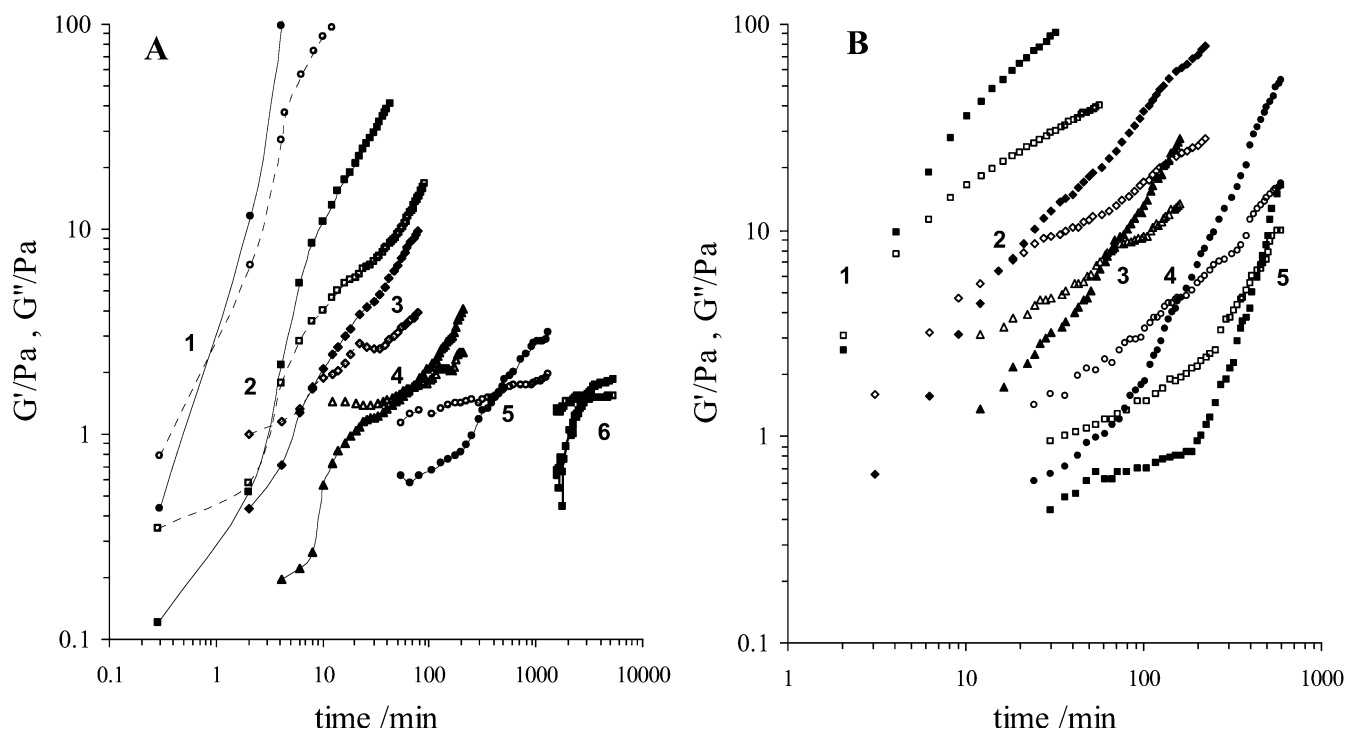


Fig. 2A,B Viscoelastic moduli (G' —filled symbols, G'' —open symbols) as a function of time during curing experiments ($\omega = 5$ rad/s) at different temperatures: **A** oil sample B (1—40 °C; 2—41 °C; 3—42 °C; 4—43 °C; 5—44 °C; 6—45 °C); **B** oil sample C (1—46 °C; 2—48 °C; 3—49 °C; 4—50 °C; 5—52 °C)

thus G' was higher than G'' after the desired curing temperature was reached.

The value of the modulus corresponding to the G' – G'' cross-over was dependent on oil composition, being higher for the oil sample with the higher content of high molecular weight paraffins. The low wax content of oil sample A, and lower molecular weight, is responsible for an incipient gel formation for which no meaningful measurements were obtained close to the G' – G'' cross-over time. Therefore, only the results obtained for oil samples B and C were analysed.

Figure 3 shows the temperature dependence of gelation rate, taking as the reciprocal of gel-time (Lopes da Silva et al. 1995). On the assumption that this gelation rate is directly proportional to the rate of intermolecular association to form a gel, it is evident that its temperature-dependence is different for oil samples B and C, indicating that compositional differences may influence the aggregation mechanism among paraffin crystals, at least at this initial gelation stage.

Gel formation under isothermal conditions

During quenching and isothermal annealing of the oils, the elastic modulus of the interlocking lattice of wax

crystals increases as the elastic character of the network ($\tan \delta(G''/G')$ decreases). Figure 4 shows representative isothermal cure curves (storage modulus (G') vs time) for oil samples A, B and C. The curing profile is similar to that of other thermoreversible gels (e.g. te Nijenhuis 1997). The storage modulus increases as a result of the increasing junction zones density between wax crystals. The ageing process is much faster at low than at high

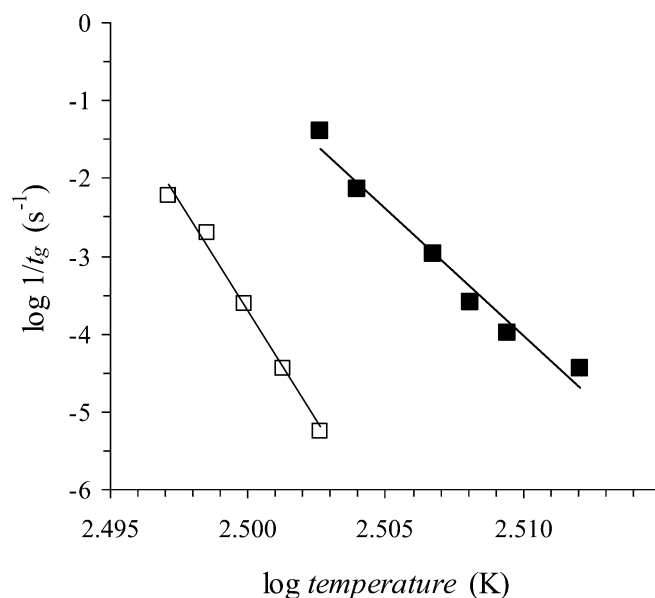


Fig. 3 Temperature dependence of the gelation rate ($1/t_g$) for oil samples B (open squares) and C (filled squares)

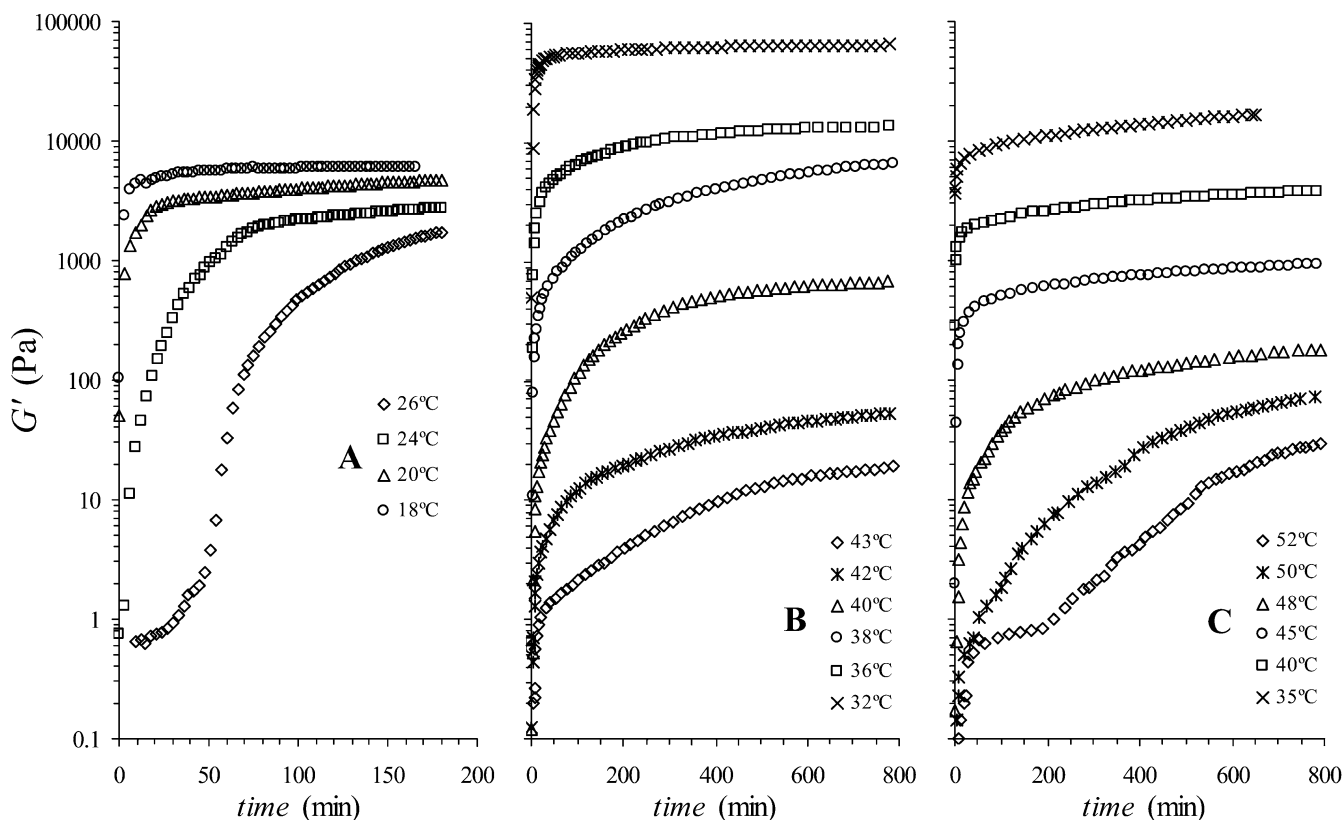


Fig. 4 Storage modulus (G') plotted against ageing time for several curing temperatures. Oscillatory frequency 5 rad/s, strain 0.05%. **A**—oil A; **B**—oil B; **C**—oil C

temperatures. During the initial ageing period G' had a great variation covering about three orders of magnitude, especially at the lower temperatures. At the higher temperatures, close to the gelation temperature, an induction period is perceptible, especially for oils A and C. This period becomes longer accordingly, as when the ageing temperature is higher.

After the rapid increase in elasticity within the gel, G' keeps increasing slightly and continuously as a result of the reinforcement of the network by slower formation and rearrangement of elastic active bonds/junction zones, reaching a pseudo plateau region. A true equilibrium modulus was not reached even after long ageing periods, especially for temperatures close to the $G'-G''$ cross-over point, i.e. for the lower concentration of crystallised material (after more than 96 h in some cases), meaning a continuous reorganisation of the particulate network.

Some disagreement is observed among previous reported results concerning the occurrence of ageing of crude oils under static isothermal conditions. Reports can be found on the isothermal increasing of the gel strength (Singh et al. 2001; Wu et al. 2002), but also on the absence of ageing effects or on their very low, often insignificant effect on gel structure (Rønningsen 1992;

Chang et al. 2000). These disagreements were attributed to poor temperature control during the experiments or to the compositional differences of the oils (Chang et al. 2000). Our tests for the three different oils under careful control of the shear and thermal history have shown that the ageing and strengthening of the wax-oil gels do occur, especially for more incipient crystal networks at temperatures close to the gelation temperature. The apparent disagreement can then be attributed to the different degree of supercooling used in different studies.

Under quiescent conditions the paraffin crystals are known to form lamellar structures, with thickness of the order of the size of a paraffin molecule (Kané et al. 2003). During ageing, even in the absence of temperature-composition gradients, the occurrence of Ostwald ripening, as evidenced in a previous work (Coutinho et al. 2003), may cause changes in crystal microstructure and a reorganization and coarsening of the initial space-filling network. The reinforcement of the network by ageing and the higher shear elastic modulus attained may be explained by the formation of stacks of crystalline lamellar structures.

Viscoelasticity of fully cured gels

After ageing until the moduli had become stationary, frequency and stress sweep tests were performed to characterize the viscoelastic behaviour of the gels.

Typical behaviour of the storage modulus (G') as a function of strain is shown in Fig. 5. Generally, for all wax-oil gels analysed, the limit of linearity γ_o was very low and close to the resolution limit of the rheometer. For these gels, van der Waals' forces are expected to be the sole interactions between crystals and crystals aggregates. This high strain sensitivity behaviour is related to the low energy interactions between structural units building up the gel, a typical behaviour of particulate colloidal gels. Here we define the value of γ_o as the experimental strain beyond which G' deviates more than 5% from its maximum well resolved value.

Comparison of the mechanical spectra obtained for oils A–C at similar weight fractions of crystallised material revealed important differences on their viscoelastic behaviour. An example of this behaviour is shown in Fig. 6, for the three aged oil gels at a volume fraction of crystallised material of 0.8%.

Interpretation of this behaviour is complicated by the fact that the extent of interactions between wax crystals cannot be varied independently of the temperature or concentration. Generally, the long term behaviour is predominantly solid-like, G' dominates over G'' , but the network of interlocking crystals is rather imperfect and has a weak gel-like character. Both moduli show some degree of frequency dependence, meaning that rearrangements are taking place within the gel on the time scale analysed and are responsible for important dissipative processes within the deformation period. For oils A and B the loss mechanisms occur especially at the

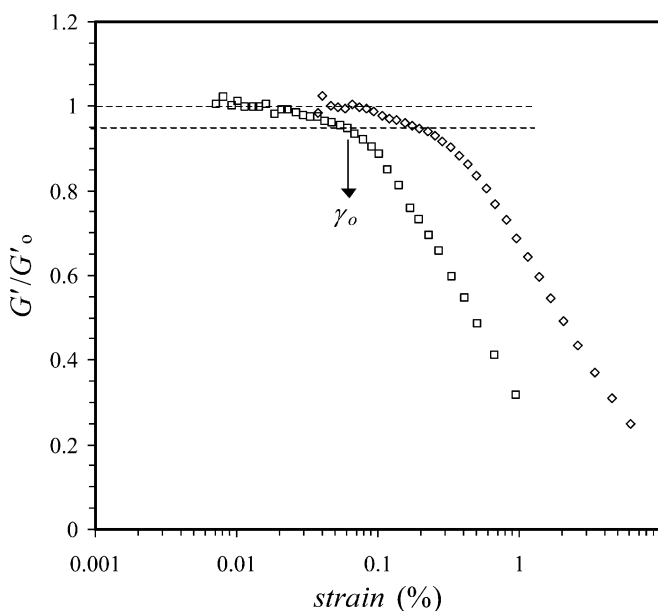


Fig. 5 The reduced storage modulus (G'/G'_o) as a function of strain for oil B gels, frequency 1 rad/s: (open squares) 38 °C; (open diamonds) 43 °C. G'_o denotes for the G' at the beginning of the stress sweep experiment, after meaningful results were obtained, and γ_o for the strain limit of linearity (defined in text)

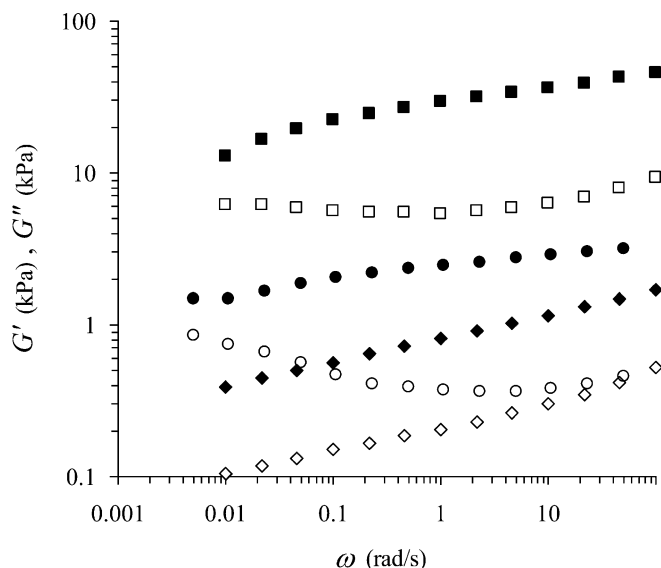


Fig. 6 Linear viscoelastic moduli (G' —filled symbols, G'' —open symbols) as a function of angular frequency ω at volume fraction $\phi = 0.8\%$, after ageing of wax oil gels: circles—oil A; squares—oil B; diamonds—oil C

lowest frequencies probed, but for oil C both moduli showed essentially the same frequency dependence over the time range analysed. This behaviour may be imparted by a high degree of porosity of the network, which trap a large fraction of oil and non-crystallised material, contributing to the relatively high viscous character of the gel. The stiffer structure developed in oil B seems to be related to a higher saturation and crystallinity of the waxes forming on this fluid which seems to contradict the oil type assigned to this oil by the supplier (Table 1). In fact, as can be observed in Fig. 7, where we compare the X-ray diffraction patterns obtained for the waxes precipitated from oils B and C, the oil sample B displays a higher degree of crystallinity than oil C. The structure that develops in the oils below the wax appearance point is dependent on the wax content and also on the presence of other material that may reduce the crystallinity of the structure.

On the assumption that the colloidal aggregates building up the gel network behave as stochastic mass-fractals on a scale which is large compared to the primary crystal size, both the elastic modulus (G') and the strain limit of linearity (γ_o) of the gel are expected to scale as a function of the particle volume fraction (ϕ) according to power law relationships (Buscall et al. 1988; Shih et al. 1990):

$$G' \sim \phi^A$$

$$\gamma_o \sim \phi^B$$

where the exponents A and B are related to the fractal dimension of the system.

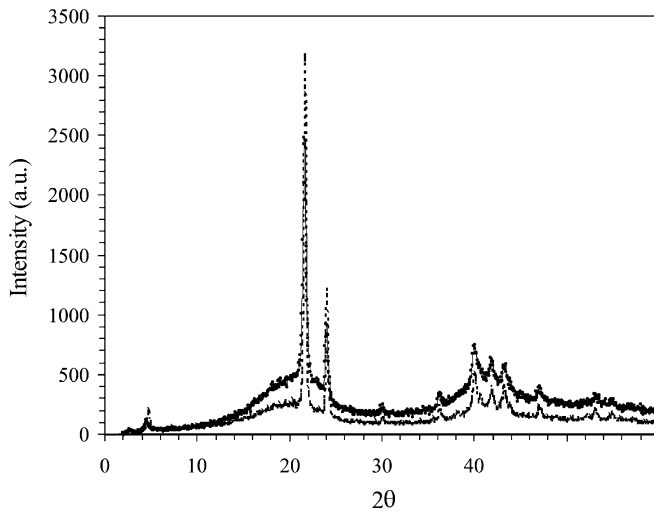


Fig. 7 X-Ray diffraction patterns obtained for the waxes precipitated from oils B (*dotted line*) and C (*bold line*)

Accordingly to the general model derived by Wu and Morbidelli (2001), these exponents are defined as

$$A = \beta / (d - d_f)$$

$$B = (d - \beta - 1) / (d - d_f)$$

where

$$\beta = (d - 2) + (2 + x)(1 - \alpha)$$

is a constant, related to x , the backbone fractal dimension or tortuosity of the network, and to α , a constant in the range $[0,1]$ which depends on the relative weighting of strong-link ($\alpha=0$) vs weak link ($\alpha=1$) behaviour initially proposed by Shih et al. (1990). For a three-dimensional system ($d=3$) β ranges between 1, for $\alpha=1$, and $3+x$, for $\alpha=0$.

An example of the elastic modulus and limit of linearity dependencies on the volume fraction of crystals is shown in the log-log plots in Fig. 8 for oil C. Both G'_o and γ_o show power-law behaviour upon particle concentration, accordingly to the A and B exponents values shown in Table 2. The fractal concept seems then to apply.

The values of the limit of linearity (γ_o) as a function of the volume fraction of crystals (ϕ) exhibit negative slopes, thus indicating a strong-link regime according to Shih et al. (1990), which is known to be applicable at low volume fractions. The dependence of γ_o on ϕ is however relatively small, meaning that these wax crystal networks behave accordingly to the transition regime of the Wu and Morbidelli (2001) model. Therefore, it is expected that the interactions between aggregates predominate over the interactions between primary particles, the crystals, but both kind of interactions contribute to the overall elasticity.

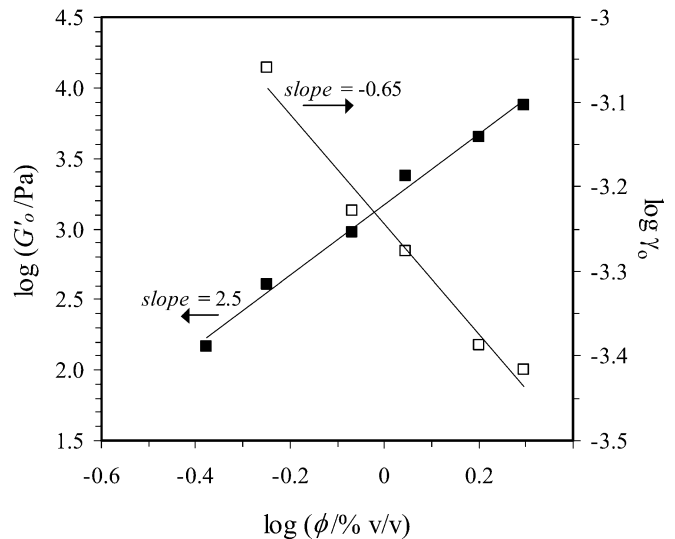


Fig. 8 Pseudo-equilibrium storage modulus (G'_o) and limit of linearity (γ_o) as a function of volume fraction of crystallised material for oil C

Table 2 Scaling parameters for the cured wax-oil gels

Oil	A	λ^a (Pa)	B	d_f	β
A	1.9	4.3×10^3	-0.37	1.7	2.47
B	2.9	3.7×10^4	-0.40	2.2	2.32
C	2.5	1.5×10^3	-0.65	1.9	2.70

^aPre-exponential factor in the power law scaling of G' on ϕ ($G' = \lambda \phi^A$), a constant independent of the volume fraction, but dependent on the size of the primary particles and on the interactions between them (Narine and Marangoni 1999)

The fractal dimension was deduced from the elastic modulus dependence on the volume fraction of particles, yielding values between 1.7 and 2.2 (Table 2). The low fractal dimensionality indicates elongated substructures. The three different waxy gels demonstrated fractal dimensions that are not very different, but the range of G' values for the three systems, reflected on the λ values (Table 2), a parameter dependent on the size of the primary particles and on the interactions between them (Narine and Marangoni 1999), shows significant differences, especially between oil B and the other two systems. The slightly higher fractal dimension obtained for oil B gels may be related with a greater degree of order in the crystal packing within the aggregates than those systems with lower fractal dimension, resulting in a coarser network.

Conclusions

The crystallization of high molecular weight n -paraffins at temperatures below the wax appearance temperature

(cloud point) originates a gelled network of interacting crystal clusters that imparts peculiar viscoelastic behaviour to the system. The waxy gels have some characteristics typical of particulate colloidal gels, such as the very low strain limit of linearity, but a high degree of network imperfections enabling molecular rearrangements within the gel.

Despite their compositional differences, the similarity of the mechanical behaviour displayed by the oils studied is quite remarkable, indicating that in all cases the gel-like organisation of the waxy material results from the formation of identical structures in all oils. The stiffer structure developing in oil B seems to be related to a higher saturation and crystallinity of the waxes forming on this fluid which seems to contradict the oil type assigned to this oil by the supplier. The structure that develops in the oils below the wax appearance point seems to be related not only to the wax content but also

to the presence of other material that may reduce the crystallinity of the structure.

The presence and the importance of the ageing of the wax was established under isothermal conditions. It must result from a coarsening of the crystallites present in the oil and it is more important close to the gel point where its full development is very slow, taking several days to occur.

Assuming that the created clusters have a fractal structure, the fractal dimension was deduced from the elastic modulus dependence on the volume fraction of particles, yielding values between 1.7 and 2.2. The low fractal dimensionality indicates elongated substructures. These results, together with the very high elastic modulus obtained at low volume fractions of crystallised material, are indicative of network structures with high degree of porosity.

References

- Buscall R, Mills PDA, Goodwin JW, Lawson DW (1988) Scaling behavior of the rheology of aggregate networks formed from colloidal particles. *J Chem Soc, Farad Trans I* 84:4249–4260
- Chang C, Boger DV, Nguyen QD (2000) Influence of thermal history on the waxy structure of statically cooled waxy crude oil. *SPE J* 5:148–157
- Cordoba AJ, Schall CA (2001) Solvent migration in a paraffin deposit. *Fuel* 80:1279–1284
- Coutinho JAP, Daridon, JL (2001) Low-pressure modeling of wax formation in crude oils. *Energy Fuels* 15:1454–1460
- Coutinho JAP, Pauly J, Daridon JL (2001) A thermodynamic model to predict wax formation in petroleum fluids. *Braz J Chem Eng* 18:411–422
- Coutinho JAP, Lopes da Silva JA, Ferreira A, Soares MR, Daridon JL (2003) Evidence for the aging of wax deposits in crude oils by Ostwald ripening. *Petrol Sci Technol* 21:381–391
- Creek JL, Lund HJ, Brill JP, Volk M (1999) Wax deposition in single phase flow. *Fluid Phase Equil* 158–160:801–811
- Daridon JL, Pauly J, Coutinho JAP (2001). Solid-liquid-vapor phase boundary of a North Sea waxy crude: measurement and modeling. *Energy Fuels* 15:730–735
- Dirand M, Chevallier V, Provost E, Bouroukba M, Petitjean D (1998) Multi-component paraffin waxes and petroleum solid deposits: structural and thermodynamic state. *Fuel* 77:1253–1260
- Kané M, Djabourov M, Volle J-L, Lechaire J-P, Frebourg G (2003) Morphology of paraffin crystals in waxy crude oils cooled in quiescent conditions and under flow. *Fuel* 82:127–135
- Lin YG, Mallin DT, Chien JCW, Winter HH (1991) Dynamical mechanical measurement of crystallization induced gelation in thermoplastic elastomeric poly(propylene). *Macromolecules* 24:850–854
- Lopes da Silva JA, Gonçalves MP, Rao MA (1995) Kinetics and thermal behaviour of the structure formation process in HMP/sucrose gelation. *Int J Biol Macromol* 17:25–32
- Lopes da Silva JA, Gonçalves MP, Doublier JL, Axelos MA (1996) Effect of galactomannans on the viscoelastic behaviour of pectin/calcium networks. *Polym Gels Networks* 4:65–83
- Musser BJ, Kilpatrick PK (1998) Molecular characterization of wax isolated from a variety of crude oils. *Energy Fuels* 12:715–725
- Narine SS, Marangoni AG (1999) Fractal nature of fat crystal networks. *Phys Rev E* 59:1908–1920
- Rønningsen HP (1992) Rheological behaviour of gelled, waxy North Sea crude oils. *J Petrol Sci Eng* 7:177–213
- Scanlan JC, Winter HH (1991) Composition dependence of the viscoelasticity of end-linking poly(dimethylsiloxane) at the gel point. *Macromolecules* 24:47–54
- Shih WH, Shih WY, Kim SI, Liu J, Aksay IA (1990) Scaling behavior of the elastic properties of colloidal gels. *Phys Rev A* 42:4772–4779
- Singh P, Fogler HS, Nagarajan N (1999) Prediction of the wax content of the incipient wax-oil gel in a pipeline: an application of the controlled-stress rheometer. *J Rheol* 43:1437–1459
- Singh P, Venkatesan R, Fogler HS, Nagarajan N (2000) Formation and aging of incipient thin film wax-oil gels. *AIChE J* 46:1059–1074
- Singh P, Youyen A, Fogler HS (2001) Existence of a critical carbon number in the aging of a wax-oil gel. *AIChE J* 47:2111–2124
- te Nijenhuis K (1997) Thermoreversible networks: viscoelastic properties and structure of gels. *Adv Polym Sci* 130. Springer, Berlin Heidelberg New York

-
- te Nijenhuis K, Winter HH (1989) Mechanical properties at the gel point of a crystallizing poly(vinyl chloride) solution. *Macromolecules* 22:411–414
- Venkatesan R, Ostlund JA, Chawla H, Wattana P, Nyden M, Fogler HS (2003). The effect of asphaltenes on the gelation of waxy oils. *Energy Fuels* 17:1630–1640
- Wardhaugh LT, Boger DV (1991) The measurement and description of the yielding behavior of waxy crude oil. *J Rheol* 35:1121–1156
- Winter HH (1987) Can the gel point of a cross-linking polymer be detected by the G' - G'' crossover? *Polym Eng Sci* 27:1698–1702
- Winter HH, Chambon F (1986) Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. *J Rheol* 30:367–382
- Wu H, Morbidelli M (2001) A model relating structure of colloidal gels to their elastic properties. *Langmuir* 17:1030–1036
- Wu CH, Wang KS, Shuler PJ, Tang Y, Creek JL, Carlson RM, Cheung S (2002) Measurement of wax deposition in paraffin solutions. *AIChE J* 48:2107–2110