Colloid Polym Sci 278:783–788 (2000)
© Springer-Verlag 2000

SHORT COMMUNICATION

G. Cassin
I. Appelqvist
N. Bossu
I. T. Norton

Stress-induced alignment of fibres in a particulate matrix

Received: 5 October 1999
In revised form: 21 December 1999
Accepted: 21 January 2000

G. Cassin (✉) · I. Appelqvist
N. Bossu · I. T. Norton
Unilever Research Colworth
Colworth House, Sharnbrook
Bedfordshire, MK44 1LQ, UK

Abstract In this article, experimental evidence for the influence that steric interaction and orientational coupling have on the orientation of cellulose fibre dispersed in a particulate matrix is given. The filler coefficient of the fibre suspension is used as a probe to follow the average fibre orientation. It is shown that the fibres do not order into a nematic phase after numerous shear stress steps. From the evolution of the filler coefficient as a function of the time the stress was applied, a rate constant for reorientation was determined. Even in the dilute regime, its value depends on the fibre volume fraction. Results obtained with various fibre and particle sizes have been scaled onto a master curve, where it is shown that the rate of reorientation increases with the fibre–particle size ratio.

Key words Microgel · Microcrystalline cellulose · Fibre reinforcement · Orientational properties

Introduction

Due to their strong reinforcing property and their wide occurrence in everyday life, fibre suspensions have been intensively studied [1–14]. The nonlinear effects induced by the filler's shape anisotropy are of special importance with regard to the mechanical properties of these suspensions. The rheology of fibre suspensions depends strongly on the average fibre orientation within the embedding matrix [8–13]. For instance, it has been shown that as the oscillatory shear amplitude applied to a fibre-reinforced plastic increased, the complex viscosity gradually decreased due to gradual alignment of the fibre in the flow direction [11]. Another aspect that fibre suspensions present is that such systems are known to show normal stress differences under shear conditions [4, 14]. The generation of normal stress differences that lead to a display of normal forces arises from the fact that under flow conditions the microstructure of the material becomes anisotropic. When fibres are dispersed in a particulate matrix, steric correlations between fibres and particles arise and contribute to the impact the shear field has on the average fibre orientation. Edwards and Mounfield [15] studied the packing of systems composed of spherical and elongated grains. They showed that even at maximum close packing a suspension of fibres dispersed in spheres would not order nematically. The reason the two constituents of the granular system do not phase-segregate is related to the orientational couplings, not only between rods, but also between rods and spheres. The purpose of the present study was to provide experimental evidence concerning the influence that steric interaction and orientational coupling have on the average orientation of a fibre when dispersed in a particulate matrix.

We investigated the rheological behaviour of dispersions of cellulose fibres embedded in a particulate matrix made from agar microgels [16–20]. Microgel dispersions, also termed fluid gels, display a dominant elastic component with a slight frequency dependence [19, 20]. Using successive steady shear stress steps, the influence of very low shear rate on fluid gels was studied. It has been shown that under the external constraint the gel particles rearrange to increase the packing density of the system [21]. In the present study, the orientation of the fibres was monitored using the same stress-controlled procedure. As the suspending matrix exhibits a yield stress, rotary Brownian diffusion of the fibres cannot occur and the filler coefficient of the fibre suspension was used as a probe to follow the average fibre orientation. The influence of the fibre volume fraction and the fibre–gel particle size ratio on their rearrangement under the external constraint was investigated.

Materials and methods

Agar fluid gels

The preparation of fluid gels is described in previous work [19, 21]. Agar fluid gels were made up as 3% polymer weight using commercial agar (agar Luxara-1253 from Arthur Branwell & Co.). All samples were prepared using Millipore bidistilled water. The fluid gels were prepared in a stirred vessel using various shaft speeds. Particle size analysis was carried out on agar fluid gels using a Mastersizer-X from Malvern. In order to get representative particle size distributions, the obscuration levels were in the range 15–20%. The refractive index of a 3% agar gel was estimated to be 1.3367. The values of the mean particle diameter obtained over the volume distribution, $D[4, 3]$, as a function of the shaft speed in the stirred vessel are reported in Table 1.

Microcrystalline cellulose and calibrated glass beads

Microcrystalline cellulose (MCC) is a purified, partially depolymerised α-cellulose extracted from speciality grades of wood pulp. Two grades of MCC were used in this work: GP-1256 and GP-1251 provided by FMC-Avicell. GP-1256 and GP-1251 have a bulk density of 0.28 and 0.25 g/cm^3, respectively. The density of the fibre was estimated by volumetry to be 1.55 g/cm^3. Micrographs of diluted dispersions of Avicel GP-1256 and GP-1251 in water are shown in Fig. 1. The crystalline particles have a rodlike shape of average length 50 and 150 μm, respectively. The other filler particles used in this study were calibrated glass beads obtained from BDH Chemicals. The approximate diameter of these beads was 400 μm; their density was 2.3 g/cm^3.

Preparation of the fibre dispersions

Agar fluid gels (3% w/w) containing various amounts of filler particle were prepared. The volume fraction of fibres was determined from the density of the fibre based on the fact that no swelling of the fibres occurred in an aqueous environment.

Table 1 Values of the average gel particle diameter over the volume distribution, $D[4, 3]$, as a function of the processing shaft speed for 3% agar fluid gel

Shaft speed (rpm)	$D[4, 3]$ (μm)
200	8.95
400	4.90
600	3.30
1000	2.00
1200	1.85
1400	1.55

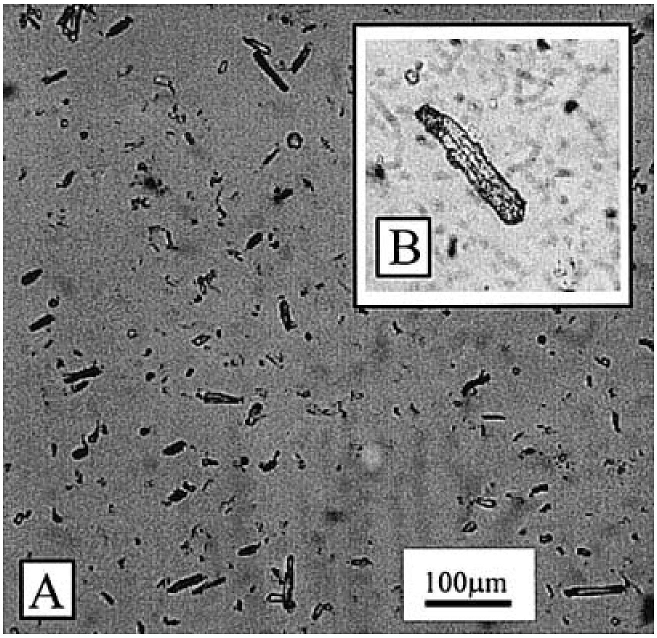

Fig. 1 Micrographs of diluted microcrystalline cellulose dispersions in water. **A** Avicell GP-1256, **B** Avicell GP-1251

The reduced packing fraction, ϕ^*, was used as a normalised concentration to describe the packing of the filler in the system [22]. The reduced packing fraction is defined as $\phi^* = \phi/\phi_\mathrm{m}$, where ϕ and ϕ_m are the filler volume fraction and the filler maximum packing fraction, respectively. The maximum packing fraction of the cellulose fibres was estimated from the ratio of the fibre bulk density and the fibre density. The value of the maximum packing fraction of Avicell GP-1256 and 1251 was 0.18 and 0.16, respectively. The maximum packing fraction of the glass beads was assumed to be equal to the volume fraction of a random close packing of spheres ($\phi_\mathrm{m} = 0.64$). Another parameter to characterise fibre dispersions is the number density, ρ, defined as

$$\rho = 4\phi/\pi d^2 L \ , \tag{1}$$

where ϕ, L, and d are the fibre volume fraction, the fibre length, and the diameter, respectively. In this work, the rheological behaviour of the suspensions was studied with the condition $\rho \ll 1/L^2 d$ satisfied for both grades of fibres, indicating that actual contact between rods is rare [1, 2].

Rheological characterisation

A Carrimed CSL500 rheometer fitted with a large-gap double-concentric-cylinder geometry [23] was used to investigate the viscoelastic behaviour of the samples. Prior to further rheological characterisation, the extent of the linear viscoelastic region of the samples was determined. The frequency spectra were recorded at a fixed strain of 0.2%, a value for which the fluid gels were within the linear viscoelastic region. To avoid wall slips, the metal walls of the Couette cylinder were roughened with sandpaper. The samples were covered with mineral oil to prevent water evaporation. All the measurements were made at 10 °C.

Results

Viscoelastic properties of the filled systems

The volume fraction of fibre (Avicell GP-1256) added to the fluid matrix ranged from 0.6 to 8.3%, corresponding to a reduced packing fraction, ϕ^*, between 0.03 and 0.46. To quantify the effect of the fibres on the rheological properties of the fluid gel, a filler coefficient, *F*, was used. It is defined as the ratio between the storage modulus of the filled system and the storage modulus of the matrix at an oscillatory frequency of 1 Hz. The evolution of the filler coefficient as a function of the volume fraction of the fibre is depicted in Fig. 2. A number of theoretical models [5, 24, 25] have been tested for predicting the elastic moduli of the fluid agar gels filled with MCC fibres. None of these models could adequately explain the data obtained. This is probably because the models assume that the fibres are infinitely larger than the entities forming the suspending medium, which is not the case in the system under study.

The evolution of the suspension viscosity as a function of the shear stress can be seen in Fig. 3. The suspensions showed a strong shear thinning behaviour, illustrated by the decrease in the viscosity as a function of the shear stress. No flow of the suspension was recorded unless the suspensions were acted upon by an apparent yield stress. The reinforcement of the system induced by the fibres is seen by the increase in the yield stress as a function of the fibre volume fraction.

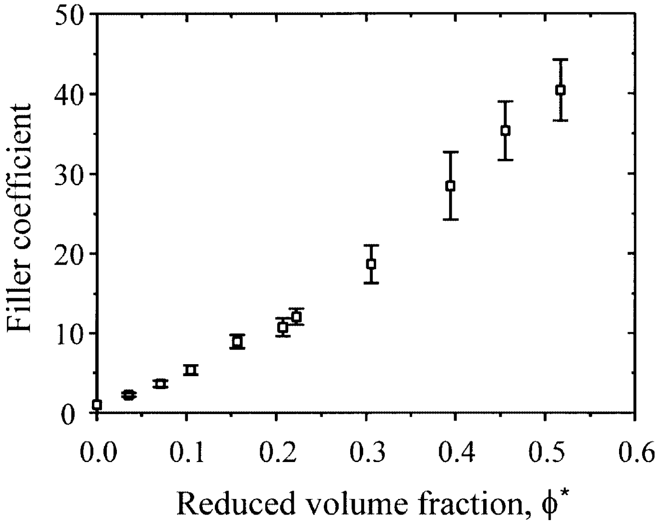

Fig. 2 Evolution of the filler coefficient as a function of the fibre reduced packing fraction, ϕ^*. Data obtained with fibre GP-1256

Influence of stress-controlled conditioning on the viscoelastic behaviour of agar fluid gels filled with fibres and spheres

A steady stress was applied for 15 min on the fibre dispersion, then the stress was released and the sample was allowed to relax for 15 min. For all the experiments, the applied stress was 3 Pa, a value for which bulk flow of the suspension does not occur (Fig. 3). The filled matrix showed an increase in the shear modulus as a function of the number of conditioning steps; however this increase was less significant than for the fluid matrix alone (Fig. 4). Consequently, the filler coefficient

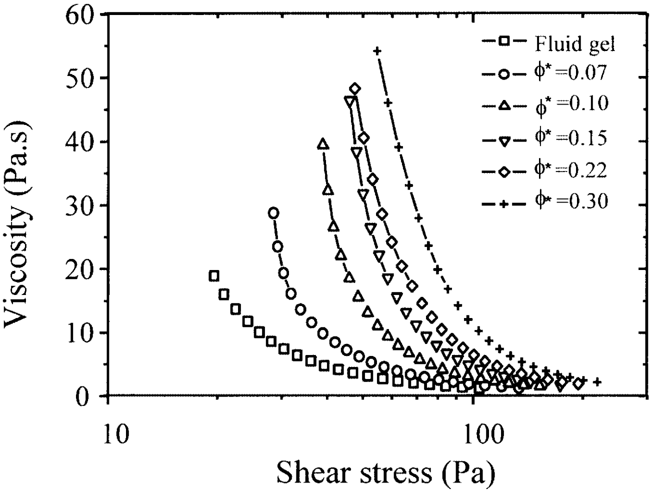

Fig. 3 Evolution of the viscosity as a function of the shear stress for fluid gels containing microcrystalline cellulose: Avicell GP-1256

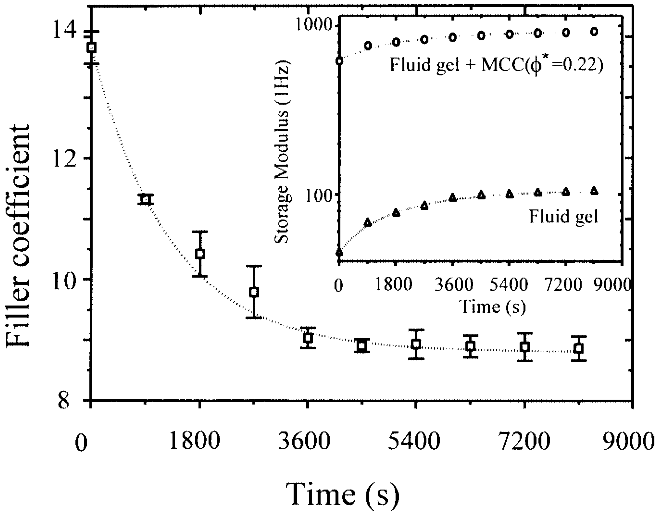

Fig. 4 Evolution of the filler coefficient of agar fluid gels containing fibres (GP-1256, $\phi^* = 0.22$) as a function of the time a stress of 3 Pa was applied. *Inset*: evolution of the storage modulus for a 3% agar fluid gel and for a fluid gel filled with fibres (GP-1256, $\phi^* = 0.22$)

decayed as a function of the time the stress was applied. Successive conditioning steps were applied to a fluid gel filled with micrometric glass beads (Fig. 5). The filler coefficient was constant over successive shear stress steps; therefore, the anisotropic shape of the MCC particles was responsible for the decrease in the filler coefficient.

Influence of the fibre reduced volume fraction, ϕ^*

The conditioning treatment was applied to fluid gels containing various amounts of MCC. For all the volume fractions studied, the filler coefficient decayed with the time the stress was applied. These curves were fitted with a simple exponential law defined as

$$F(n) = F_0 \exp(-kt) + F_\infty[1 - \exp(-kt)] \ , \qquad (2)$$

where F_0 and F_∞ are the initial value ($t = 0$) and the asymptotic value ($t \to \infty$) of the filler coefficient. The rate constant, k, indicates the efficiency of the reorientation process induced by the external constraint. The best fit of Eq. (2) to the experimental data according to the least-squares criterion gives an estimation of F_0, F_∞, and k. The values obtained for various reduced volume fractions of fibres are reported in Table 2. The evolution of k as a function of the fibre volume fraction is depicted in Fig. 6.

Influence of the fibre–gel particles size ratio, θ

Using different gel particle sizes and fibre grades, it was possible to use the size ratio, θ, defined as the ratio of the average fibre length to the gel particle diameter. The effect induced by shear stress steps on fibre dispersions (GP-1256 and GP-1251, $\phi^* = 0.17$) in various fluid gels whose average gel particle diameter ranged from 9 to 1 μm (Table 1) was investigated. The dispersions displayed a filler coefficient that decayed as a function of the conditioning time. Every curve was analysed to estimate k and to monitor its evolution as a function of θ (Table 3). To take into account the fact that at the same volume fraction, fibres of different size have different number densities, the decay rate constant had to be normalised by the number density, ρ. Hence, the data can be scaled onto a master curve, where the evolution of the normalised decay rate constant, k/ρ, as a function of θ is shown (Fig. 7).

Table 2 Initial values, F_0, asymptotic values, F_∞, and decay rate constant, k, obtained from the decay of the filler coefficient as a function of the conditioning time for various fibre reduced packing fractions, ϕ^*. Data obtained with fibre GP-1256. The shear stress applied was 3 Pa

Fibre volume fraction	ϕ^*	F_0	F_∞	$k \times 10^3$ (s^{-1})
0.006	0.03	2.7	1.6	0.92 ± 0.04
0.019	0.10	6.5	4.1	0.88 ± 0.05
0.028	0.15	10.6	6.2	0.80 ± 0.02
0.040	0.22	13.6	8.6	0.70 ± 0.04
0.055	0.30	23.3	13.0	0.75 ± 0.01
0.083	0.46	42.7	24.1	0.72 ± 0.01

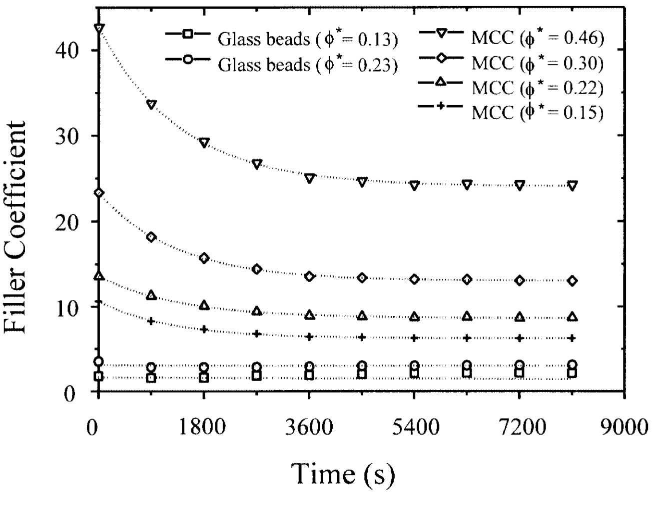

Fig. 5 Evolution of the filler coefficient of agar fluid gels containing fibres (GP-1256) and micrometric glass beads at various reduced packing fractions. The shear stress applied was 3 Pa

Discussion

Under a steady shear stress, the storage modulus of a fluid gel increases (Fig. 4, inset). This has been explained

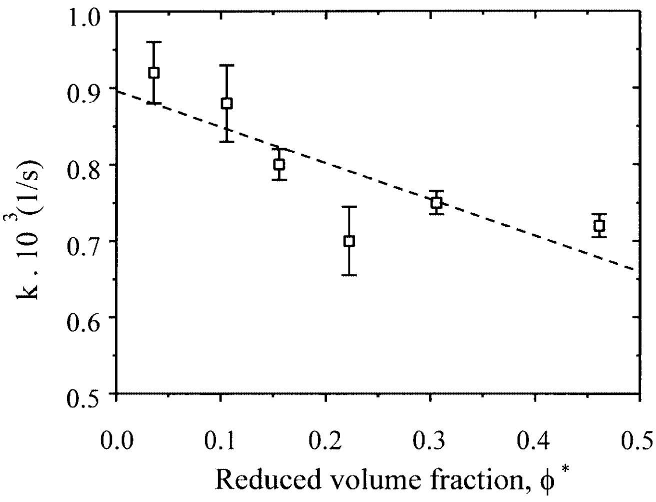

Fig. 6 Evolution of the decay rate constant, k, as a function of the fibre reduced packing fraction (GP-1256)

Table 3 Values of the normalised rate constant for reorientation, k/ρ, obtained from the decay of the filler coefficient as a function of the time the stress (3 Pa) was applied for various fibre–gel particle size ratios, θ. The number density, ρ, and the size ratio were calculated for an average fibre length of 50 and 150 μm for the fibres GP-1256 and GP-1251, respectively. The number density of the two fibres (GP-1256, GP-1251) corresponding to a reduced packing fraction, $\phi^* = 0.17$, is 7974 and 295 mm^{-3}, respectively

θ (GP-1256)	$k \times 10^3$ (s^{-1})	$k/\rho \times 10^8$	θ (GP-1251)	$k \times 10^3$ (s^{-1})	$k/\rho \times 10^7$
5.6	0.09 ± 0.04	1.1 ± 0.6	22.6	0.011 ± 0.005	0.38 ± 0.2
10.2	0.52 ± 0.05	6.5 ± 0.6	40.1	0.53 ± 0.10	18.0 ± 3.4
15.1	0.41 ± 0.20	5.1 ± 2.2	60.0	0.25 ± 0.11	8.66 ± 3.3
27.0	1.61 ± 0.12	20.1 ± 1.1	99.5	1.08 ± 0.11	37.0 ± 3.8
32.2	1.20 ± 0.48	15.0 ± 5.5	106.4	0.64 ± 0.21	21.6 ± 7.1

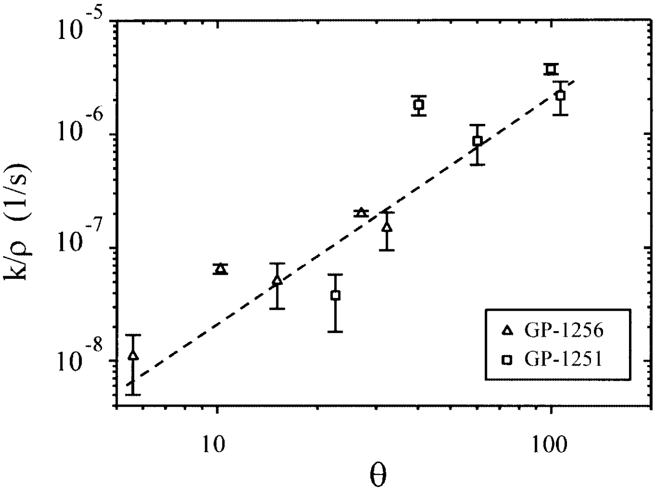

Fig. 7 Evolution of the normalised rate constant for reorientation, k/ρ, as a function of the fibre–gel particle size ratio, θ. The number density, ρ, and the size ratio were calculated for an average fibre length of 50 and 150 μm for the fibres GP-1256 and GP-1251, respectively

by a rearrangement of the particle packing leading to compaction of the system [21]. For fluid gels filled with fibres, the increase in the shear modulus was less significant (Fig. 4). Consequently, the filler coefficient decayed as a function of the time the stress was applied. The fluid gel filled with spheres showed a constant filler coefficient over successive steps; this suggests that the anisotropy of the filler particles is responsible for the decrease in the filler coefficient. On the other hand, shear-induced particle migration processes within the measuring cell can be discarded since the corresponding shear rates applied during the creep experiments were very low: ($10^{-6} < \dot{\gamma} < 10^{-4}$ s^{-1}). Moreover, an increase in the gel particle packing induced by the fibre can be ruled out as an explanation of the decay of the filler coefficient. The stress-induced compaction of the fluid gel was found to be inversely proportional to the initial reduced packing fraction of the particle [21]. If an increase in the gel particle packing induced by the fibres had been responsible for the less significant increase in the storage modulus, k would have been proportional to the fibre volume fraction. It is shown in Fig. 6 that this is not the case: the decay rate decreases with an increase in fibre volume fraction.

It is most probable that the decay of the filler coefficient as a function of the conditioning time is due to changes in the average orientation of the fibres. When an external constraint is applied, the fibres minimise the surface they offer to the shear stress and they tend to have their main axis aligned to the shear field [11–13]. The stress applied was lower than the apparent yield stress of the dispersion; therefore, the change in the fibre orientation cannot be due to the bulk flow of the gel particles, but rather to small adjustments of the particle orientation within the matrix. As the embedding matrix exhibits a yield stress the fibres are trapped and any change in their average orientation is not subsequently randomised by thermal agitation. An interesting feature is that the value of the filler coefficient after numerous conditioning steps is still higher than the value obtained for a suspension filled with hard spheres at the same reduced volume fraction (Fig. 5). This suggests that the fibres do not reach a state of full alignment, in which they would be parallel to the external constraint. Even after being subjected to long conditioning a certain level of disorder remains in the suspension. The reason the fibres cannot fully align is due to the presence of gel particles that fit into the spaces between the fibres. The alignment of the fibres with respect to the shear field is also hampered by fibre–fibre steric interaction, which is indicated by the decrease in the rate constant for reorientation with the fibre reduced volume fraction (Fig. 6). Steric interactions appear at a low fibre number density ($\rho \ll 1/L^2d$), which suggests that orientational couplings between fibres are mediated via the matrix of gel particles rather than transmitted from fibre to fibre via direct contact. Additional evidence for the effect of fibre–gel particle steric interaction on the orientational properties of the fibre comes from the fact that the normalised rate constant for reorientation, k/ρ, increases with the θ (Fig. 7). When the fibres are of similar size as the gel particles, i.e. $\theta \simeq 1$, the fibres orientational properties are negligible as any change in orientation of the fibre is hampered by the gel particles' steric exclusion. In contrast, for large fibres, i.e. $\theta \gg 1$, the gel particles' steric interactions with the fibres are less important, which allows the fibres to align further in the shear field. These results support the statistical mechanical analysis Edwards and Mounfield [15] carried out on the packing of systems composed of spherical and elongated grain.

Conclusions

It is shown that the average orientation of fibres dispersed in a viscoelastic particulate matrix can be monitored by means of successive steps of steady stress. The fibres never reach a state of full alignment because a nematic ordering of the fibres is hampered by fibre–fibre and fibre–gel particle steric interactions. The results show that the fibre's orientational properties depend on the fibre–gel particle size ratio.

References

1. Doi M, Edwards SF (1978) J Chem Soc Faraday Trans II 74:560–570
2. Doi M, Edwards SF (1978) J Chem Soc Faraday Trans II 74:918–932
3. Wierenga AM, Philipse AP (1998) Colloids Surf A 137:355–372
4. Ramazani A, Ait-Kadi A, Gremla M (1997) J Non-Newtonian Fluid Mech 73:241–260
5. Chow TS (1980) J Mater Sci 15:1873–1888
6. Wierenga A, Philipse AP, Lekkerkerker HNW, Boger DV (1998) Langmuir 14:55–65
7. Solomon MJ, Boger DV (1998) J Rheol 42:929–949
8. Fan X, Phan-Thien N, Zheng R (1998) J Non-Newtonian Fluid Mech 74:113–135
9. Fan CF, Hsu SL (1989) J Polym Sci Part B Polym Phys 27:2605–2619
10. Termonia Y (1994) J Polym Sci Part B Polym Phys 32:969–979
11. Kim JK, Song JH (1997) J Rheol 41 (5):1061–1085
12. Besun N, Ozguclu B, Peker S (1997) Colloid Polym Sci 275:567–579
13. Stover CA, Koch DL, Cohen C (1992) J Fluid Mech 238:277–296
14. Zirnsak MA, Hur DU, Boger DV (1994) J Non-Newtonian Fluid Mech 54:153–193
15. Edwards SF, Mounfield CC (1994) Physica A 210:290–300
16. Brown CRT, Norton IT (1991) European Patent EP 355908
17. Hedges ND, Norton IT (1991) European Patent EP 432835
18. Chalupa WF (1994) US Patent Application 94-265524
19. Foster T, Brown CRT, Norton IT (1998) In: Williams PA and Phillips GO (eds) Gums and stabilisers for the food Industry 9. Royal Society of Chemistry, London, pp 259–269
20. Frith WJ, Lips A (1996) In: Williams MC (ed) Proceedings of the XIIth International Congress on Rheology, Quebec City. pp 558–559
21. Cassin G, Appelqvist I, Normand V, Norton IT (2000) Colloid Polym Sci
22. Barnes HA (1989) In: Barnes HA; Hutton JF and Walters K (eds) An introduction to rheology. Elsevier, Amsterdam, pp 115–137
23. Normand V, Ravey JC (1997) Rheol Acta 36:610–617
24. Frisch HL, Simla R (1956) In: Rheology theory and applications. Ch 14, pp 525–613, Enrich F.R. (ed)
25. Guth E (1945) J Appl Phys (16)21: 20–25