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Rheological characterization of dry-formed networks of rayon fibres

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The viscoelastic properties of low-density dry-formed fibre networks have been evaluated by dynamic mechanical measurements in shear. The fibres used were rayon fibres of different diameters (13, 30 and 60 μm) and lengths (2, 4 and 6 mm). The effects of network density and grammage on the viscoelastic properties of the network were demonstrated. An important objective of this study was to assess relations between mechanical properties and fibre or network characteristics. The primary mechanical parameters used to describe the networks were the storage modulus G'_0 measured at very low imposed strain amplitudes (in the linear region) and the critical strain γ_C at which the network yields significantly. It was noted that if the network is to be able to withstand high deformations it should exhibit a high value of γ_C, which in turn, is promoted by a short free segment length between fibre crossings and a large number of contact points per fibre in the network. Long and thin fibres provide an advantage in this context. The modulus G'_0 appeared to be related to the ratio of the free segment length to the fibre diameter. A lower value of this ratio corresponds to a higher G'_0 value and an improved load transfer through the network structure. The networks studied here should in general be regarded as weak compared with other types of networks, e.g. paper. © *1998 Chapman & Hall*

1. Introduction

Cellulosic fibres are used as absorption materials in various types of hygiene products. The core in hygiene products such as disposable diapers (nappies) is today a cellulosic network of low density. This network core is almost exclusively dry-formed. This means that flowing air is used as transport medium for the suspended fibres during the forming of the core. As a result, no permanent hydrogen bonds are formed between the fibres constituting the npetwork. The insufficiency of the inter-fibre bonds in the dry-formed fibre network results in a low mechanical strength in the network [1]. Since hydrogen bonds are absent in dry-formed structures, the strength of such networks must depend on other structural parameters. Alternatively, when aiming at improving the mechanical performance of such materials, those factors that are responsible for the integrity of the network must be evaluated. Interesting parameters can be the normal or frictional forces between fibre-crossing segments, the bond stiffness, the fibre properties and the entanglement of the fibres.

Experience has indicated that mechanical failure of the fibre network is a very common cause of customer complaints. This failure of the network often leads to a liquid distribution problem in a hygiene product which can then be directly related to a poor performance of the network.

Earlier work on the characterization of the mechanical properties of dry-formed hygiene products has been mainly focused on the determination of network strength with the PFI network strength tester [2]. Since this method is based on forcing a piston through the network, it is only remotely related to the fundamental mechanical properties of the network. Furthermore, the test does not simulate the mechanical forces exerted on the network during its use in practice.

Hence, to characterize the fundamental mechanical properties of the network and, as a continuation, to find mechanical or structural parameters which relate to the end-use performance of the product, it is necessary to use other types of laboratory equipment. For polymeric materials, it is known that oscillatory viscoelastic measurements can provide valuable information regarding the structure [3]. This is also the technique chosen in this investigation. The dynamic–mechanical measurements were here performed with a Bohlin VOR Rheometer.

The object of this work was to describe the structure of the dry-formed fibre network and its properties. The effects of the mechanical properties of the fibres and of the dimensions of the fibres on the mechanical properties of dry-formed networks were evaluated. The dependence of the network properties on structural characteristics and on the bonding between the fibres is also discussed, as well as the elastic properties of a fibre network. The fibres used in the experiments were rayon fibres with different lengths and diameters. The importance of frictional forces between the fibre

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segments with regard to the mechanical properties of the network will be addressed in a later work.

2. Theoretical considerations

2.1. Important parameters for the characterization of fibre networks

In order to describe a network and its properties, it is important to assess which factors are required to characterize the structure. The network structure is to a large extent governed by the fibre characteristics and the contacts between the fibres, but the technique chosen for forming the network is, directly or indirectly, also of considerable importance.

The mechanical properties of the network are obviously influenced by the mechanical properties of the fibre as well as by its dimensions and shape. Earlier work has shown that there is a correlation between the modulus of the network and the longitudinal elastic modulus of the individual fibre [4]. The network used in that work can be regarded as being primarily two-dimensional and well bonded. The fibre length and thickness also affect the mechanical properties of the network. A long fibre has for example a larger number of fibre-to-fibre contact points per fibre. This results in a network in which the applied deformations are transmitted more effectively than in a network of short fibres. A thin fibre can be more entangled in the network, than a thick fibre, and in that way provide a greater stability and extensibility to the network.

The network properties depend not only on the fibre properties but also on the network structure and on the bonding and the friction between the fibres. Network density, grammage, free fibre segment length and number of fibre-to-fibre contacts per fibre are all important structural parameters. In network theories, the network density is normally the primary structural parameter characterizing the network. The free fibre segment length and the number of fibre-to-fibre contacts per fibre can be evaluated from the model of Komori and Makishima [5]. Underlying that model are three assumptions:

1. The fibres are straight cylinders
2. The fibres are randomly oriented
3. End-to-end or end-to-side contacts are neglected

The free fibre segment length between fibre-to-fibre bonds, shown schematically in Fig. 1, can in terms of that model be expressed as

$$S = \frac{2V}{\pi d l_{\text{tot}}} \tag{1}$$

where S = free fibre segment length (m); V = volume of network (m^3); d = fibre diameter (m); l_{tot} = total length of fibres in volume V (m).

When S is known, the number of fibre contacts per fibre, n_f, can be evaluated as

$$n_f = \frac{l}{S} \tag{2}$$

where l = fibre length (m).

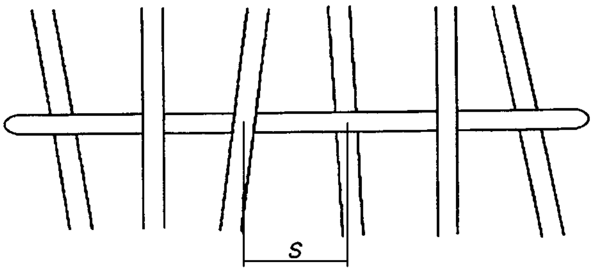

Figure 1 The free segment length S between fibre-to-fibre bonds in a network.

The mechanical properties of the fibre bonds can have a strong influence on the ultimate properties of the network. Stiff and strong bonds are able to withstand an applied stress effectively before they break and the network ruptures. The properties of the fibre bonds do not normally have any pronounced effect on the stiffness or elastic properties of the network unless the stiffness of the bonds is very low relative to that of the fibre [6]. This situation may however apply in the case of the networks investigated here.

2.2. Network theories

Several models have been suggested to describe the elastic properties of a fibre network [cf. 4, 7, 8]. These models describe bonded networks. There are, however, large differences between bonded networks and the unbonded networks used in this investigation. Theories for bonded networks are nevertheless mentioned as an analogy which can be useful even in the case of unbonded networks. Expressed in a somewhat simplified way, theories of this type often model the network modulus as the product of two factors, one related to the fibre stiffness and the other describing the network characteristics. A simple way to model the elastic properties of two-dimensional networks which are isotropic in the plane is to express the elastic properties of the network in terms of the longitudinal elastic modulus of the fibres and the ratio of the density of the network to that of the fibre material [9]

$$E_{\text{nw}} = \frac{1}{3} E_f \phi \frac{\rho_{\text{nw}}}{\rho_f} \tag{3}$$

where E_{nw} = elastic modulus of the network; E_f = longitudinal elastic modulus of the fibre; ϕ = a coupling efficiency factor, between 0 and 1; ρ_{nw} = network density; and ρ_f = fibre density.

It is evident in this equation that the density is a very important factor in network mechanics. It has been shown experimentally [9] that the network modulus increases with increasing density. The coupling efficiency factor, ϕ, in Equation 3 accounts for the influence of the fibre length and it also describes how the applied deformation is transmitted from fibre to fibre through the network. An increase in fibre length or in network density leads to a higher ϕ factor. Weak bonds with low stiffness lead to a low ϕ factor and provide a network with a low elastic modulus [10]. The ϕ factor can also be modified to account for the fact that there is certainly a distribution of fibre lengths.

The fibres are normally not randomly oriented in the plane, and Equation 3 can be modified to account for the influence of fibre orientation. One example for a two-dimensional structure is [10]

$$E_{nw} = \frac{1}{3} E_f \phi \frac{\rho_{nw}}{\rho_f} (6-4a_1+a_2)(1-\nu_{xy}\nu_{yx}) \quad (4)$$

where E_{nw} is the elastic modulus of the network in the main orientation direction of the fibres. The terms a_1 and a_2 describe the fibre orientation distribution and ν_{xy} and ν_{yx} are the Poisson's ratios of the network.

2.3. Theories to describe ultimate properties

Besides the elasticity of the network, there is also a need to model or characterize the ultimate performance of the network. One parameter that may be useful for this purpose is the yield stress. Experimental data on fibres in suspension, even that a type of unbonded network, have in several investigations been expressed in terms of a correlation between the yield stress of the network and the consistency C_m [11–13]. The data were fitted to a power law equation of the type

$$\tau_{nw} = aC_m^b \quad (5)$$

where C_m is the fibre concentration given in weight per cent and τ_{nw} the yield stress. The constants a and b depend on the type of pulp, degree of beating etc. Values of a between 1.18 and 24.4 and of b between 1.26 and 3.02 have been reported [11].

A power law resembling that in Equation 5 has also been used in other situations. de Ruvo *et al.* [14] approximated the in-plane strength of paper (a type of two-dimensional network) by a power law function of the density

$$\sigma_p = \frac{1}{3} k \left(\frac{\rho_p}{\rho_f}\right)^n \sigma_f \quad (6)$$

where σ_p = tensile strength of paper; σ_f = tensile strength of fibre; ρ_p = paper density; ρ_f = fibre density; and k and n = constants.

In general, it is substantially more difficult to model the strength characteristics of the network, and existing models are not as detailed as those used for the elastic properties. However, it is quite clear that the density of the network is also a parameter of major importance for the strength properties, cf. Equations 5 and 6. For completeness, it should be mentioned that there are several other models predicting the strength of paper structures. They are, however, not considered here.

Attempts have furthermore been made to analyse the relations between geometrical structures and mechanical properties of networks in a theoretical way with computer simulations. Berg and Svensson [15] and Salomonsson [16], for example, modelled networks as a truss with beams and nodes. Such simulations are not considered here either.

The purpose of the present paper is to describe the structure as well as the mechanical properties of dry-formed fibre networks. The properties are presented in terms of storage modulus, critical strain and elastic energy related, for example, to fibre length, network density, free segment length and number of fibre-to-fibre contact points.

3. Experimental procedure

3.1. Materials

The fibres used were rayon fibres from Svenska Rayon AB, Sweden, cut to suitable lengths by Bernhard Steferdt AB, Tyringe. Three fibre weights have been used: 1, 5 and 20 dtex (g/10 000 m) and three fibre lengths: 2, 4 and 6 mm. These fibres had not been surface treated. Details of the fibres are given in Table I. More precise data on the fibre dimensions were obtained with the STFI-Fibermaster [17], Table II. The arithmetic average fibre thicknesses were 13.2 ± 0.4 μm for the 1 dtex fibre and 30.2 ± 0.4 μm for the 5 dtex fibre. It was not possible to evaluate the thickness of the 20 dtex fibre with the STFI-Fibermaster; instead its thickness was estimated from the dtex numbers and the results from the STFI-Fibermaster for the other two fibres to be ca. 60 μm. The fibre form according to the STFI-Fibermaster is defined as the ratio of the fibre length, l, to the diagonal, m, of the surrounding rectangle (see Fig. 2 for definitions of these quantities). Scanning electron micrographs of the rayon fibres, obtained with a Stereoscan 360 from Cambridge Instruments, are shown in Fig. 3. The cross-section of the fibres was actually not perfectly circular as is evident from the micrographs but for the purpose of this work this is disregarded, i.e. the fibres are treated as cylinders with a circular cross-section.

TABLE I Fibre characteristics: product specification according to Svenska Rayon AB, Sweden

Fibre			1 dtex	5 dtex	20 dtex
dtex	g/10 000 m		0.9–1.1	4.5–5.5	18–22
Strength[a]	cN/dtex	dry min	1.5	1.6	1.3
		wet min	0.7	0.7	0.6
Elongation[a]	%	dry	14–19	20–28	20–28
		wet	14–23	22–30	22–30
Elastic modulus[b]	(GPa)		7.1	6.8	6.6

[a] The strength and elongation of the fibres were measured with a Fafegraf M from Herbert Stein, Germany.

[b] The longitudinal elastic modulus of the fibres was measured with a specially designed equipment for tensile testing. The load cells, Bofors U2D1, were specially adjusted to handle small forces.

TABLE II Fibre dimensions according to the STFI-Fibermaster [17] (for definition of fibre form see Fig. 2)

Fibre	Length (mm, ± 0.03 mm)		Thickness (μm, ± 0.04 μm)		Form (%)	
	Arithmetic average	Weight average	Arithmetic average	Weight average	Arithmetic average	Weight average
1 dtex 2 mm	2.27	2.58	13.4	13.7	91	88
1 dtex 4 mm	4.24	4.80	13.1	13.4	83	81
1 dtex 6 mm	5.62	6.39	13.1	13.3	83	81
5 dtex 2 mm	2.24	2.31	32.0	32.1	96	96
5 dtex 4 mm	4.46	4.63	29.1	29.2	96	95
5 dtex 6 mm	6.25	6.61	29.1	29.3	90	89

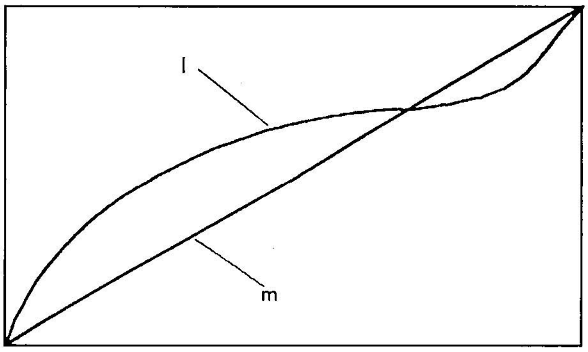

Figure 2 Definition of the fibre form (l/m) according to the STFI-Fibermaster.

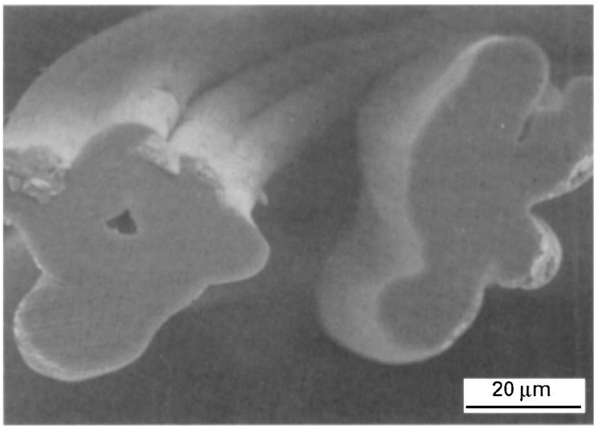

Figure 3 Scanning electron micrographs of the rayon fibres.

If the dtex values are recalculated from the measured values, it is found that these values are not the same as the given values. This results from the fact that the cross-section is not perfectly circular.

3.2. Sample preparation

In order to remove all contamination from the manufacturing process, the fibres were first diluted to a concentration of 0.8% in distilled water and then washed for 10 000 revolutions in a standard SCAN-disintegrator (SCAN-M 2:64). After washing, the fibres were dried and conditioned at 23 °C and 50% RH. The fibres were then defibrated in a Kamas hammermill H 01 (Kamas Industri AB, Sweden). The rotor speed and the diameter of the holes in the sieving plate were chosen, for each type of fibre, to give an optimal network strength as measured according to a method by PFI [2]. The operating conditions for the mill and the values of the optimal network strength are given in Table III.

TABLE III Operating conditions for the Kamas hammermill and the maximum network strength

Fibre	Rotor speed at maximum network strength (r.p.m)	Diameter of the holes in the sieving plate (mm)	Maximum network strength (N)
1 dtex 2 mm	4000	8	9.2
1 dtex 4 mm	4000	12	26.0
1 dtex 6 mm	4000	without sieving plate	40.9
5 dtex 2 mm	4000	6	1.2
5 dtex 4 mm	3000	8	6.6
5 dtex 6 mm	2000	12	20.4
20 dtex 4 mm	4000	6	1.0
20 dtex 6 mm	3000	12	3.2

Feeding rate of the fluff pulp: 2 g/s

After defibration, fibre networks were formed according to the Kroeyer method [18], i.e. by using two whisks which distribute the fibres over a net. The fibres fall through the net into a mould for forming test specimens (for the mechanical evaluation). In order to visualize the fibre orientation in the network 2% of dyed fibres were added when the network was formed. The fibres were almost randomly oriented in the plane perpendicular to the cylinder axis (see Fig. 4), but the structure appeared to be layered along this axis. It may be expected that these test specimens are actually transversely isotropic.

3.3. Measurements of the elastic properties in shear

Oscillatory viscoelastic measurements which are known to yield valuable information regarding the structure of materials [3], were made. Dynamic–mechanical measurements can also be performed at different strain levels which means that information regarding the undisturbed structure can be obtained as well as the imposed strain level at which the structure starts to deteriorate. The dynamic–mechanical measurements were performed with a Bohlin VOR Rheometer (Bohlin Reologi AB, Sweden) at room temperature.

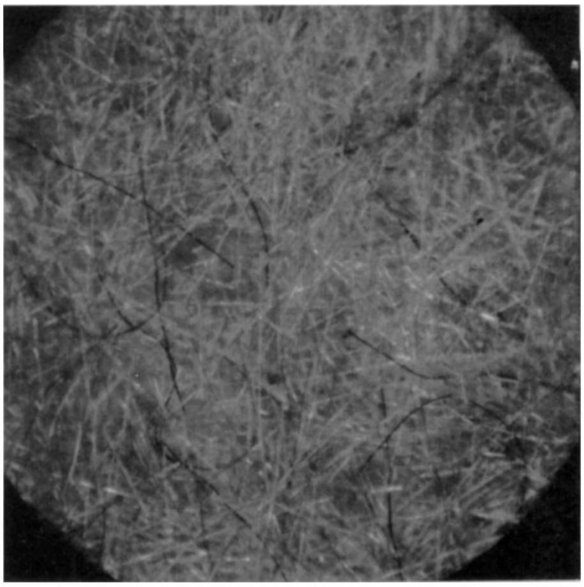

Figure 4 Network containing 2% dyed fibres. The photograph shows the plane perpendicular to the cylinder axis (fibre thickness 30 μm, fibre length 4 mm).

The test specimens were inserted between serrated plates with a diameter of 30 mm and subjected to a torsion around the cylinder axis. The frequency was 1 Hz and the applied shear strain amplitude was varied between 0.2 and 20 mrad. The density of the network was varied by changing the distance between the discs (between 2.5 and 15 mm). In this way networks with densities of 33, 50, 67 and 100 kg m^{-3} were obtained. In some cases, bulk (the inverse of the network density) was used to characterize the networks. The corresponding bulk values obtained by compression in the rheometer were 0.030, 0.020, 0.015 and 0.010 $\text{m}^3\,\text{kg}^{-1}$.

3.4. Data treatment and evaluation of the results

The primary data from the dynamic mechanical measurements were analysed as follows. G' is the storage shear modulus of the network. In general, the storage modulus decreased as the strain amplitude increased. Actually G' was fairly constant for small strains and the value of the storage modulus at a strain amplitude of 0.0007 was taken as G'_0, i.e. the undisturbed shear modulus of the network, cf. Fig. 5. The intersection of the two straight lines depicted in Fig. 5 gives a critical strain γ_C. For strains larger than γ_C the network gradually breaks down. Another way of expressing this is that the network is regarded as being approximately linearly viscoelastic at strains lower than γ_C.

In addition to the critical strain γ_C, the ultimate properties of the network were described by the stored elastic energy at γ_C and the yield stress corresponding to the critical strain. The stored elastic energy, W_{el}, when the network yields was calculated as

$$W_{\text{el}} = \frac{1}{2} G'_0 (\gamma_c)^2 \qquad (7)$$

The yield stress was obtained from the expression

$$\tau = G'_0 \gamma_c \qquad (8)$$

4. Results

4.1. The strain dependence of G': general observations

Fig. 6 shows the storage shear modulus as a function of the strain amplitude for networks consisting of fibres of different lengths (ca. 2, 4 and 6 mm). The diameter of the fibres was constant, 30 μm, and the network density was also kept constant, 100 kg m^{-3}, as well as the grammage 500 g m^{-2}. The 6 mm fibre clearly provided a network of low storage modulus and high critical strain and the 2 mm fibre a network of high storage modulus and low critical strain. It should be remembered that the number of fibres per volume unit decreased as the fibre length was increased.

The influence of different fibre diameter (13, 30 and 60 μm) on the storage shear modulus is shown in Fig. 7. The length of the fibres was 4 mm and the network density was kept constant at 100 kg m^{-3}, as well as the grammage at 500 g m^{-2}. The thick fibre of 60 μm, led to a network with a high storage modulus

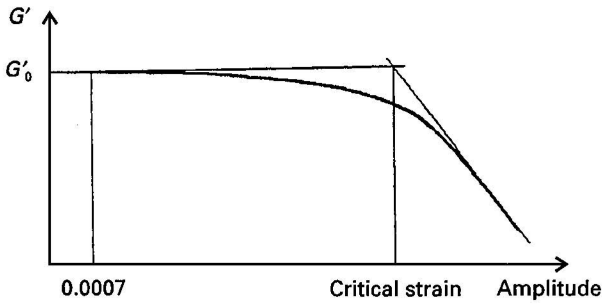

Figure 5 The primary data from the dynamic–mechanical measurements.

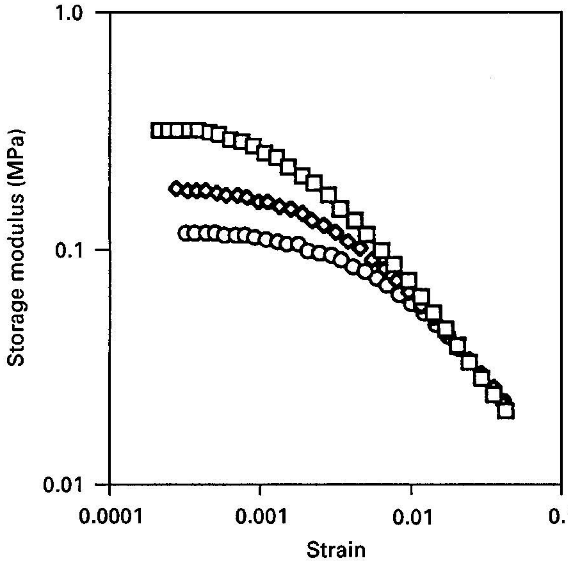

Figure 6 The storage shear modulus as a function of strain amplitude for networks based on fibres of different lengths. Fibre diameter 30 μm, grammage 500 g m^{-2} and network density 100 kg m^{-3}. (□) 2 mm; (◇) 4 mm; (○) 6 mm.

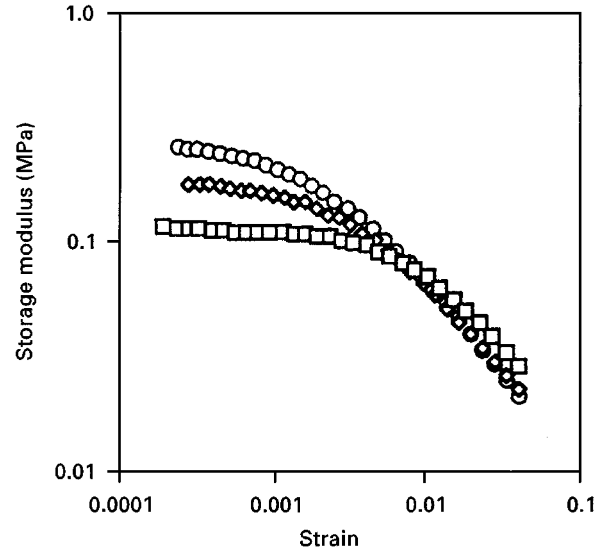

Figure 7 The storage shear modulus as a function of strain amplitude for networks based on fibres of different diameters. Fibre length 4 mm, grammage $500\,\mathrm{g\,m^{-2}}$ and network density $100\,\mathrm{kg\,m^{-3}}$. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

and a low critical strain whereas the thin fibre of 13 μm, resulted in a network with a low storage modulus and a high critical strain. The number of fibres per unit of volume decreased when the fibre diameter increased.

Fig. 8 shows G' versus the strain amplitude for networks based on 4-mm long and 30-μm thick fibres. This graph illustrates the influences of network density and grammage on the strain dependence of G'. Obviously the grammage had a negligible effect, whereas an increase in density from 33 to $100\,\mathrm{kg\,m^{-3}}$ raised the G'_0 value from ca. 0.03 to approximately 0.15 MPa. The critical strain increased with increasing network density. The network density had a similar effect on the mechanical parameters of networks based on fibres with other lengths and diameters.

4.2. Influence of fibre dimensions and network density on G'_0 and γ_c

Fig. 9 shows that G'_0 increased as the network became denser as a result of the compression in the rheometer. This increase was more pronounced in the case of the shorter fibres. As already mentioned, a similar effect of the density on the modulus was observed when the fibre diameter was changed from 30 μm to 13 or 60 μm. The magnitude of G'_0 was, however, reduced as the diameter decreased. The grammage of the samples was here kept at $500\,\mathrm{g\,m^{-2}}$.

Figs 10 and 11 summarize the effects of fibre dimensions and network density on the critical strain level when the grammage was $500\,\mathrm{g\,m^{-2}}$. The critical strain increased with increasing fibre length and decreasing fibre diameter. The increase in γ_c with increasing fibre length was more pronounced for the thinnest fibres of 13 μm. Increasing the network density by compression made the network stronger, i.e. the critical strain increased.

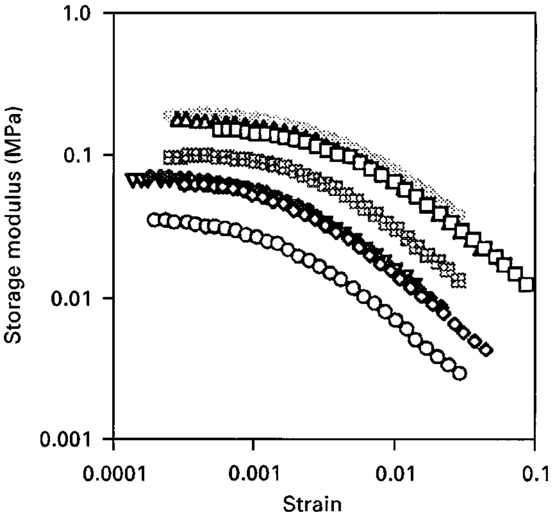

Figure 8 The storage shear modulus as a function of strain amplitude for networks based on fibres of different grammages and densities. (□) grammage $250\,\mathrm{g\,m^{-2}}$, density $100\,\mathrm{kg\,m^{-3}}$; (◇) $250\,\mathrm{g\,m^{-2}}$, $50\,\mathrm{kg\,m^{-3}}$; (○) $250\,\mathrm{g\,m^{-2}}$, $33\,\mathrm{kg\,m^{-3}}$; (△) $500\,\mathrm{g\,m^{-2}}$, $100\,\mathrm{kg\,m^{-3}}$; (■) $500\,\mathrm{g\,m^{-2}}$, $66\,\mathrm{kg\,m^{-3}}$; (◆) $500\,\mathrm{g\,m^{-2}}$, $50\,\mathrm{kg\,m^{-3}}$; (⊡) $750\,\mathrm{g\,m^{-2}}$, $100\,\mathrm{kg\,m^{-3}}$; (▽) $750\,\mathrm{g\,m^{-2}}$, $50\,\mathrm{kg\,m^{-3}}$.

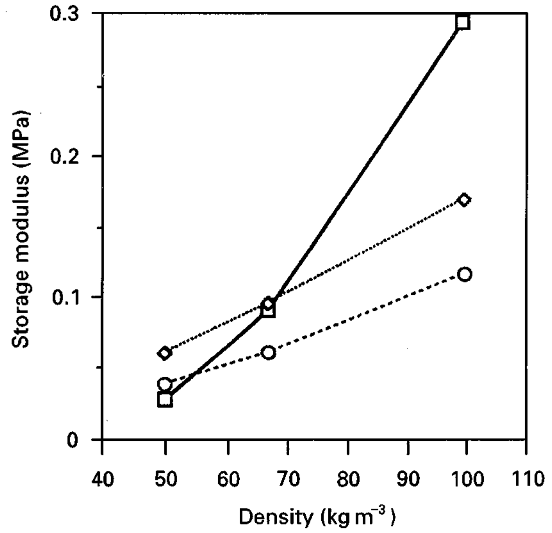

Figure 9 The storage shear modulus as a function of network density for networks based on fibres with different lengths. Fibre diameter 30 μm, grammage $500\,\mathrm{g\,m^{-2}}$. (□) 2 mm; (◇) 4 mm; (○) 6 mm.

5. Discussion

5.1. Elastic modulus of the network

The elastic modulus of networks and fibre-reinforced composite materials at a given density normally increases when the fibres used are longer. This was not the case in this investigation. On the contrary, there was a tendency for the modulus to decrease as the fibres became longer. This behaviour is not easy to explain as the number of contact points in the fibre network was only marginally affected by the fibre length (at a given density and fibre diameter). One possible reason for the decrease in shear modulus may be the character of the contact points between the fibres. The load exerted on the network is transmitted through the structure via those points. When the

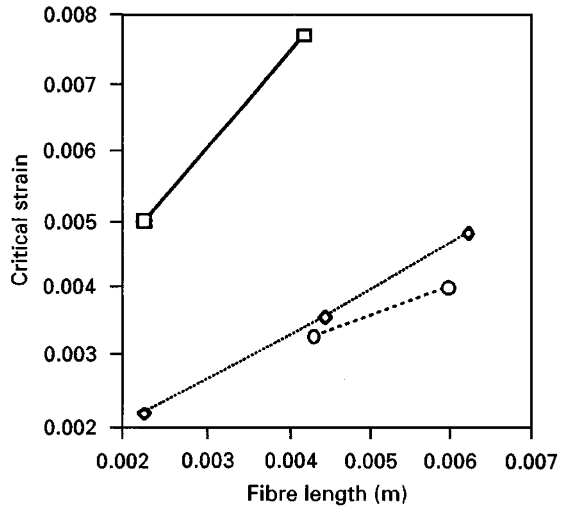

Figure 10 The critical strain of the network as a function of fibre length for fibres with different diameters. Grammage 500 g m^{-2}, density 100 kg m^{-3}. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

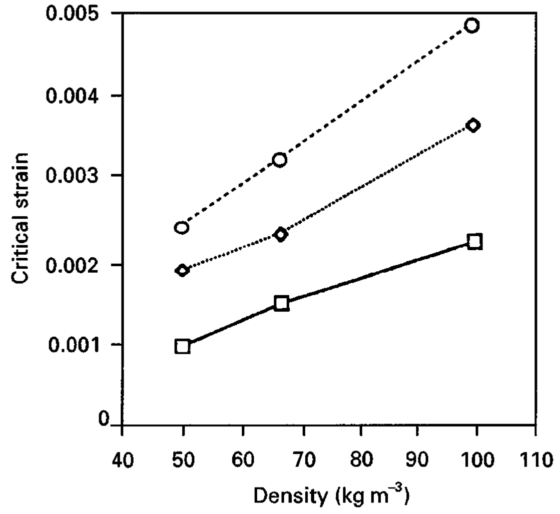

Figure 11 The critical strain as a function of the network density for networks based on fibres with different lengths. Fibre diameter 30 μm, grammage 500 g m^{-2}. (□) 2 mm; (◇) 4 mm; (○) 6 mm.

network is formed using long fibres, the (initial) density of the network is low compared to the initial density of the network formed by short fibres. It is possible that a distinction has to be made between contact points formed initially as a result of the forming process and contact points between fibres resulting from the compression of the network. At a given network density, the proportion (or the number) of the latter contact points is greater when longer fibres constitute the network. If such contact points are less rigid than those initially formed, then the result would be a lower modulus with increasing fibre length in agreement with the experimental results.

The modulus of the network increased as the fibres became thicker. This is not unexpected because an increase in fibre diameter raises the stiffness of the fibre and obviously also the shear stiffness of the network. The results of this study clearly indicate that it is not sufficient to use only the density to characterize the network from a mechanical point of view. Supplementary structural characteristics are required.

The coupling efficiency factor, ϕ, in Equation 3 is very small for these structures, of the order of 0.005. This means that the network is weak and actually cannot transmit the load in an effective way. The reason is that the network density is very low and/or that the bondings are not sufficiently stiff. Hollmark *et al.* [9] noted that the coupling efficiency factor became rather small for networks with a density of about 100 kg m^{-3}.

5.2. The influence of structural parameters on the storage shear modulus

The maximum storage modulus G'_0 can also be presented as a function of the number fibres per unit volume. This is shown in Fig. 12 for fibres with different lengths and constant diameter of 30 μm, and in Fig. 13 for fibres with different diameters and constant fibre length of 4 mm. The grammage was in both cases 500 g m^{-2}. The number of fibres per unit volume were changed by compressing the networks to different extents, i.e. by changing the density. As expected, an increase in the number of fibres at a given length or diameter resulted in an increase in the G'_0 value and, for a given number of fibres per unit volume, thick and long fibres are to be preferred if a network of high stiffness is aimed at. However, if a simple structural parameter characterizing the network is sought, the number of fibres per unit volume is not an ideal choice as different relations are obtained depending on the fibre length or diameter. The same applies to other structural characteristics such as the number of contact points per fibre or the number of contact points between fibres per unit volume.

A network parameter of interest in this context is the free fibre segment length (see Equation 1). The maximum storage modulus of the network is shown as a function of the free fibre segment length in Fig. 14.

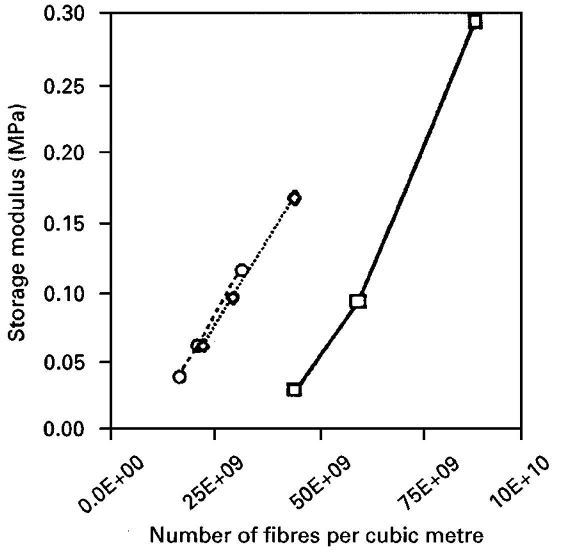

Figure 12 The storage shear modulus as a function of the number of fibres per cubic metre for fibres with different lengths. Fibre diameter 30 μm, grammage 500 g m^{-2}. (□) 2 mm; (◇) 4 mm; (○) 6 mm.

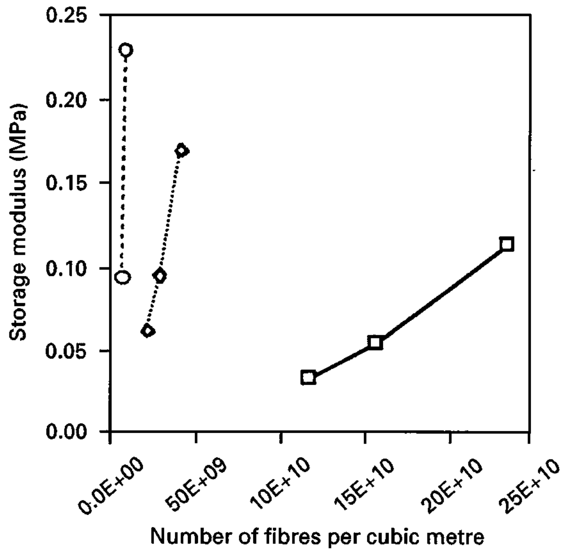

Figure 13 The storage shear modulus G'_0 as a function of the number of fibres per cubic metre in the network for fibres with different diameters. Fibre length 4 mm, grammage 500 g m^{-2}. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

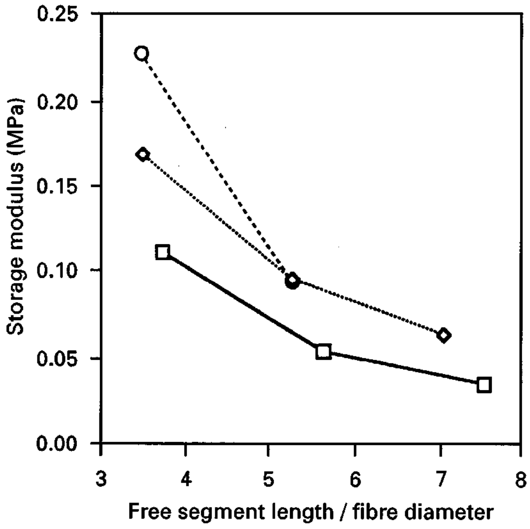

Figure 15 The storage shear modulus G'_0 as a function of the free segment length divided by the fibre diameter for fibres with different diameters. Fibre length 4 mm, grammage 500 g m^{-2}. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

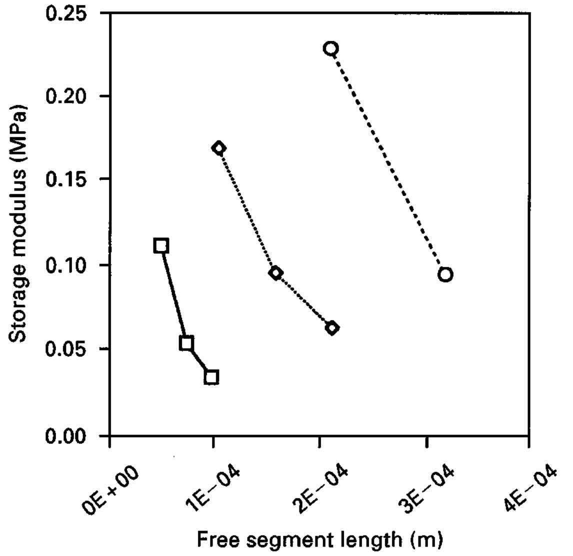

Figure 14 The storage shear modulus G'_0 of the networks as a function of the free segment length for fibres with different diameters. Fibre length 4 mm, grammage 500 g m^{-2}. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

The length of the fibres was 4 mm, and the grammage was kept constant, 500 g m^{-2}. The thin, 13 μm, fibre required a shorter free segment length in the network than the thick, 60 μm, to provide a given storage modulus. A decrease in the free segment length for fibres of a given thickness obviously led to a higher storage shear modulus.

In the Introduction, it was mentioned that normal forces between crossing segments could be important for the network stiffness. If so, a correlation between the ratio of the free segment length S to the surface moment of inertia of a cylinder (cross-section of the fibre) and the shear modulus would be expected. No such correlation was however found for these networks. The use of the ratio S/d, where d is fibre diameter, appeared, however, to be more rewarding, as shown in Fig. 15. In this case the networks were based on 4-mm long fibres and the grammage was 500 g m^{-2}. The stiffness data here appear to fall on approximately the same line, i.e. a kind of master curve was obtained.

Approximately the same relation as that in Fig. 15 was also obtained for networks based on the 2- and 6-mm long fibres. This indicates that the ratio between the free segment length and the fibre diameter can be an important structural parameter. In a well-bonded network, which is not subjected to any superimposed compression, this ratio has been shown to be important for the stress transfer between the fibres. A low value of S/d indicates that each fibre is effectively loaded and this promotes the stiffness of the network, i.e. the stress is transferred relatively effectively throughout the structure. The results shown in Fig. 15 also indicate that the stress on the loaded network is transmitted through the structure via a bending of crossing fibre segment and perhaps via a shearing of bonded regions.

However, a word of caution might be appropriate. Although the modulus of the network was improved by decreasing the free segment length (normalized with regard to the fibre diameter), the networks studied here should still be regarded as relatively weak, since the modulus of the fibres are not used very effectively due to the low network density. Furthermore, and perhaps quite importantly, the relation depicted in Fig. 15 was obtained for networks where the density was changed by compression of the samples. This means that the segment length was changed by external means and that the structure is perhaps not representative for an uncompressed network of similar density. The relation shown in Fig. 15 may be valid in some sense for structures that are not compressed, but this warrants a separate investigation.

5.3. The influence of structural parameters on the critical strain

In a sense, there was a more straightforward relation between structural parameters and the critical strain than that observed with the storage modulus. The γ_C value for the networks increased almost linearly with increasing number of contact points per fibre. This is shown in Fig. 16 for networks made of fibres with different lengths and constant diameter of 30 μm, and in Fig. 17 for networks made of fibres with different diameters, and a constant fibre length of 4 mm. The network grammage was 500 g m^{-2} and the network density varied from 50 to 100 kg m^{-3}. Thus, the more well-bonded the fibres are in the network, the larger strain amplitudes must be applied before the network yields.

In Fig. 18, the critical strain of the network is shown as a function of the free fibre segment length for fibres with different diameters. The length of the fibres was kept constant at 4 mm, as well as the network grammage at 500 g m^{-2}. In general, the critical strain seemed to increase exponentially with decreasing free segment length. Networks containing long and thin fibres and of high density consist of fibres with short free segment lengths and have a high number of contact points per fibre. Those networks exhibit a high critical strain and are able to withstand significant shearing deformation before they break down. Information about this kind of results has not been found in the literature.

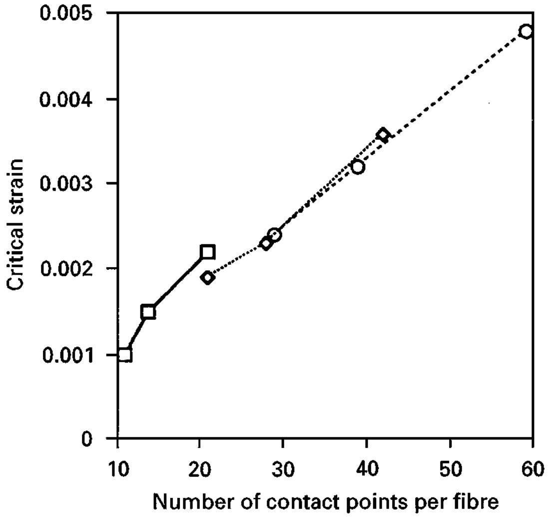

Figure 16 The critical strain of the networks as a function of the number of contact points per fibre for fibres with different lengths. Fibre diameter 30 μm, grammage 500 g m^{-2}. (□) 2 mm; (◇) 4 mm; (○) 6 mm.

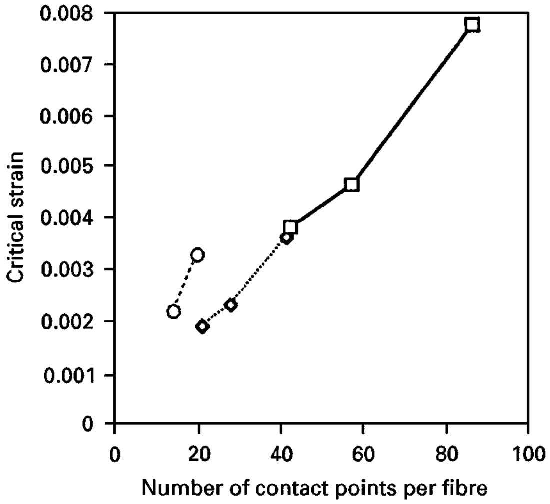

Figure 17 The critical strain of the networks as a function of the number of contact points per fibre for fibres with different diameters. Fibre length 4 mm, grammage 500 g m^{-2}. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

5.4. Evaluation of the stored elastic energy and the yield stress

An alternative way to characterize the ultimate properties of the fibre network is to evaluate the stored elastic enery at the critical strain γ_C. The elastic energy here reflects to a large extent the corresponding influence of the structural parameters on γ_C. This is not unexpected in view of Equation 7. The dependence of the elastic energy on the network density is shown in Fig. 19 for fibres with different lengths and constant diameter of 30 μm, and in Fig. 20 for fibres with different diameters and constant length of 4 mm. The network grammage was 500 g m^{-2} in both cases. A high density resulted in a high elastic energy stored in the network before significant yielding. A network consisting of thin and long fibres was able to store more elastic energy before it ruptured than a network made of thick and short fibres. High elastic energy at γ_C implies that the network is strong and possesses the ability to deform before it yields. It may be that the stored elastic energy is a parameter that can be useful for characterizing the end-use performance of the type of structure considered here. Further work is, however, required in order to substantiate this.

Fig. 21 shows the yield stress ($= G'_0 \gamma_c$) as a function of the volume concentration of fibres in the network for all the different fibres in this investigation. The experimental data can be fitted to a power law

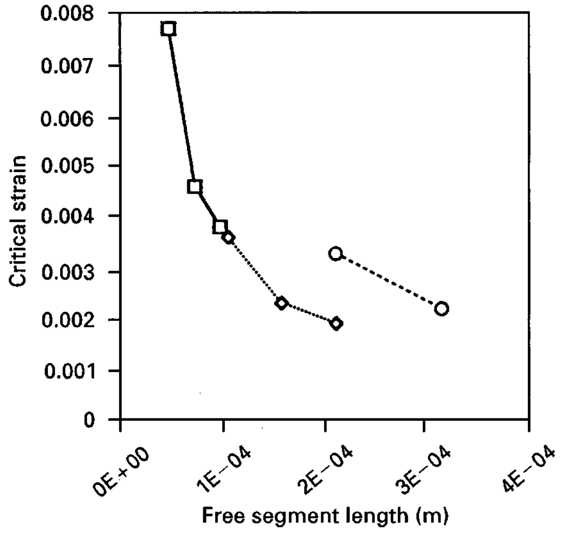

Figure 18 The critical strain of the networks as a function of free segment length for fibres with different diameters. Fibre length 4 mm, grammage 500 g m^{-2}. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

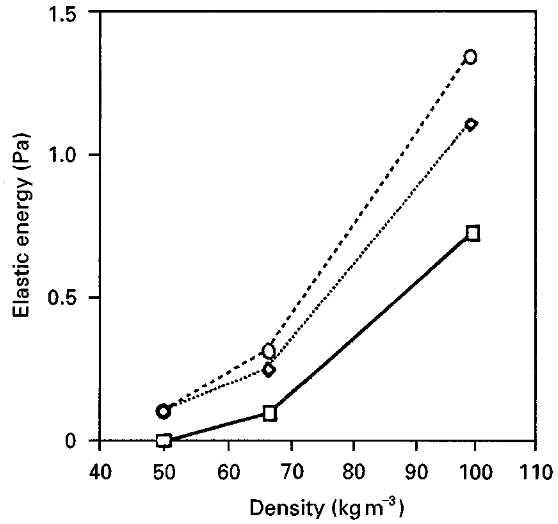

Figure 19 Stored elastic energy before yielding as a function of the network density for networks based on fibres with different lengths. Fibre diameter 30 μm, grammage 500 g m^{-2}. (□) 2 mm; (◇) 4 mm; (○) 6 mm.

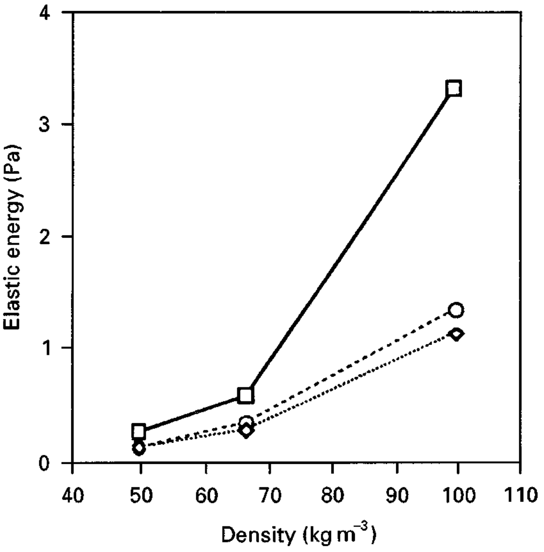

Figure 20 Same as for Fig. 19 but for networks based on fibres with different diameters. Fibre length 4 mm, grammage 500 g m^{-2}. (□) 13 μm; (◇) 30 μm; (○) 60 μm.

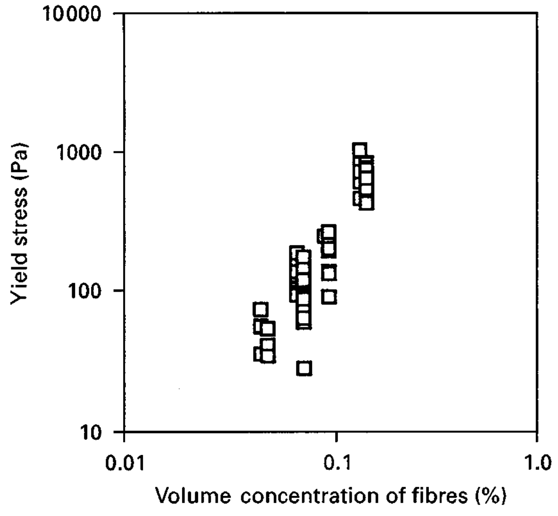

Figure 21 The yield stress of the network versus the volume concentration of fibres.

expression of the type given by Equation 5 with $a = 5.15$ and $b = 2.60$ with the coefficient of determination 0.88. The experimental scatter is obviously quite significant but in general the results arranged themselves approximately along the common line described by the power law expression regardless of the fibre dimensions. No clear relation between the yield stress and the structural parameters could be ascertained. This may be taken as an indication that the yield stress is not a suitable parameter for optimizing or characterizing the network structure with regard to its mechanical performance.

6. Conclusions

The most important results of this study can be summarized as:

1. Rheological measurements can provide relevant information regarding the relation between the structure of the network and its mechanical properties.
2. If the network is to be able to withstand high deformations prior to yielding, it should be based on long and thin fibres. From a mechanical point of view, the network should then be characterized by high values of the critical strain γ_C and of the stored elastic energy W_{el}. High values of these parameters are promoted by a short free segment length S and a large number of contact points per fibre, n_f in the network.
3. The stiffness of the network can be characterized by the storage shear modulus G'_0 evaluated at small applied strain levels. For fibres with the same chemical composition, the modulus of the network appeared to be determined or influenced by the ratio between the free segment length and the diameter of the fibres.
4. The networks studied here should be regarded as rather weak. This is a consequence of the low degree of inter-fibre bonding of the structure and the low network density, which provides a less effective load transfer throughout the structure.
5. To predict the stiffness of the dry-formed network, a knowledge of the network density and of the elastic modulus of the fibres constituting the network is not sufficient.

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