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The effect of additives on the mechanical properties of dry-formed fibre networks

C. ASKLING, LARS WAGBERG
SCA Research AB, Box 3054, S-85003 Sundsvall, Sweden
M. RIGDAHL
Swedish Pulp and Paper Research Institute STFI, Box 5604, S-11486 Stockholm, Sweden

The effects of thermal bonding and friction-changing additives on the mechanical properties of dry-formed cellulosic networks have been evaluated. Calcium carbonate particles and a cationic surface active agent were used to change the coefficient of friction of cellulose (Chemothermo mechanical pulps; (CTMP) and rayon fibres. The parameters used to describe the networks were the storage modulus G_0' (measured at low strain amplitudes) and the critical strain γ_c (at which the network yields) obtained from the dynamic–mechanical measurements and the maximum force F_{max} measured with a shear tester. The mechanical properties of the networks were improved as a result of the thermal bonding, which promotes stress transfer through the network structure. The friction-changing additives changed the ability of the fibres in the network to disentangle before the network ruptures. This change was, in the first place, reflected in corresponding changes in the critical strain γ_c and the maximum strength F_{max} of thd dry-formed networks. © *1998 Chapman & Hall*

1. Introduction

Cellulose fibres constitute the absorption core in hygiene products such as diapers. This core is almost always a dry-formed network of low density. Such networks usually have a rather low mechanical strength due to insufficient interfibre bonding [1, 2]. The mechanical strength is, however, of considerable importance, because too low a strength may result in crumbling or crack formation in the diaper which is of course a disadvantage with regard to the performance of the product. There is obviously a need to improve the basic understanding of how parameters such as interfibre friction, bond strength and bond stiffness affect the mechanical strength properties of dry-formed cellulosic networks.

Earlier work has shown that the low strength of dry-formed structures can be attributed to a poor stress transfer between the fibres and that the strength can be improved by adding a binder material [1, 3] or bicomponent fibres [4]. Other authors have discussed the importance of the fibre surface finish for the relation between fibre properties and the performance of the end-use products [5, 6], but knowledge in this area is limited.

Dynamic–mechanical measurements have been shown to provide valuable information regarding the relation between fibre properties, the structure of dry-formed networks and the mechanical properties of these networks [7, 8]. This type of analysis was also employed in this work in order to evaluate the influence of fibre surface treatment and bond characteristics on the properties of dry-formed networks. The ultimate properties of networks were evaluated using a specially designed equipment for shear strength testing [8].

The main object of the present work was to describe how the mechanical properties of a dry-formed network of cellulose or rayon fibres were affected by introducing strong bonds between the fibres in the network and by treating the fibre surfaces with additives which affect the friction between the fibres. The investigation is divided into two parts. The first part deals with the effect of introducing strong bonds into networks by thermal bonding with bicomponent fibres. In the second part, the influence of friction-reducing as well as friction-increasing agents on the mechanical properties of the fibre networks is evaluated.

2. Experimental procedure

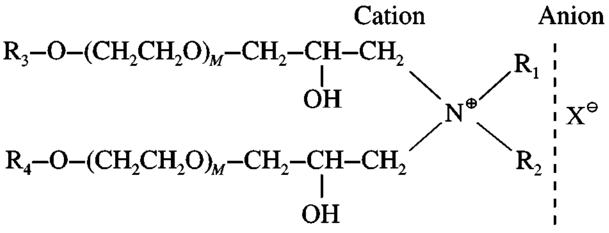
2.1. Materials

The pulps used in the first part, i.e. when strong bonds were introduced into the network, were two flash-dried chemothermo mechanical pulps (CTMP) produced on two occasions, both from SCA Graphic Sundsvall AB, Sweden, and delivered in bale form. The pulps had different fibre lengths (weight average): 2.41 ± 0.03 and 2.24 ± 0.03 mm, denoted CTMPa and CTMPb in this paper. The pulps were defibrated in a hammermill to optimal network strength as measured according to [9]. The rotor speed was 2600 rpm, the diameter of the holes in the sieving plate 15 mm and the feeding rate 200 g min^{-1}. The hammermill is described in more detail in [8].

Prior to the forming of networks, CTMPa was mixed with bicomponent fibres (Danaklon, Denmark) in different proportions. The bicomponent fibres, which consisted of a core of polypropylene with a surrounding shell of polyethylene, were 4 mm long and the fibre weight was 3.3 dtex (g 10 000 m^{-1}). The networks were then thermally bonded at 128 °C for 15 min in an oven from Werner-Mathis AG, Switzerland. The polyethylene shell of the bicomponent fibre melted at 125 °C whereas the polypropylene core had a melting temperature considerably higher than the bonding temperature.

Strong bonds between the fibres in networks were also achieved by treating CTMPb fibres with Tecseal, an ethylene-acrylic acid-copolymer (EAA) from Trüb Emulsions Chemic AG, Switzerland. The pulp fibres were sprayed with a water-based dispersion of the copolymer in an air stream [10]. Different percentages by weight of the EAA relative to the weight of the dry fibres were added (5, 10 and 20%). A reference sample which was sprayed with only water, was also prepared. Prior to forming the networks, the treated fibres were defibrated in a kitchen mixer (Braun Multimax MX 32, Germany) for 20 s. The networks were then thermally bonded at 112 °C fo 15 min in the previously mentioned oven. Scanning electron micrographs (Fig. 1) indicate that the applied EAA formed a rather homogeneous film on the fibre surface. The figure also shows the reference fibres without EAA.

The CTMPa-fibres were also used in the second part of this study together with rayon fibres (Svenska Rayon AB, Sweden) with a length of 4 mm and a fibre weight of 5 dtex. The friction coefficient between the fibre surfaces was lowered with a cationic surface active agent, Berocell 584 (Eka Nobel AB, Sweden), which has the general formula:



where R_1 and R_2 are alkoxy groups with 12–22 carbon atoms; R_3 and R_4 are alkyl-substituted phenolic groups with 14–46 carbon atoms; M is from 1 to 10; and X is an alkylene oxide tenside.

The rayon fibres were disintegrated in a standard disintegrator (SCAN-M 2:64) at a concentration of 0.8% in distilled water for 10 000 revolutions and were then dewatered in order to remove contaminations from the manufacturing process. After this treatment, the fibre suspensions were again diluted to a concentration of 0.8% with distilled water. The CTMP pulp was disintegrated but not washed. Different amounts of the cationic agent were added to suspensions of CTMP or rayon fibres, which then were stirred for 10 min before dewatering. The different amounts of the surfactant were 0, 3 and 10 mg g^{-1} pulp. After

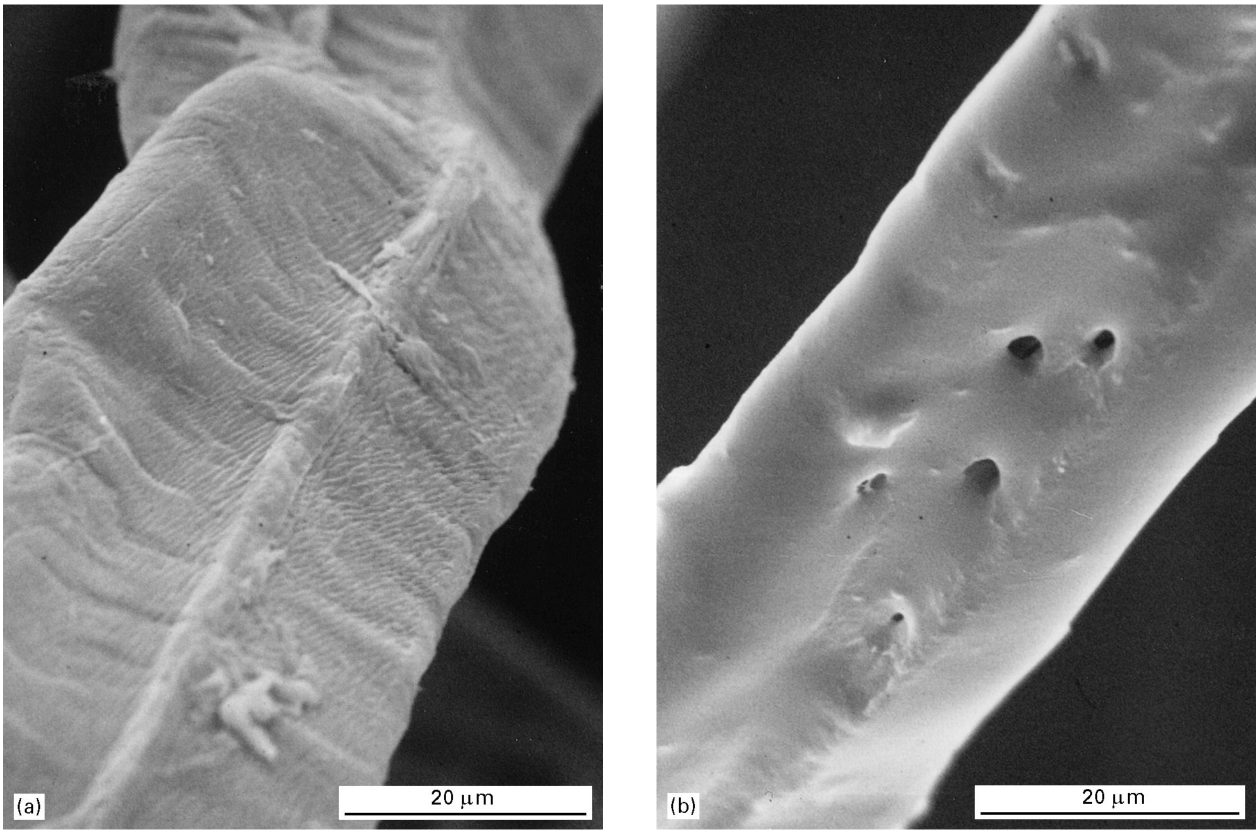


Figure 1 Scanning electron micrographs of CTMPb fibres (a) without EAA and (b) covered with EAA.

drying at 23 °C and 50% RH, the fibres were defibrated in order to produce an optimal network strength determined according to [9]. The CTMP was defibrated under the same conditions as before, and the rayon fibres were defibrated in a Kamas hammer mill H 01 (Kamas Industri AB, Sweden), fitted with a sieving plate with 8 mm holes, at a rotor speed of 3000 r.p.m.

In order to increase the friction coefficient, the CTMPa fibres and the rayon fibres were sprayed with a calcium carbonate suspension (Hydrocarb HO, Hustadsmarmor AS, Norway). A reference sample was sprayed with distilled water only. Before the spraying, the CTMP was defibrated as described above, and the rayon fibres were disintegrated and dewatered as above and then dried at 23 °C and 50% RH. As shown by the scanning electron micrograph in Fig. 2, the $CaCO_3$ particles were not entirely evenly distributed on the fibre surface (CTMP in this case), and some degree of particle aggregation could be noted.

2.2. Sample preparation

After preparation of the fibres, fibre networks were formed with a test specimen former described in detail in SCAN-C33 : 80. The former was equipped with special tubes which formed test specimens suitable for the different mechanical evaluations. The density of the networks was $100\,\mathrm{kg\,m^{-3}}$ (unless otherwise stated) and the grammage was $500\,\mathrm{g\,m^{-2}}$ in all experiments. The density and the grammage were calculated on the basis of the fibre weight without taking into account the additives.

2.3. Dynamic–mechanical analysis

The dynamic–mechanical measurements were performed with a Bohlin VOR rheometer (Bohlin Reologi AB, Sweden) at room temperature. The samples were conditioned at 23 °C and 50% relative humidity (RH) before the measurements were performed. The test specimens, with a diameter of 30 mm, were inserted between serrated plates 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.

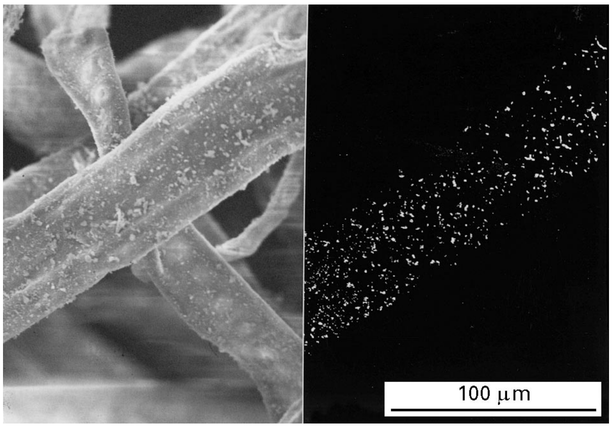


Figure 2 Scanning electron micrographs of the CTMPa fibres covered with calcium carbonate.

In the dynamic–mechanical analysis, the storage shear modulus G' was evaluated as a function of the shear strain amplitude of the applied sinusoidal deformation (Fig. 3). 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 shear modulus of the undisturbed network (cf. Fig. 3). The intersection of the two straight lines depicted in Fig. 3 gives the critical strain γ_c. Somewhat simplified, it may be said that for strains larger than γ_c the network gradually breaks down. Another way of expressing this is to say that the network is regarded as being approximately linearly viscoelastic at strains lower than γ_c.

2.4. Strength properties of the network

Since measurements with the Bohlin VOR provide information on the micromechanics of the networks, it was considered vital as a complement, to evaluate the macroscopic network properties of the same networks in order to relate to the end-use performance of the networks. The strength properties were then evaluated by measuring the maximum force which the network could withstand and the work of deformation to break in the shear mode, using specially designed equipment. The following standard procedure was used for the shear testing of the dry-formed networks. Test specimens with dimensions of 30 × 50 mm were mounted with a clamping distance of 15 mm, schematically shown in Fig. 4, and sheared at a deformation rate of $1\,\mathrm{mm\,s^{-1}}$. During the deformation, the force was continuously recorded by a load cell mounted on one of the clamps. In order to be able to record the small forces involved, special load cells, Bofors U2D1 (Bofors AB, Sweden), were used. The force was plotted as a function of the deformation, as is shown schematically in Fig. 5, and the following entities were defined: F_{max} = maximum force recorded; γ_{max} = (deformation/clamping distance) at maximum force.

Prior to the measurements, the samples were conditioned overnight at 23 °C and 50% RH and the tests were then conducted under the same conditions.

The ultimate properties of the CTMP-networks bonded with the bicomponent fibres could not be

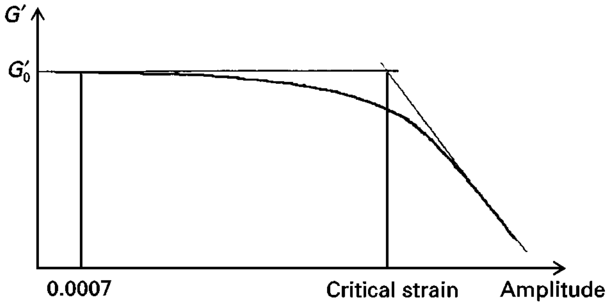


Figure 3 Schematic presentation of the relation between G' and the shear strain amplitude.

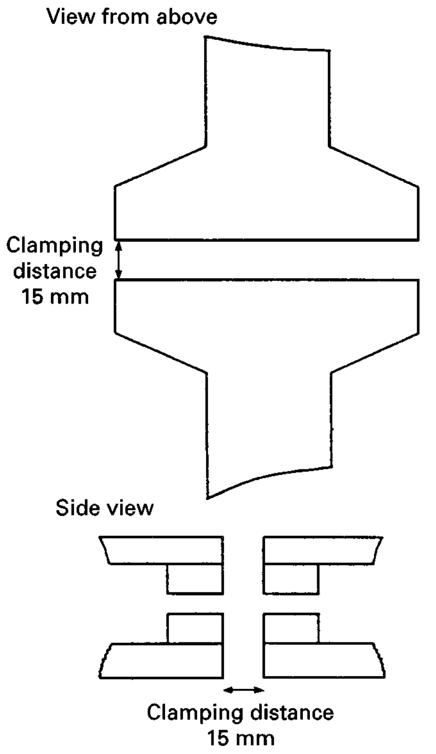


Figure 4 Schematic drawing of the clamps of the shear tester.

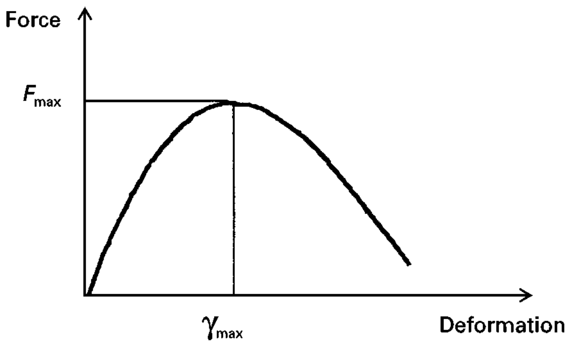


Figure 5 Schematic diagram of the relation between the applied force and the shear deformation when measurements were made using the specially designed mechanical tester.

determined in the shear mode with specially designed equipment. The mechanical performance of these networks was instead evaluated in the tensile mode with this equipment, and the measurements were complemented with measurements performed with a conventional tensile tester, Alwetron TCT 10 (Lorentzen and Wettre AB, Sweden). The mechanical properties of the networks were also characterized by determining the network strength using the PFI-network strength tester [9].

2.5. Friction coefficient

In order to quantify the change in the friction properties of the fibre surfaces caused by the addition of the calcium carbonate and the cationic surfactant, the friction coefficient between prepared sheets was determined. Calcium carbonate was sprayed onto the surface of newsprint made of 100% TMP (thermomechanical pulp, SCA Graphic Sundsvall AB, Sweden) and the cationic agent was added to the CTMP suspension, using the same method as described earlier, before sheets were formed. The friction measurements were performed according to ASTM-P 1984-87 with an IMASS SP-102-3M90, equipment from IMASS, USA. Several attempts were made to measure the friction coefficient between a treated rayon thread and a network of impregnated fibres or the friction coefficient between two treated rayon threads. These attempts were not, however, successful and the above-mentioned method was therefore chosen in order to obtain quantitative data relating to the effects of the different additives.

3. Results and comments

3.1. Mechanical properties of bonded dry-formed networks

The first part of this study was focussed on the introduction of strong bonds into the network structure. Fig. 6 shows the storage modulus, G'_0 of networks consisting of CTMPb treated with different amounts of EAA. Obviously G'_0 increased with increasing amount of EAA due to improved bonding and improved stress transfer throughout the structure.

The shear strength $F_{\max}$ of the networks (with a density of 50 kg m^{-3}) measured with the shear tester also increased with increasing amounts of EEA, in a manner similar to the increase in G'_0. There appears however to be a minimum amount of EEA required to raise the strength level ($F_{\max}$) above that obtained by a water treatment only. The densities of the bonded networks analysed by the two methods were different because it was impossible to press the bonded network (it would be crushed) before the shear testing. The test with the rheometer did not however need any pre-pressing, since the density could be determined in the equipment.

Strong bonds can also be obtained in the network with the bicomponent fibres, and Fig. 7 shows the storage modulus, G'_0, of networks based on CTMPa and bicomponent fibres as a function of the content of the latter fibres. Thermal bonding was shown to be a very effective process for raising the shear stiffness G'_0. Increasing the amount of bicomponent fibres from 0 to 100% (no CTMP fibres) increased the value of G'_0 from ca. 0.18 to approximately 0.66 MPa. In a sense, the bicomponent fibres and EEA can be regarded as equally effective. The addition of 20% of either the components increased the modulus of the network by ca. 0.2 MPa (cf. Figs 6 and 7).

The influence of the concentration of the bicomponent fibres in networks with a density of 55 kg m^{-3} on the maximum tensile force is also shown in Fig. 7. With the exception of the network based only on the bicomponent fibres (100%), the tensile strength increased with increasing concentration of the bicomponent fibres. The apparent decrease in strength when the network consisted only of the synthetic fibres is probably due to slip of the test specimens in the clamps. It should be pointed out that the tensile strength was in this case measured with two different testers. For the specimens containing the two lowest

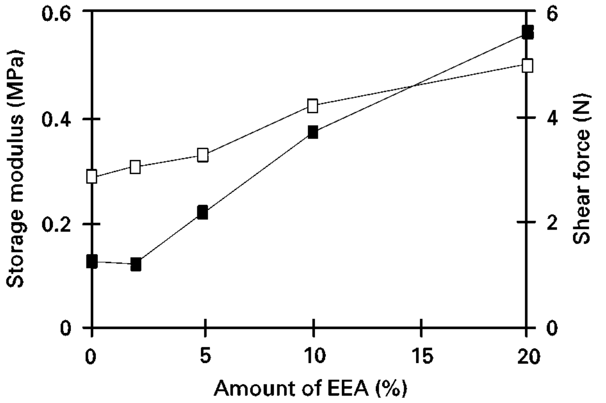


Figure 6 The storage modulus G'_0 (□) and the maximum shear force F_{max} (■) of networks based on CTMPb fibres treated with different amounts (% by weight) of EAA. The network density was approximately 100 kg m^{-3} (G'_0) and 50 kg m^{-3} (F_{max}).

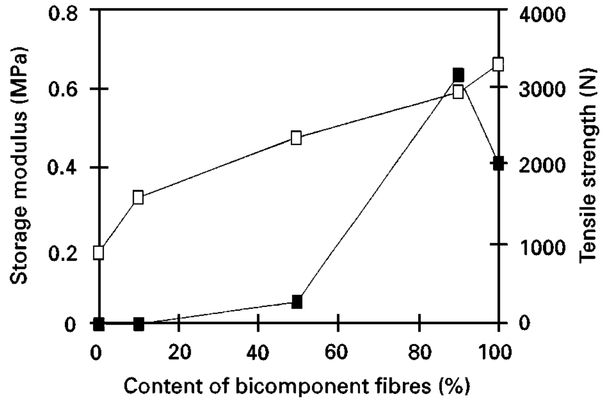


Figure 7 The storage modulus G'_0 (□) and the tensile strength F_{max} (■) of networks based on CTMPa and bicomponent fibres versus the content of bicomponent fibres. The network density was approximately 100 kg m^{-3} (G'_0) and 55 kg m^{-3} (F_{max}).

concentrations of the bicomponent fibres (0 and 10%), the specially designed tester was used, whereas the universal tensile tester was employed for the other samples.

3.2. Friction properties

The CTMPa fibres and rayon fibres were treated with friction-increasing or friction-reducing agents in order to evaluate how the fibre surface finish and the interaction between the fibres influenced the mechanical properties of the network. Calcium carbonate, $CaCO_3$, was here chosen as the friction-increasing agent. The suitability of $CaCO_3$ as such an agent is illustrated by Fig. 8 where the coefficient of friction between treated sheets is shown as a function of the amount of calcium carbonate applied on the surface of a sheet of newsprint. Both the static and the kinetic friction coefficient increased appreciably when 1 g m^{-2} of $CaCO_3$ was applied. Higher amounts of the mineral did not however have any further effect on the friction properties. The influence of calcium carbonate on the storage modulus and the maximum shear force, F_{max}, is shown in Fig. 9 for networks based on CTMPa fibres or rayon fibres. The treatment of the CTMP with $CaCO_3$ led to a very slight increase in both G'_0 and F_{max}. Treatment of the rayon fibres led, however, to a different result. G'_0 was slightly reduced by the mineral treatment, whereas the shear strength F_{max} was improved quite markedly. The improvements in the mechanical parameters of the networks were relatively smaller than the increase in the friction coefficient (cf. Fig. 8). Treatment of the fibres with $CaCO_3$ raised the critical strain γ_c significantly, as shown in Fig. 10; especially when the network was based on rayon fibres.

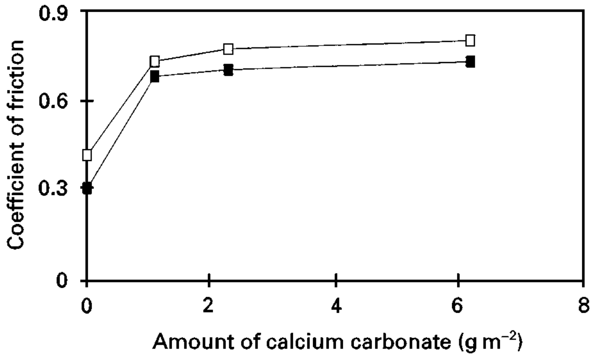


Figure 8 The coefficient of friction between treated sheets as a function of the amount (g m^{-2}) of calcium carbonate applied to the surface of a sheet of newsprint. □ static; ■ kinetic.

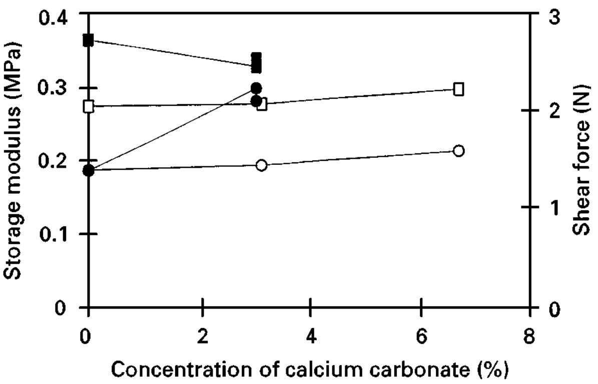


Figure 9 The storage modulus G'_0 and the maximum shear force F_{max} versus the concentration of calcium carbonate for networks consisting of CTMPa or rayon fibres. (□) CTMP G'; (■) rayon G'; (○) CTMP F_{max}; (●) rayon F_{max}.

A cationic surface active agent was used as the friction-reducing agent. The suitability of this compound for that purpose is illustrated by Fig. 11, where the coefficient of friction between treated sheets is given as a function of the amount of surface active agent in CTMPa sheets. The treatment reduced both the static and the kinetic friction coefficients.

The friction-reducing agent had no great effect on the G'_0-value (see Fig. 12) either for networks consisting of CTMPa fibres or for those based on rayon fibres. The critical strain γ_c decreased significantly however when the content of the friction-reducing agent was increased (Fig. 13). The effect was more pronounced when the rayon fibres constituted the network structure. Fig. 12 also shows the effect of the surface active agent on F_{max}. This measure of the shear strength of the network changed in the same way as γ_c; i.e. it decreased when the fibres were treated with

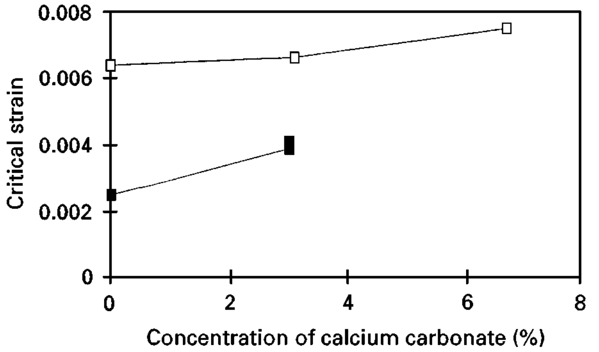


Figure 10 The critical strain versus the concentration of calcium carbonate for networks consisting of CTMPa (□) or rayon (■) fibres.

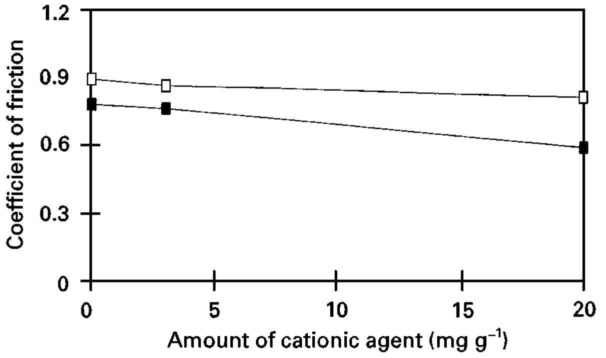


Figure 11 The coefficient of friction between treated CTMPa sheets as a function of the added amount of cationic surface active agent. (□) static; (■) kinetic.

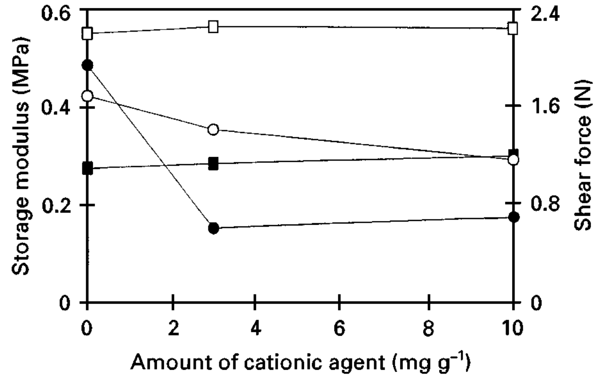


Figure 12 The storage modulus and the maximum shear force as a function of the added amount (mg g^{-1}) of cationic surface active agent for networks based on CTMPa or rayon fibres. (□) CTMP G'; (■) rayon G'; (○) CTMP $F_{\max}$; (●) rayon $F_{\max}$.

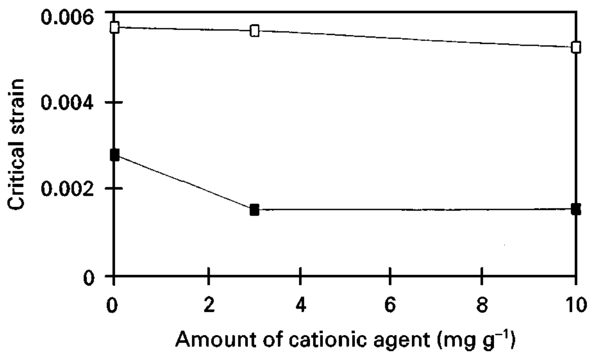


Figure 13 The critical strain as a function of the added amount (mg g^{-1}) of cationic surface active agent for networks based on CTMPa (□) or rayon (■) fibres.

the friction-reducing agent, and the effect was greater for the networks based on rayon fibres.

4. Discussion

The addition of bicomponent fibres and the EEA treatment of the CTMPb produced strong and stiff bonds in the network structure after heating. This is indicated by the pronounced improvements in both the storage modulus G_0' and the strength $F_{\max}$. It is not likely that the number of fibre bonds is appreciably increased by the incorporation of bicomponent fibres in the network or by the EEA treatment. This is not therefore the reason for the increase in the G_0'-values. Instead the thermal bonding increases the bond stiffness and then improves the stress transfer between the fibres. This can be expressed in terms of a higher structure coupling factor as shown by Westerlind [3], cf. also Askling *et al.* [7]. This improvement in stress transfer efficiency raises the stiffness and strength of the network.

The fibre-to-fibre friction can be changed with different surface active agents [5, 6, 11]. In this investigation, calcium carbonate and a cationic surfactant were used as friction-increasing and friction-reducing substances, respectively. The storage modulus for the network consisting of fibres treated with friction agents did not change as much as the friction coefficient at a given treatment level. This may be because the number of active fibre-to-fibre contact points is the same even after the surface treatment of fibres and because the bond stiffness is not sufficiently changed to have an effect on the G_0' value.

The tendency of the fibres to disentangle was however affected by the friction agents. Calcium carbonate improved and the cationic surfactant worsened the ability of the fibres in the network to disentangle before the network started to rupture. This is indicated by the higher and lower values of the critical strains, γ_c, respectively.

Earlier results [8] indicated a correlation between the values of the mechanical properties obtained with different test methods. It was however emphasized that the correlation held true for networks of fluff pulp defibrated in different ways if they were based on the same type of fibre surface finish. When the surface properties of the fibres are changed with friction agents, no such correlation between the storage modulus and maximum shear force was found. Instead, the shear tester gives values which appear to be more related to the disentanglement of the fibres in the network, which is to a great extent influenced by the surface properties of the fibres. It is thus not surprising that γ_c and $F_{\max}$ appear to be affected by the friction-changing additives in a similar manner, whereas the value of G_0' is almost unaffected.

5. Conclusions

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

1. The bond stiffness increased when strong bonds were introduced into dry-formed fibre networks by

thermal bonding. This may be interpreted in terms of a higher structure coupling factor and a better stress transfer throughout the network.

2. Surface friction agents change the tendency of the fibres to disentangle before the network ruptures. This is indicated by the increase in the critical strain (improved resistance towards disentanglement) and in the shear strength for fibres treated with calcium carbonate and by corresponding decreases in networks based on fibres treated with a cationic surfactant. These effects were more pronounced when rayon fibres with smooth surfaces were used.

3. The storage modulus (which quantifies the stiffness of the undeformed network) was not however influenced by the friction-changing additives in a manner that could be clearly related to the friction properties. This indicates that this kind of treatment had only a minor effect on the number of fibre contacts in the structure and on the bond stiffness.

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References

1. J. A. VILLALOBOS, The drying and curing of dry-formed webs. *Tappi* **64**(9) (1981) 129.
2. A. DE RUVO, H. HOLLMARK, S. HARTOG and C. FELLERS, Dry-formed vs wet-formed – a comparison of mechanical properties (in Swedish). *Sv. Papperstidn.* **85**(7) (1982) 16.
3. B. WESTERLIND, Mechanical properties of dry-formed and other low density papers, PhD Thesis, Royal Institute of Technology, Stockholm, Sweden, (1985).
4. S. TOMIOKA, Use of bicomponent fibre for thermally bonding air laid structures and some specific product applications, *Insight* **81**, (1981), Advanced forming/bonding Conferences, Paper 2.
5. H. L. RÖDER, Measurements of the influence of finishing agents on the friction of fibres. *J. Textile Inst.* **44**(6) (1953) 247.
6. H. G. JONG, Yarn-to-yarn friction in relation to some properties of fiber materials. *Textile Res. J.* **63**(1) (1993) 14.
7. C. ASKLING, L. WAGBERG and M. RIGDAHL, Rheological characterization of dry-formed networks of rayon fibres, *J. Mater. Sci.* **33** (1998) 2005.
8. C. ASKLING, L. WAGBERG and M. RIGDAHL, Effects of the process conditions during dry-defibration on the properties of cellulosic networks, *J. Mater. Sci.* **33** (1998) 1517.
9. PFI-Method of 1981, Measurement of network strength in dry fluffed pulps, The Norwegian Pulp and Paper Res. Inst. Box 250, Vinderen, Oslo 3, Norway, (1981).
10. R. EK, Dispersing fibrous materials in gas flow where e.g. wood pulp is fed into nozzle near point at which channel diverges, Swedish Patent SE 8008196-1, Oct. 3, (1985).
11. M. HARDING and T. GRANT, Influence of pulp properties on absorbent properties, *Absorbency* **89**, (1989), 2nd International PIRA Conference, Paper 8.

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