The Effect of Cellulose–Solvent Interaction on the Mechanical Properties of Bonded Fibrous Structures

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Synopsis

The mechanical properties, i. e., the tensile strength, tensile modulus, elongation at rupture, and tensile energy absorption (work of rupture), of a dry-formed network of cellulose fibers are shown to be substantially improved by impregnation of the network with organic solutions of poly(vinyl acetate) (PVAC). With the exception of the tensile strength, the improvement of the mechanical properties in the dry state is, however, dependent not only on the polymer content, but also on the interaction between the solvent and the cellulose fibers constituting the network. A solvent which interacts strongly with cellulose produces a stiffer and less ductile network than a more inert liquid. It is suggested that this effect is the result of a change in the cellulosic network structure itself. The solvents used in this study were methanol, acetone, ethyl acetate, chloroform, and toluene.

INTRODUCTION

Interest in dry-formed networks of cellulose fibers and their properties has been steadily increasing during recent decades. This is naturally related to the possibility of producing dry-formed paper sheets and similar products.[1–6] The dry-forming technique has several potential advantages over the conventional wet process,[5] not least with regard to economic investment requirements. However, the strength of the dry-formed network is insufficient for many purposes. This is due to the poor stress transfer through a deformed network or, equivalently, the low degree of interfiber coupling.[1,4,7] In practice, the means generally adopted of enhancing the strength characteristics is to add a synthetic, polymer-based, binder. The binder can be added to the network, e. g., by spraying a latex onto both sides of the dry-formed web, which is the most common technique,[2] or by immersing the sheet in an organic solution of a polymer.[7] A significant improvement in strength and ductility of the network is obtained with both procedures.

The aim of the present work has been to study the effect of the type of organic solvent for the binder on the mechanical properties of the dry-formed sheet. For this purpose, the mechanical properties of dry-formed networks which had been immersed in a number of different solutions of the same polymeric binder and then dried were compared. Here poly(vinyl acetate) (PVAC) was chosen as binding material since it is soluble in a relatively large number of organic liquids. As solvents we have used methanol, acetone, ethyl acetate, chloroform, and toluene. These liquids are expected to exhibit different degrees of interaction with cellulose fibers and also with PVAC itself.

In an earlier work,[7] the influence of polymeric binders on the mechanical properties of dry-formed networks was studied and discussed in terms of the
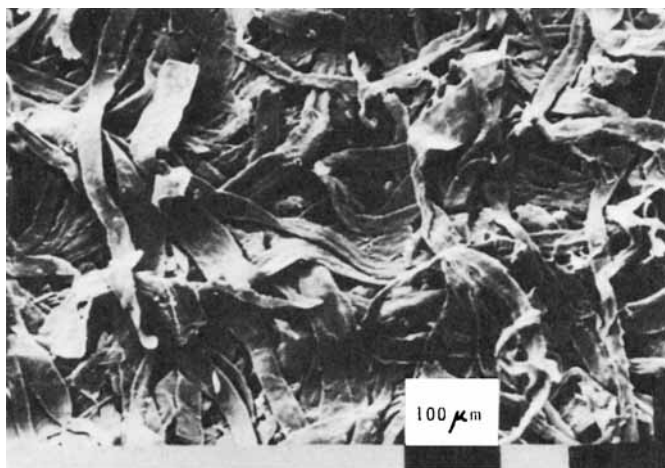
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Fig. 1. Scanning electron micrograph of the network structure.

nature of the polymeric binder and the binder distribution. The binding ma-
terial was, as in the present paper, added by means of solution impregnation,
and the binder content was less than 10% by weight. From this study, it was
concluded that the structure of the cellulose network itself was also of significance
for the final properties of the bonded network or sheet. In particular, when the
network was immersed in an aqueous solution of the polymeric binder or when
a water-based latex was used as a binder, a minimum amount of binding material
(ca. 2%) was required to affect the strength and stiffness of the network signifi-
cantly. On the other hand, when the network was impregnated with an organic,
less polar, solution of the binder, a change in the mechanical properties was ob-
served at the lowest polymer contents used. This behavior was interpreted as
being the result of the interaction between water and cellulose, i. e., the fibers
in the dry-formed network swell in the presence of water and upon drying this
results in an increase in the local inhomogeneity of the network; the number of
contact areas between fibers decreases and the distance between surfaces in-
creases. It may then not be unrealistic to assume that a small amount of binding
material (less than 2%) cannot improve the mechanical properties of the network.
For liquids which interact to a smaller degree with cellulose than water, effects
of this type are expected to be absent or less pronounced, which agrees with the
reported results.[7] For the sake of clarity it should be mentioned that dry-formed
fiber structures are normally very inhomogeneous compared with wet-laid
structures, i. e., the fibers are curled, wrinkled, and maybe even damaged to some
degree (cf. Fig. 1 and Ref. 1).

Before turning to the experimental results of this study, it should be pointed
out that a series of experiments on wet-formed paper sheets which is very relevant
in this context has been performed by Robertson.[8] He measured the tensile
properties of paper strips when they were immersed in various liquids, including
those used in this work, and he found that, e. g., the reduction in strength due
to the immersion strongly depended on the nature of the organic fluid. For the
liquids used in this work, the reduction in strength was largest for methanol and

decreased in the order acetone, ethyl acetate, chloroform, and toluene. The reduction in strength was in most cases mirrored by the swelling behavior of the sheets, i. e., a large strength reduction corresponded to a larger degree of swelling. From Robertson's investigation, it was concluded that the liquids which interacted to the lowest degree with cellulose, i. e., caused the smallest reduction in tensile strength, were those which had a low cohesive energy density and a relatively large molar volume.

EXPERIMENTAL

Materials

The dry-formed network was produced from a commercial grade of bleached kraft fluff pulp which had been defibrillated in a commercial disc refiner.

The binding material, poly(vinyl acetate), was added to the fiber network at room temperature in the form of a solution. The weight average molecular weight of the PVAC-grade was ca. 500,000.

The solvents methanol, acetone, ethyl acetate, chloroform, and toluene were laboratory grades which were used without further purification.

Methods

Impregnation. The dry-formed laboratory sheets, which were made in a sifting apparatus, were consolidated between moist felts using a roll press. After being dried, the sheets were immersed in a polymer solution of appropriate concentration and then allowed to air-dry without restraint. All experiments were performed on sheets that had been conditioned at 23°C and 50% RH. Prior to the impregnation the basis weight of the sheets was of the order of 75 g/m^2 and the density ca. 350 kg/m^3.

Mechanical Properties. The tensile stress–strain behavior was measured at 23°C and 50% RH using a horizontal tensile tester (Lorentzon and Wettre), and the strength, the elongation at rupture, the initial (tangent) modulus, and the work of rupture (tensile energy absorption) were evaluated. The width of the sample strip was 50 mm, the length 100 mm, and the strain rate 1.7×10^{-3} s^{-1}.

RESULTS AND COMMENTS

Effect of Immersion in Solvents without PVAC

Before discussing the efficiency of PVAC as a binding material when dissolved in organic solutions, it is important to establish the effect of the solvent alone. The networks were immersed in the different organic liquids until saturated and then air-dried. For comparison, some strips were immersed in water and air-dried. Table I gives the solubility parameters of the solvents and their molar volumes. The letter after the solubility parameter indicates the degree of hydrogen bonding (p poor, m moderate, and s strong). According to Robertson's proposal, methanol, which, with the exception of water, has the highest cohesive energy density (square of the solubility parameter) and the smallest molar vol-

TABLE I
Solubility Parameter (δ) and Molar Volume (V) of the Liquids

	δ (cal/cm^3)$^{1/2}$	V (cm^3)[a]
Toluene	9.1 p	106.6
Ethyl acetate	9.1 m	98.5
Chloroform	9.3 p	80.9
Acetone	9.9 m	74.0
Methanol	14.5 s	40.7
Water	23.4 s	18.05

[a] Ref. 8.

ume, should interact more strongly with cellulose than the others. Next in order of degree of interaction comes acetone, while chloroform and ethyl acetate are expected to behave rather similarly. Toluene, which has the lowest cohesive energy density and the largest molar volume, should affect the cellulose fibers to the smallest extent. This is confirmed by strength and swelling measurements.[8] It should be mentioned that although PVAC, which has a solubility parameter of 9.4 (cal/cm^3)$^{1/2}$, in soluble in all these liquids, chloroform is the best solvent of the five.

Table II, gives the mechanical properties of the dry-formed networks after immersion in the different solvents and subsequent air drying. This table also includes data for strips which had been water-immersed, and the mechanical properties of sheets which had not been immersed in any liquid at all (control samples). Concentrating first on the specific tensile strength, i. e., the nominal tensile strength (σ_B) divided by the network density (ρ), it is seen that immersion in water reduces the strength from ca. 0.7 N m/g to 0.3 N m/g, which must be regarded as a strong influence. When the sheets are immersed in toluene, the reduction is smaller, to ca. 0.5 N m/g, while the other solvents reduce the strength to an intermediate value (ca. 0.4 N m/g). The specific tensile modulus (E/ρ) is reduced in a similar manner. The largest reduction is again observed for the network which has been soaked in water, while toluene does not appear to appreciably affect the stiffness. The influence of solvent immersion on the elongation at rupture (ϵ_B) is also given in Table II. Prior to any immersion, ϵ_B is ca. 1.2%. Toluene, ethyl acetate, acetone, and chloroform do not affect the ductility of the network to any greater extent, while a slight increase is perhaps noted when water and methanol are used.

TABLE II
Mechanical Properties of Dry-Formed Networks Immersed in Different Liquids and Then Air-Dried

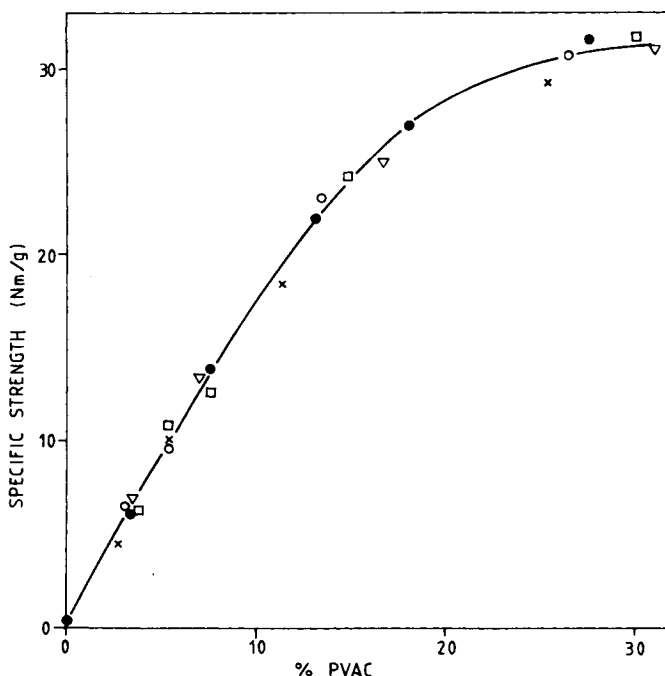| Liquid	σ_B/ρ (N m/g)	E/ρ (N m/g)	ϵ_B (%)
Toluene	0.5	80	1.0
Ethyl acetate	0.4	50	1.3
Chloroform	0.4	40	1.1
Acetone	0.4	40	1.4
Methanol	0.4	40	1.9
Water	0.3	20	2.1
Control (no immersion)	0.7	80	1.2

Fig. 2. Specific strength (σ_B/ρ) vs. the content of PVAC in the sheets. The differents solvents for PVAC are: (●) acetone; (○) ethyl acetate; (x) toluene; (▽) methanol; (□) chloroform.

These results indicate that a liquid which interacts with cellulose causes an increase of the inhomogeneity of the already very disordered structure of the dry-formed cellulose network. It may be remarked that for sheets which have been immersed in the liquids no clearly discernible rupture actually occurs. During deformation, several debonded zones progress perpendicular to the loading direction. The mechanical properties of these networks thus appear to be largely determined by the entanglement of the fibers. Evidently the disrupture of the dry-formed network on immersion is so dramatic that fiber surfaces are not close enough to establish bonding.

Effect of Solvent on the Binding Efficiency of PVAC

Figure 2 shows the specific tensile strength of the fiber network vs. the content of PVAC in the sheets. As indicated in the figure, the polymer has been dissolved in the various organic solvents given in Table I. The nature of the solvent used clearly has no influence on the specific strength of the bonded sheets. All the experimental points arrange themselves along a common curve, at least over the range here investigated (up to ca. 30% PVAC by weight). The very strong influence of the polymer on the strength should be noted; the specific tensile strength increases from a value of less than 1 N m/g for an unbonded sheet to well over 30 N m/g. The strongest increase is observed for polymer contents below 10%; above this value a saturation level appears to be gradually approached.
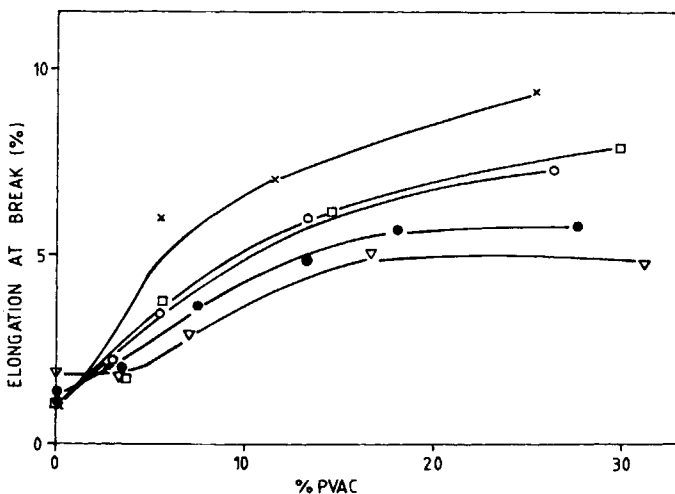
Fig. 3. Elongation at rupture (ϵ_B) of the networks vs. the amount of PVAC. Keys for the solvents are the same as in Figure 2.

Thus, perhaps somewhat surprisingly, the degree of cellulose–liquid interaction has no effect on the strength of dry-formed networks bonded by means of solution impregnation. Such an influence can, however, be noted in the extensibility of the networks. Figure 3 shows the elongation at rupture as a function of the content of PVAC (in the sheets) dissolved in the different organic liquids. The ϵ_B values increase in the order: methanol, acetone, ethyl acetate, chloroform, and toluene. This is true over the major part of the PVAC-content range. For lower contents of PVAC (below 5%), there is no clear trend. In this case, the order in which the solvents increase the elongation at rupture is exactly the opposite of that found by Robertson[8] for the magnitude in strength reduction of wet-laid paper sheets when immersed and tested in various liquids. This shows that the specific interaction between cellulose fibers and a given organic liquid has a fundamental bearing on the properties of a dry-formed structure even after bonding and drying. The interaction is, however, not primarily reflected in the strength of the sheet but rather through its extensibility. The difference between solvents is not merely a marginal effect; cf., e. g., ϵ_B at 25% PVAC for sheets immersed in a toluene solution (ϵ_B almost 10%) with that of sheets impregnated with the PVAC-methanol system ($\epsilon_B \approx 5\%$).

The work of rupture (W_b), i. e., the area under the stress–strain curves, is shown vs. the content of PVAC (in the sheets) dissolved in the different liquids in Figure 4. Again, the network immersed in the solution (toluene) with the lowest degree of interaction with cellulose requires the highest work of rupture, and, consequently, methanol-immersed sheets have the lowest rupture energy. The order of the different solvents used is the same as that found for the influence on the elongation at break. This is, of course, to be expected since W_b is in this case primarily determined by ϵ_B. It thus appears that when a solvent which is rather inert with respect to cellulose is used, the inhomogeneous character of the network is not further increased, and a tougher and more ductile bonded structure is therefore produced.
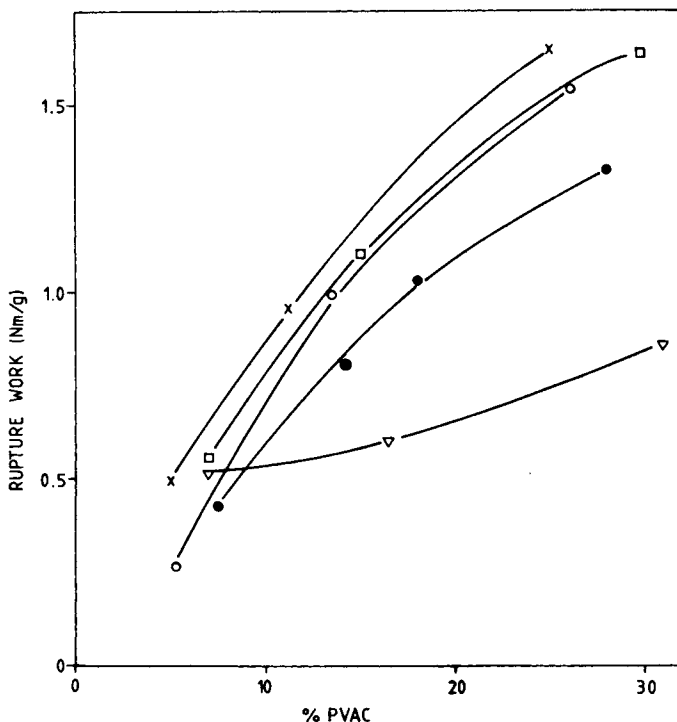
Fig. 4. Work of rupture (W_b) of the networks vs. the amount of PVAC. Keys for the solvents are the same as in Figure 2.

The data for the specific tensile modulus shows more experimental scatter than the other parameters, but some general trends can nevertheless be noted. The sheets which have been immersed in a solvent which interacts strongly with cellulose are in general appreciably stiffer, i. e., less deformable, than those saturated with less aggressive liquids such as toluene. For instance, the network which has been immersed in the acetone solution and subsequently dried has a specific tensile modulus of ca. 2300 N m/g at a PVAC content of 18%, whereas a sheet containing about the same amount of PVAC which has been treated in a toluene solution has a markedly lower stiffness, ca. 1800 N m/g.

DISCUSSION

In this paper it has been shown that immersion of a dry-formed network structure in an organic solution of poly(vinyl acetate) is a very effective binding technique with regard to strength improvement (cf. also Ref. 7). The change in mechanical properties is, however, affected by the degree of interaction between the solvent used and the cellulose material. A strong interaction seemingly results in a stiffer and more brittle structure. There is no doubt that effects of this kind are important in practical applications and should be taken into consideration.

The difference in ductility between the PVAC-impregnated networks is probably not due to any plasticizing effect of the residual organic solvent.

Torsional pendulum experiments performed on impregnated and dried strips gave the same value of the glass transition temperature of PVAC as that obtained with samples of the pure polymer. This indicates that there is no plasticizing effect of the solvent at all. Measurements of this kind are reported in Ref. 7.

At this stage it is difficult to give a detailed model for the observed mechanical behavior of the PVAC-reinforced networks. More experimental work is obviously required. From Figure 2 it is evident that the strength of the bonded sheet is a function of the PVAC-content but that it is independent of the type of solvent used. It is plausible that the network strength is determined by the strength of the fiber–polymer–fiber bonds.[7] The results given in Figure 2 suggests that the total effective size (or volume) of such bonds is independent of the solvent used. It is, however, not clear whether the bond breakage is of a cohesive nature, i. e., the polymer film ruptures, or of the adhesive kind (failure along the interface). Furthermore, it is likely that the extensibility of the polymer itself is not affected by the nature of the solvent after drying. The difference in ductility, modulus, and work of rupture (tensile energy absorption) when various solvents are used must then be traced to the deformability or the state of the cellulosic network.

It seems that a model which may satisfactorily explain the observed behavior is a straightening of the fiber segments when the network is immersed in a solvent which interacts with the cellulosic fibers. This effect may be a result of stress release or softening of bonded or kinked parts. A noninteracting solvent leaves the highly deformable network inert and establishes bonds at suitable joints. The result is an equally strong structure where the interacting solvent yields a material with high modulus and low stretch and the more inert solvents give the
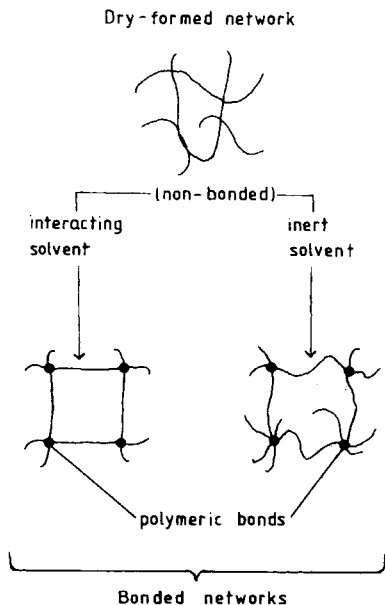

Fig. 5. Schematic illustration of the effect on the network structure of a solvent interacting strongly with cellulose and of a more inert solvent.

opposite effect. This is illustrated schematically in the model given in Figure 5. The straightening of the fibers will also occur when the sheets are impregnated with the organic liquids alone, i. e., without the binder PVAC. As mentioned earlier, in this case no binding of the network will take place, only a disrupture of the structure, resulting in a general reduction in mechanical properties (depending on the organic liquid used).

Finally, it should be recalled that most commercial dry-formed paper products are bonded by spraying a water-based latex onto the web. In view of the results above and of the fact that water interacts very strongly with cellulose, this procedure is of no benefit to the product, since it can cause an initial breakdown of the network structure.

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