Introduction of Polymers into Fibrous Structures by Solution Impregnation

M. RIGDAHL, B. WESTERLIND, H. HOLLMARK, and A. DE RUVO,
*Swedish Forest Products Research Laboratory, Paper Technology
Department, S-114 86 Stockholm, Sweden*

Synopsis

Dry-formed networks of cellulose fibers, produced with a laboratory device, have been impregnated with aqueous solutions of poly(vinyl alcohol) or solutions of poly(vinyl acetate) in acetone. In both cases, the strength and stiffness of the networks increase several times compared with the unmodified structure. When aqueous solutions are used, it appears that a minimum amount of poly(vinyl alcohol) is required (ca. 2 wt %) to increase the strength appreciably, but when poly(vinyl acetate) dissolved in acetone is used, as a binder, the strength improves even at the lowest level of polymer addition. For the systems studied here, the elongation at rupture increased with increasing polymer concentration. In most cases, the amount of polymer in the network structure was less than 10 wt %. Some results from impregnations using other polymeric systems, e.g., latices, are also reported.

INTRODUCTION

Low density dry-formed network structures usually have rather poor mechanical strength properties. This is true of networks composed of synthetic fibers as well as of those based on native cellulose fibers (and also other types of nonwovens). For dry-formed cellulose fiber structures, the low mechanical strength is often interpreted as being due to unsufficient interfiber bonding.[1,2] It has also been pointed out that dry-formed structures are structurally very inhomogeneous, i.e., the fibers are curled, wrinkled, maybe slightly damaged, etc., which may yield rather high local stress concentrations and thus reduce the strength of the sheet.[1] The wide distribution of the tensile strength values of dry-formed sheets supports this suggestion.[1] An alternative explanation of the low strength (and stiffness) is that the stress transfer between fibers is poor in dry-formed networks of cellulose fibers. The strength of nonwovens (based on synthetic fibers or cellulose) is usually raised by adding a synthetic (polymer-based) binding material (see, e.g., Refs. 1–4). In practice, the amount of synthetic binder used for dry-formed paper sheets can be of the order 20%,[5] and for other nonwovens it may even be higher. For economic reasons, it would be desirable to decrease this level substantially. The primary aim of the present work is to describe how the mechanical properties of a dry-formed cellulosic network are influenced by the application of low amounts of synthetic binders, in the first place, poly(vinyl acetate) and poly(vinyl alcohol). Two different modes of behavior are noted, relating to the nature of the solutions used for these impregnation studies. When the network (dry-formed sheet) is immersed in an aqueous solution of poly(vinyl alcohol), a minimum amount of polymer is required to significantly improve the mechanical properties of the network. This pattern

of behavior was not observed when the fiber structure was impregnated with an organic solution of the binding material [poly(vinyl acetate)]; an increase in strength and stiffness of the sheet was noted even at the lowest polymer content. Before reporting on the results of these impregnation studies, it may be worthwhile to review some facts concerning the efficiency of binding materials. Although this study is focused on dry-formed networks of cellulose fibers, the results may also have some bearing on other types of nonwovens.

Binding Materials

Synthetic binders have been extensively used in nonwoven materials, including wet-laid paper products. Although there is a large volume of literature on this subject, the basic mechanisms for the effect of the binders on the end product are, however, apparently not completely understood. Questions remain to be answered concerning the relationship between the type of binder and the resulting properties of the nonwoven material, the importance of binder distribution, the adhesion between binder and the fibrous network, curing or annealing times and temperatures, etc. It is quite obvious that the situation is very complex and that there are many factors influencing the performance of a given binder.[2,6]

A synthetic binder can be added to the dry-formed paper (or any other nonwoven structure) in the form of latex, powder, fibers, or a solution. For dry-formed products, the latex form has been used in most cases, and such systems have, consequently, been studied in greater detail than the others. Typical latices used in this connection are those based on styrene–butadiene rubbers, vinyl acetate copolymers, acrylic copolymers, and vinyl chloride copolymers. The latex systems can be applied to the dry-formed structures by means of impregnation (saturation) or spraying. In practice the latter technique is usually preferred, although both spraying and impregnation appear to be more efficient than the beater addition technique sometimes used for wet-laid nonwovens.[7,8]

The type of polymer used may influence the properties of the sheet. In general, the softer the latex, the softer and more ductile is the nonwoven product.[8] Sometimes the glass transition temperature (T_g) of the polymer is used as a rough guideline for estimating the degree of softness. This may be of value in some cases, but the absolute value of the modulus of the polymer in the rubbery state is also an important factor. Many latices are also thermally crosslinked after impregnation to enhance the strength properties.

The distribution of the polymer within the sheet also strongly affects the physical properties of the network structure, and binder migration during drying or curing can present a problem. Troesch and Hoffmann[9,10] have shown that migration is considerably slowed down when the latices are thermosensitized. This means that the latex coagulates at a certain temperature and further migration is thus partly prevented. They further found that fine coagulated agglomerates yielded better strength properties than coarser ones.[9,10] In extensive work by Alince et al.[11–15] on the effect of cationic styrene–butadiene latex on wet-laid paper the importance of the polymer distribution was carefully investigated. It was noted that the latex was most effective (from the point of reinforcement efficiency) when the fiber was uniformly covered by the latex. It

was also concluded that polymeric bonds are superior to the normal type of bonding between cellulose fibres. This point is further discussed later in this paper.

If two different polymer systems are used together as strength improvers, synergistic effects may occur, further enhancing the properties of the non-woven.[16]

It should also be mentioned that Robertson in a very extensive work[17] studied the mechanical behavior of wet-laid paper sheets impregnated with polymer solutions and latices. He found that the change in strength of such sheets is to a large degree determined by the mechanical properties of the polymer. A similar behavior is observed in the present work for dry-formed networks, but the effect of polymeric binders on the strength appears to be more pronounced for those initially rather weak dry-formed structures.

Aims of the Present Work

The object of this work has been to study the influence of small amounts of polymeric materials (usually less than 10 wt %) on the mechanical properties of dry-formed networks of cellulose fibers. The polymer has been impregnated into the network by immersion, since we felt that this technique may be more reproducible than spraying. Two different polymers have been used as binding materials; poly(vinyl acetate) dissolved in acetone and poly(vinyl alcohol) dissolved in water. The difference in the final network properties between these systems may cast some light upon the stress transfer mechanisms in the bonded sheet. This relates especially to the nature of the solvent used for these impregnation studies, i.e., aqueous vs. organic solutions. For comparison, some results obtained with low amounts of latices are also reported.

EXPERIMENTAL

Materials

The dry-formed web was produced from a commercial grade of fluff pulp (bleached sulphate), which had been defibrated in a commercial disc refiner. The density of the dry-formed sheets was ca. 300 kg/m^3 and the basis weight about 80 g/m^2.

The synthetic binding materials were added to the fiber network (sheet) in the form of a solution. Poly(vinyl acetate) (PVAC) with a weight average molecular weight of ca. 500,000, was dissolved in acetone at room temperature. Poly(vinyl alcohol) (PVOH) was dissolved in water at 90°C. The PVOH used was a fully hydrolyzed grade (98.4%).

Methods

Impregnation

The dry-formed laboratory sheets, which were made in a sifting apparatus, were consolidated between moist felts in a roll press. The sheets were dried and then impregnated by immersion in a polymer solution of an appropriate con-

centration.   The sheets were held in the solution until saturated.   The sheets were allowed to air-dry without restraints and were then weighed to determine the polymer uptake.   All experiments reported were performed on sheets that had been conditioned at 23°C and 50% RH.

Mechanical Properties

The tensile stress–strain behavior was measured at 23°C and 50% RH using a horizontal tensile tester (Lorentzen and Wettre).   The initial (tangent) tensile modulus as well as the tensile strength and elongation at rupture were evaluated. The width of the paper strip was 50 mm and the strain rate $1.7 \times 10^{-3} s^{-1}$.   The wet strength was determined under the same conditions and with the same equipment.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs were obtained using a Cambridge 600 Microscope.

Dynamic Mechanical Measurements

Dynamic mechanical spectroscopy was employed to determine the glass transition temperature of the polymer in the fiber network.   The measurements were made using a Torsional Braid Analyser operating at ca. 1 Hz.

RESULTS AND COMMENTS

Mechanical Properties and Structure of Unbonded Dry-Formed Network

Figure 1 shows a typical stress–strain curve of the dry-formed paper sheet (network).   The stress is here given as the specific stress, i.e., the stress (σ) di-
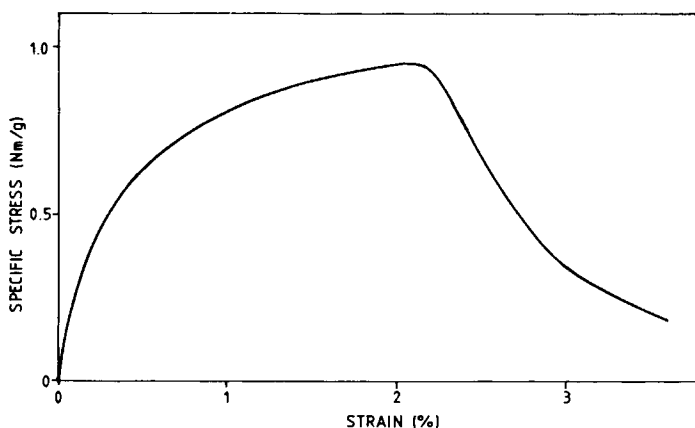

Fig. 1. Specific stress (σ/ρ) vs. strain (ϵ) for an unmodified dry-formed paper sheet during a tensile test.
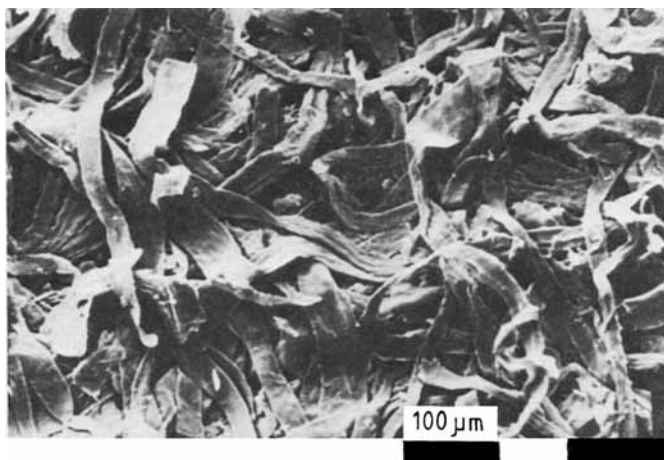
Fig. 2. Scanning electron micrograph of the structure of dry-formed paper.

vided by the network density (ρ). The maximum value of the registered specific stress is here termed specific strength. Typical values of the specific tensile strength (tensile index), specific elastic modulus (E/ρ), and elongation at rupture are $1 \text{ N} \cdot \text{m/g}$, $100 \text{ N} \cdot \text{m/g}$, and 2%, respectively. It is seen in Figure 1 that the stress attains a maximum value and then decreases as the elongation proceeds. This is due to the creation of microcracks, yielding zones of debonded material, "ripples," as the deformation increases.[1] These microcracks slowly decrease the load-bearing capability of the sheets. In contrast to wet-laid paper, the dry-formed sheets were in this case isotropic in the paper plane.

Figure 2 is a scanning electron micrograph of the structure of the dry-formed network. As has been earlier reported,[1] the fibers are wrinkled and curled or
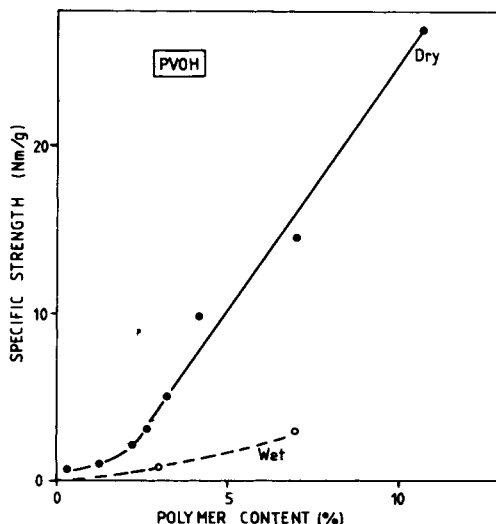

Fig. 3. Dry and wet strength of PVOH-reinforced dry-formed network as a function of the polymer content.

sometimes highly deformed. This structure gives a relatively inhomogeneous impression, and it is probable that the number of contact points (or the size of the contact area) between the fibers is rather low.

Mechanical Properties of the Network Structure Impregnated with Aqueous Solutions of Poly(vinyl Alcohol)

Figure 3 shows the specific tensile strength of the dry-formed sheets vs. the content of PVOH. Here the tensile strength for a sheet without binder was obtained from measurements on a sheet which had been soaked in water and then allowed to dry without restraint. This treatment obviously reduces the strength from ca. 0.8–1.0 N · m/g (cf. Fig. 1) to ca. 0.5 N · m/g. This experiment was performed merely to study the effect of water immersion alone.

The poly(vinyl alcohol) obviously has a dramatic influence on the mechanical behavior of the dry-formed structure. A concentration of ca. 10% PVOH results in a 30-fold increase in strength. The PVOH grade itself has a specific strength in the absence of cellulose fibers of ca. 40 N · m/g. The increase in strength of the network from ca. 0.5 N · m/g to ca. 27 N · m/g with ca. 10% PVOH must be traced back to a better stress transfer between the fibers in the presence of the polymeric phase. A similar effect on the tensile strength of paper has also been noted for wet-laid papers by Alince[12] and Engman et al.,[7] although the magnitude of the reinforcement efficiency is not of the same order as that observed with the dry-formed networks investigated here.

Figure 3 indicates that a minimum amount of polymer is required to obtain a marked increase in specific strength (tensile index). Below ca. 2% the influence of the binder is almost negligible. This point is further discussed in a later section.
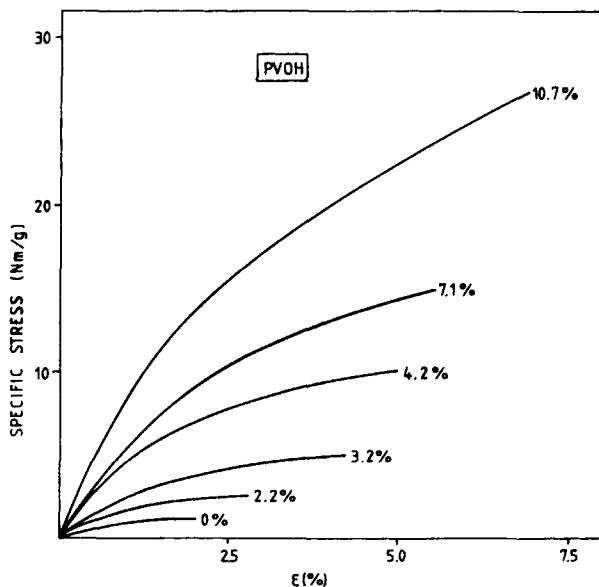

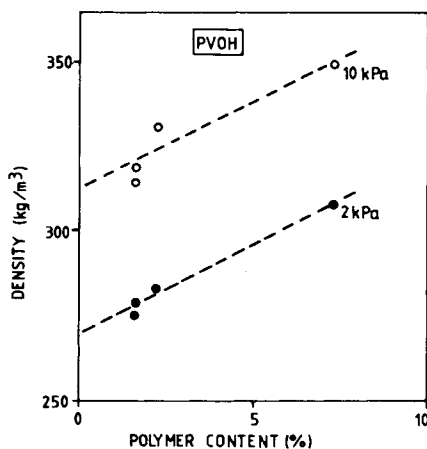Fig. 4. Stress–strain curves for dry-formed papers, containing different amounts of PVOH.

Fig. 5. The influence of PVOH on the density of dry-formed paper sheets. The density was determined from thickness measurements at pressure levels of both 10 kPa and 2 kPa, as indicated in the graph.

Since PVOH is a water-soluble polymer, the wet strength is, as expected, rather low compared with the strength in the dry state (see Fig. 3).

Figure 4 shows a series of stress–strain curves for dry-formed sheets containing different contents of PVOH. Within the range shown, the stiffness, the strength and also the elongation at rupture increase in approximately the same way with increasing amounts of polymer.

The variation in sheet density with increasing amount of PVOH is given in Figure 5. The density was calculated from caliper measurements carried out under pressures of 10 kPa and 2 kPa. There is evidently an increase in density as the PVOH concentration is raised and a simultaneous decrease in sheet thickness.

Mechanical Properties of Dry-Formed Sheets Impregnated with Poly(vinyl Acetate)

PVAC-based materials are considered to be interesting as binders for non-wovens.[18] At room temperature PVAC is a glassy (amorphous) polymer with a glass transition temperature (T_g) around 40°C. As in the case of PVOH, impregnation of dry-formed structures with PVAC dissolved in acetone has a dramatic influence on the stiffness and strength (Fig. 6). A sheet containing 15% PVAC has a specific tensile strength exceeding 20 N · m/g and the specific tensile modulus is ca. 2 kN · m/g. However, contrary to the behavior exhibited by the PVOH-saturated networks, the increase in strength and stiffness is more pronounced at lower contents (below 5%). Above this amount of PVAC, the increase in strength is only ca. 1 N · m · g^{-1}/% PVAC. The elongation at rupture increases from ca. 2.2% for an unreinforced sheet up to ca. 6.5% at a concentration of 15% PVAC.

Figure 7 shows the temperature dependence of the dynamic loss factor (tan δ) for a dry-formed paper strip containing 2.4% PVAC and for a paper (dry-formed) with no binding material. It may be noted that measurements relating to the temperature dependence of the dynamic mechanical loss factor, which
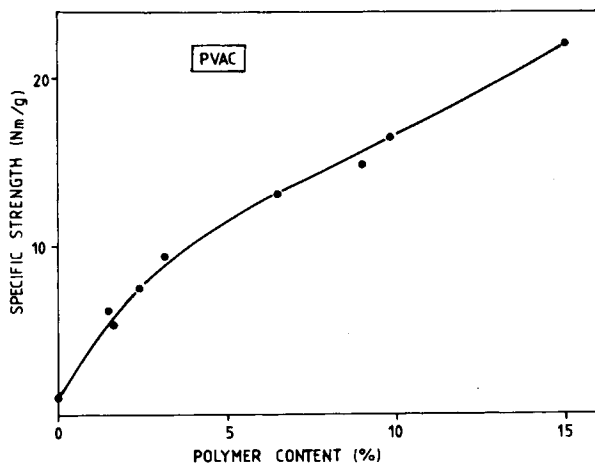
RIGDAHL ET AL.

Fig. 6. The specific strength of dry-formed networks vs. the PVAC content.

is defined as the ratio between the loss and storage modulus of a sample, is a well-known technique for characterizing and locating the glass transition temperature and secondary transitions, see, for instance, Ref. 19. For an amorphous polymer the tan δ (temperature) curve normally exhibits a maximum at the glass transition temperature. Despite the low amount of PVAC in the present case the glass transition of PVAC is very pronounced in the polymer-containing sheet, while for the unmodified structure the loss factor is almost independent of temperature in this region. Below the glass transition, the loss factor of the impregnated sheet is significantly lower than that of the untreated strip (0.0135 and 0.0325, respectively, at 23°C). This indicates that even at these low levels of polymer impregnation the polymer takes a very active part in the stress transfer mechanism. It is certainly very tempting to speculate about the role
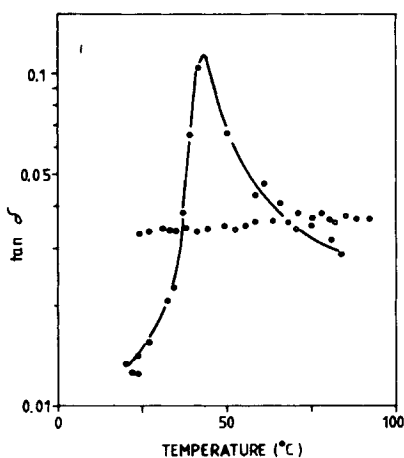

Fig. 7. Tan δ vs. temperature for dry-formed networks without binder (O) and containing 2.4% PVAC (●).

of friction in this context, i.e., the higher value of tan δ for the unreinforced sheet may be caused by friction etc. between more or less bonded cellulose fibers when the strip is subjected to periodic oscillations. The polymer binds the fibers together better yielding a lower damping. However, further experiments are needed to substantiate this point. It may be pointed out that the lowering of tan δ (below T_g) is more pronounced the higher the concentration of PVAC.

One further point concerning the dynamic mechanical measurements is worth mentioning. From Figure 6 it is evident that the lowest amount of PVAC (1.5% in this case) has the greatest relative effect on the tensile strength. For these networks, the dynamic mechanical data indicated a T_g value of 48°C, which is 7–8°C higher than that of pure PVAC. An increasing in the amount of PVAC in the dry-formed sheet resulted in a monotonic decrease in T_g down to ca. 40°C for a paper containing 9% polymer binder. This increase in T_g at low concentrations may indicate some specific polymer–fiber interaction (cf. also Refs. 20–22).

The results of a few preliminary uniaxial tensile stress relaxation tests at room temperature are displayed in Figure 8. In stress relaxation, the stress necessary to maintain a superimposed elongation is recorded as a function of the elapsed time. Obviously, even an amount of PVAC as low as 1.5% has a great influence on the long-term mechanical properties of the dry-formed paper. At longer times (>10^3 s) the stress decays more rapidly for the polymer-containing paper, and this curve in fact differs very little from the stress relaxation curve of pure PVAC (cf. Ref. 23). Again, it seems plausible that the stress transfer is to a large extent accommodated by the polymer, i.e., the interfiber bonding is of the fiber–polymer–fiber type.

Comparison with Mechanical Performance of Dry-Formed Network Structures Impregnated with Other Polymer Systems

In addition to PVOH and PVAC, a number of other polymers were used for impregnation of network structures. A complete report on the properties of these
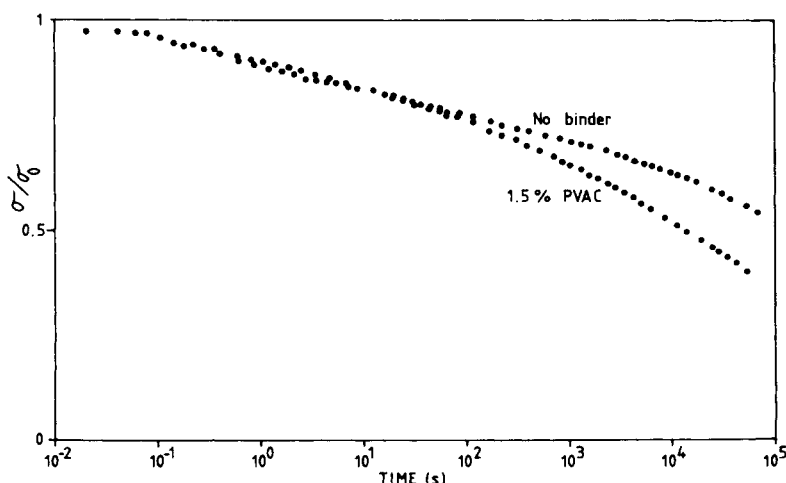

Fig. 8. Stress–relaxation curves for dry-formed paper with and without PVAC. The time-dependent stress σ is here normalized with regard to the initial stress σ_0 of the experiments.

reinforced sheets is beyond the scope of this paper. Here, the similarities and deviations from the behavior of the PVOH- and PVAC-impregnated structures will be discussed only in general terms. The polymers studied may conveniently be divided into two groups: water-based lattices (dispersions) and polymers dissolved in organic liquids.

The latex group included, e.g., a series of acrylic copolymers with different glass transition temperatures, polystyrene dispersions, and a dispersion of a ethylene–acrylic acid copolymer. With regard to the strength development of the reinforced paper sheets, the same pattern as that noted with PVOH was observed, i.e., a certain minimum concentration of binder (ca. 2%) was required to obtain a significant effect on the strength, but above this level the tensile index increased rapidly. The absolute value of the strength was not, however, as high as that observed with PVOH. The maximum values obtained with the latex systems investigated here were of the order of $9 \ N \cdot m/g$ at a content of 8% binding material. This is to be expected since the majority of the lattices studied are rather soft in comparison with, e.g., PVAC. For all binder systems the elongation at rupture increased with increasing amount of polymeric binder.

It was also found that, for a latex system with a T_g or a film-forming temperature in the vicinity of room temperature or higher, heat treatment of the reinforced structure is often beneficial for the strength development. When properly annealed, the reinforcing abilities of the dispersions studied here were rather similar at lower concentrations. The film forming capability of the latex is evidently vital for the performance of the final network structure. A similar improvement in mechanical performance due to annealing has also been reported by Alince[12,15] for wet-laid paper reinforced with styrene–butadiene and styrene lattices and by Engman et al.[7]

The second group of sheets having networks saturated with organic solutions of polymers (e.g., polystyrene and ethylene–vinyl acetate copolymers) differed somewhat in mechanical behavior from the latex-treated structures. No minimum amount of binding material was apparently necessary to increase the strength significantly. The reinforcing effect of the dissolved polymers was thus similar to that observed with PVAC, although the absolute value of the strength may not be as high as with this polymer. An increase in elongation at rupture with amount of binder was also observed with these systems.

Organic solutions of polymers may in some cases have advantages over latex systems. If a sheet is impregnated with a dispersion of an amorphous (glassy) polymer with a high T_g, e.g., polystyrene, annealing is necessary to enhance the film-forming properties of the latex to obtain a satisfactory strength level of the structure. If, however, the structure is impregnated with a solution of polystyrene in toluene, the problem of film forming is eliminated and the efficiency of the polymer is improved several times, despite the fact that no annealing procedure is employed. This is illustrated in Figure 9, which compares the relative specific tensile strength of dry-formed paper sheets impregnated with a polystyrene dispersion and subsequently dried at room temperature (no annealing) to that of sheets impregnated with a solution.

So far we have only discussed the importance of the type of polymer system to be used as a binder. The distribution of the binder in the cellulosic network is also important, since it may significantly affect the performance of the nonwoven structure.[7,9,11] This problem will be dealt with in detail in a later report.
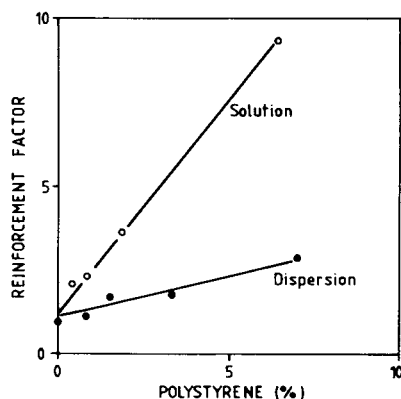
Fig. 9. The reinforcement factor of dry-formed sheets, i.e., the ratio of tensile strength of bonded to that of unbonded paper vs. the amount of polystyrene. The sheets had been impregnated with either a PS dispersion (●) or a PS solution (toluene) (O).

However, scanning electron microscopy of these networks containing low amounts of polymer revealed no immediate difference between such structures and that with no binder (Fig. 2). There are no concentrations of binding material at fiber crossings which are sometimes observed in other types of nonwovens.[24] One is led to the conclusion that the polymer covers the entire available fiber surface more or less homogeneously. This is further supported by X-ray spectroscopic analysis of dry-formed papers impregnated with a chlorine-containing polymer. Such studies, which will be reported separately, also indicate that the number of easily observable contact points in this type of network is not very large.

DISCUSSION

It has been shown that dry-formed paper has a low mechanical strength but that addition of synthetic binders such as PVAC and PVOH increases the tensile strength several times even at concentrations well below 10% (by weight). Regarding the distribution of the binding material, it has earlier been pointed out that a uniform coverage of the fibers with the binder[9,12] produces a stronger structure, i.e., the binder is more efficiently used. Binder which covers the fibers at regions away from contact points between fibers may then appear to be wasted, since it will seemingly not contribute to the strength improvement, but it may level out local stress concentrations, irregularities, etc. along the fiber length and in this way give the product a better strength profile. If so, the exact nature of the polymer is not very important, as long as a proper film of it is formed. An effect of this type will be more pronounced at low binder contents, and this may well be the reason why the influence of polymer concentration on the strength is rather similar for some of the different binding systems investigated here. Alince[15] has arrived at a similar conclusion for styrene–butadiene-reinforced paper. At higher concentrations the role of the specific binding systems will naturally be more discernible.

Since the strength of the dry-formed sheets with neither PVAC nor PVOH is low and since the tensile index increases several times with addition of less than

10% binder, it may be safe to say that the degree of interfiber bonding (hydrogen bonding, dispersion forces, etc.) is negligible. The binding between the cellulose fibers is thus primarily developed by the polymer, i.e., by bonds of the fiber–polymer–fiber type. This appears to be an efficient type of bond. For all the investigated binding systems the elongation at rupture increases with the amount of polymer, and this may also be taken as an indication of this type of bonding (cf. Refs. 15,17).

The difference between dry-formed networks impregnated with water-based systems (PVOH) and with organic solutions of polymers (PVAC) is interesting and deserves comment. It was observed that when a latex or an aqueous solution of the polymer was added to the dry-formed sheet a certain minimum quantity (ca. 2%) was needed before the strength began to increase. With organic solvents (toluene, acetone, etc.) this behavior was not noted, the strength increasing significantly even at rather low polymer contents. When the paper strip is immersed in water-based systems the interaction forces between the fibers are reduced to a very low level.[25] In addition, the fibers swell[25] and the complicated structure of the dry-formed sheet is strongly affected. It is plausible to suppose that during drying the strong influence of water will further increase the inhomogeneity of the sheet structure, e.g., the number of contact points decreases and the mean distance between individual fibers may increase, especially if, as here, the sheet is dried without restraint. This may explain why the strength decreases when a dry-formed sheet is immersed in water and then air-dried. It is thus not too difficult to imagine that a small amount of polymer (less than 2%) added under such conditions may have no great influence on such an inhomogeneous structure. When the sheet is immersed in a liquid having a lower cohesive energy than water and a relatively large molar volume, the effect on the structure will not be so drastic,[25] so that impregnation with organic solutions of polymers may be expected to be more favorable at low concentrations.

The rather remarkable influence of PVAC and PVOH on stiffness and strength, which may be difficult to reconcile within the usual concepts of composite theory, can perhaps be traced back to the improved stress transfer characteristics of the reinforced sheet. Similar effects have been reported by others.[7,11,26] In a subsequent paper, the reinforcement of networks with polymeric binders will be discussed in terms of a network theory developed by Perkins and Mark.[27]

Finally there are some aspects of polymer impregnation of dry-formed structures which have not been dealt with here. First there is the question of adhesion between polymer and cellulose. This is an area where more experimental work is certainly required. For instance, it must be established whether the network fails due to rupture of the polymer–cellulose interface or by rupture of the binder alone (or by some other mechanism). The shear strength of a polymer–fiber joint is important in this connection. A second factor which has not been discussed here is how the type of cellulose fibers affects the strength of the dry-formed sheets and, in addition, how important are factors such as curled and kinked fibers. Preliminary experiments on other types of fibers than the bleached sulphate fibers here used indicate that such factors may be very important.

References

1. A. de Ruvo, H. Hollmark, S. Hartog, and C. Fellers, *Sven. Papperstidn.*, **85**(7), 16 (1982).
2. J. A. Villalobos, *Tappi*, **64**, 129 (1981).
3. J. Dahlberg and K. Eberling, *Paperi ja Puu*, **62**, 748 (1980).
4. J. R. Starr, Tappi Engineering Conference, Atlanta, 1981, p. 417.
5. Anon., *Pulp Paper Int.*, **22** (Aug.), 38 (1980).
6. R. D. Athey, *Tappi*, **60**, 118 (1977).
7. G. Engman, E. Alfthan, and A. de Ruvo, *Tappi*, **59**, 117 (1976).
8. R. A. Gill, T. J. Drennen, E. J. Sweeney, and L. Mlynar, *Tappi*, **55**, 761 (1972).
9. J. Troesch and G. Hoffmann, *Tappi*, **58**, 138 (1975).
10. J. Troesch and G. Hoffmann, *Tappi*, **59**, 133 (1976).
11. B. Alince, M. Inoue, and A. A. Robertson, *J. Appl. Polym. Sci.*, **20**, 2209 (1976).
12. B. Alince, *Sven. Papperstidn.*, **80**, 417 (1977).
13. B. Alince, *Paper Trade J.*, **163**, 52 (March 15, 1979).
14. B. Alince, M. Inoue, and A. A. Robertson, *J. Appl. Polym. Sci.*, **23**, 539 (1979).
15. B. Alince, *J. Appl. Polym. Sci.*, **23**, 549 (1979).
16. L.-L. Chan, *Pulp Paper Mag. Can.*, **77**, T93 (1976).
17. A. A. Robertson, in *Fundamental Properties of Paper Related to Its Uses*, Cambridge, British Paper and Board Industry Federation, Vol. 1., Benn Ltd., London, 1976, p. 373.
18. P. L. Rosamilia, Tappi Paper Synthetics Conference, Washington, D.C., 1979, p. 251.
19. I. M. Ward, *Mechanical Properties of Solid Polymers*, Wiley-Interscience, London, 1971.
20. G. J. Howard and R. A. Shanks, *J. Appl. Polym. Sci.*, **26**, 3099 (1981).
21. T. Yamauchi, K. Murakami, and R. Imamura, *Jpn. Tappi*, **33**, 51 (1979).
22. E. Alfthan, A. de Ruvo, and M. Rigdahl, *Int. J. Polym. Mater.*, **7**, 163 (1979).
23. J. Kubát and L.-Å. Nilsson, *Mater. Sci. Eng.*, **52**, 223 (1982).
24. P. Fredricks, *Sven. Papperstidn.*, **74**, 233 (1971).
25. A. A. Robertson, *Pulp Paper Mag. Can.*, **65**, T171 (1964).
26. R. E. Prud'homme, *J. Appl. Polym. Sci.*, **21**, 947 (1977).
27. R. W. Perkins and R. E. Mark, Proceedings of The Role of Fundamental Research in Paper-Making, Cambridge, British Paper and Board Industry Federation, England, 1981.