

Wood Fiber–Synthetic Polymer Composites.

II. Laminates of Treated Fibers and Polyolefins

ANTHONY J. MICHELL, JANET E. VAUGHAN, and DONALD WILLIS,
CSIRO Division of Chemical Technology, South Melbourne 3205, Australia

Synopsis

Flexural properties of laminates prepared by hot pressing commercial papers and laboratory handsheets with films of polyolefins were measured following exposure to different levels of moisture. Prior to their incorporation in the laminates, the fibers, either individually or as preformed paper, were acetylated or crosslinked with formaldehyde to reduce their sensitivity to moisture. The results are compared with earlier measurements which showed that the properties of laminates based on paper precoated with polyethylene declined sharply at high relative humidities. For laminates comprising laboratory handsheets made from acetylated fibers, the decline in properties is less but the initial values under dry conditions are lower also. However, acetylation or crosslinking of preformed paper improves up to threefold the retention of flexural modulus by the laminates under the wettest conditions with no concurrent loss in this property under dry conditions, although some embrittlement of the component paper sheets is observed. Enhanced fiber alignment or the addition of 5% glass fibers to the paper does not arrest the decline in flexural properties of the laminates with increasing relative humidity. This decline differs little when other polyolefins are used but is accentuated when ethylene–vinyl acetate copolymer is the binder.

INTRODUCTION

This study forms part of a long-term program to develop wood fiber–synthetic polymer composites for use in building and packaging. In a previous paper,¹ the authors showed that at low humidities the flexural properties of laminates built up from sheets of paper extrusion-coated with low-density polyethylene compared favorably with those of glass-filled high-density polyethylene and of paper–phenolic resin laminates. However, at high humidities, these polyethylene-based laminates showed a more severe decline in their mechanical properties. Since such behavior is undesirable in a material to be used for structural purposes, means to arrest this decline in properties have been sought.

Similar problems with respect to moisture occur in paper products, where improved properties have been obtained by the use of barrier materials or by treating the fibers to make them hydrophobic. In attempts to prepare papers with reduced affinity for moisture, a number of workers^{2–5} have partially acetylated wood pulp fibers; but the processes used, while making the fiber hydrophobic, also degrade its strength. More recently, Herdle and Gandy⁶ have developed a partial acetylation technique which results in a more uniform reaction and less fiber degradation. Stamm and Beasley⁷ showed acetylation of formed paper sheets to be a rapid and efficient means of imparting dimensional stability and improved tensile properties to paper exposed to moisture. Vapor-phase acetylation of Asplund-type hardboards leads to improved dimensional stability, especially if the boards are given a preliminary heat treatment.⁸

Acid-catalyzed crosslinking with formaldehyde also improves the wet strength

and dimensional stability of paper, but again with some sacrifice of dry-strength properties.⁹⁻¹² Variations in cellulose fiber orientation and the use of small percentages of synthetic fibers unaffected by moisture have also been advocated as means of improving the properties of paper exposed to moisture.¹³

This article reports experiments in which wood pulp fibers, either free or preformed into paper, were acetylated both by the classical method^{2,5} and by the newer method of Herdle and Gandy,⁶ or were crosslinked with formaldehyde using formic acid as catalyst as suggested by Cohen.¹² The treated materials, converted where necessary into sheet form, were laminated with low-density polyethylene or ethylene-vinyl acetate copolymer (EVA) and the flexural properties of the laminates studied at varying humidities. The effects on these properties of orientation in the paper sheets, of the addition of glass fibers to the paper, and of replacing low-density polyethylene with high-density polyethylene or polypropylene were also examined.

EXPERIMENTAL

Materials

The commercial papers and pulps used were newsprint produced by Australian Newsprint Mills Ltd. and bleached waxing kraft, sack kraft, corrugating paper, and eucalypt and pine kraft lap pulps produced by Australian Paper Manufacturers Ltd. The glass fibers used were obtained by disintegration of Whatman silicate glass paper GF/A.

Since commercial low-density polyethylene packaging films were found to have too high a melt viscosity to penetrate the paper, the films used in the experimental laminates were specially blown by I.C.I. Australia Ltd. from their low-density polyethylene grades XJG-143 (MFI = 2.5, ASTM 1238 Condition E) and WNC-121 (MFI = 7.0, ASTM 1238 Condition E). The ethylene-vinyl acetate (EVA) copolymer films were made by hot pressing granules of I.C.I. Australia Ltd. Alkathene Copolymer 9840 containing 18% w/w vinyl acetate (MFI = 10, ASTM 1238 Condition T). The high-density polyethylene and polypropylene films were made similarly from Hoechst Australia GA 7260 (MFI 190/2 = 15, DIN 53735) and Shell Chemical (Australia) RM61 (MFI 230/2.16 = 9.0, BS 2782) polymers, respectively.

The flexural moduli and yield strengths of the respective polymers as measured by ASTM D790-66 were as follows: WNC-121 polyethylene, 215 MPa and 11.4 MPa; EVA copolymer 45 MPa and 3.7 MPa; high-density polyethylene 1540 MPa and 40 MPa; polypropylene 1750 MPa and 54 MPa.

Fiber Treatments

Commercial eucalypt kraft lap pulp was disintegrated in water and dried by washing with ethanol and ether.

Acetylation—Method I. Separate samples of the dry pulp were acetylated with acetic anhydride in pyridine at 40°C by the method of McKenzie and Higgins⁵ for 2 and 16 hr, giving acetyl contents of 11.3% and 14.7%, respectively, as determined by saponification with *p*-toluenesulfonic acid.

Acetylation—Method II. A further batch of the same pulp was disintegrated

in water and largely dewatered on a Buchner funnel. The wet pulp cake was acetylated with acetic anhydride in acetic acid at 27°C according to the method of Herdle and Gandy,⁶ using methanesulfonic acid as the catalyst. The resulting pulp had an acetyl content of 12.6%, determined as above.

Sheetmaking

Aligned Sheets. An Allimand ctp dynamic sheet machine¹⁴ was used to form sheets from pine kraft lap pulp which had been disintegrated for 20 min in a Valley beater.

Laboratory Handsheets From Pulps. Laboratory handsheets were made to a fixed weight from suspensions of fibers in water by using the apparatus and method of Appita Standard P 203m-62, while the same procedure, but with the apparatus modified as described by McKenzie and Higgins,⁵ was employed for sheets made from suspensions in acetone or ethanol.

Paper Treatments

Acetylation. Commercial sack kraft paper was immersed in a 0.5% solution of zinc chloride for 20 sec and then acetylated for various times with acetic anhydride in the vapor phase at 120°C according to the method of Stamm and Beasley.⁷ The acetylation levels achieved were 6.3% and 14.5% after 1 and 2 hr, respectively.

Crosslinking with Formaldehyde. The method adopted was essentially that of Cohen, Stamm, and Fahey.¹¹ All experiments were conducted at 120°C on 25 cm × 20 cm papers in a 16-l. stainless-steel box placed in an oven. Formaldehyde was generated from the required amount of paraformaldehyde placed in a dish inside the box. Volatile catalysts (ammonia, diethylamine, or formic acid) were introduced as liquids by means of a feed tube delivering to another dish at the bottom of the box, admission being made after the paper and paraformaldehyde within the box had reached the designated temperature. For experiments in which sodium hydroxide was the catalyst, each paper was immersed in aqueous sodium hydroxide for 20 sec and allowed to dry at 65% R.H. before being placed in the box. This procedure resulted in an uptake by the papers of 160% of their weight of 0.1% NaOH, and hence the dried papers contained approximately one and a half times the concentration of sodium hydroxide as the solution with which they had been treated.

The following combinations of alkali (% solution) and paraformaldehyde (g wt) were used: 0.1% NaOH, 6 g; 1% NaOH, 2 g; 5% NaOH, 2 g; 2 ml 27% aqueous ammonia, 3.2 g; 5 ml anhydrous diethylamine, 6 g. Reaction times varied from 60 to 300 min. For newsprint, 1% NaOH and 0.2 g formaldehyde were estimated to correspond to one mole of each of these reagents per mole of free ortho positions in the lignin present.

For acid-catalyzed crosslinking, formic acid was used under conditions shown by Cohen¹² to impart improved dimensional stability to paper without excessive embrittlement. Paper (20 g) was placed in the box along with paraformaldehyde (3.2 g), and formic acid (1.8 ml) was introduced. The reaction was allowed to proceed for 40–160 min, the extent of reaction being followed through observation of the change in length which occurred when the treated paper was soaked in water.⁹

Formation of Laminates

Laminates having exposed faces of paper were made by hot pressing stacks of paper sheets interleaved with polymer films and prepared so that the machine direction of all the sheets had the same orientation. The laboratory handsheets were isotropic in the plane of the sheet and therefore required no orientation.

For the various combinations of materials it was not possible to obtain laminates having identical thicknesses or proportions of fiber to polymer since the papers were only available in fixed but different weights and the range of polymer films was limited. The number of plies of each component was chosen to give a synthetic polymer content in the range of 30%–50% and a laminate thickness appropriate for flexural tests in a 3-cm-span three-point loading jig in accordance with ASTM Standard Method D790-66.

Stacks containing either WNC-121 low-density polyethylene, or the ethylene–vinyl acetate copolymer were assembled between release sheets and caul plates, placed in a press preheated to 160°C, and subjected to minimal pressure for 5 min followed by 2 MPa for 2 min. For polyethylene XJG-143, these times were extended to 10 and 5 min, respectively, while for the high-density polyethylene and polypropylene, pressing times were again 5 and 2 min but the platen temperatures were 170° and 200°C, respectively.

Testing

Laminates were conditioned and their flexural properties determined in the machine direction as reported previously.¹ The maxima of the curves of load versus extension were broad and are denoted in the text as the flexural yield strengths according to ASTM D790-66. Water-soaked specimens were tested after immersion in water for 24 hr. The actual thickness of a laminate following its conditioning was used in computing its flexural properties.

Values of flexural strain are not reported individually because they are imprecise owing to the broad maxima obtained in the stress–strain curves. However, the values of the maximum strain in the outer fiber ranged from 0.8% to 1.1% and did not appear to vary significantly with the type of treatment or with moisture content, though values for the water-wet samples tended to be in the upper part of the range.

Tests of the properties of the papers, for example, burst factor, tear factor, ring crush, and breaking length in the machine direction were carried out according to Australian Standard AS 1301-75. The reduction in linear swelling of treated paper was measured by the method of Cohen, Stamm, and Fahey.¹⁵

RESULTS AND DISCUSSION

Laminates from Acetylated Fibers

The effect of varying humidities and of water on laminates comprising laboratory handsheets of acetylated fibers and polyethylene or ethylene–vinyl acetate copolymer are shown in Tables I and II. The thickness of the laminate based on 14.7% acetylated fibers which had been sheeted from water was, on average, 6% greater than that of the corresponding laminate from water-laid untreated fibers. However, the laminates from acetone-laid 12.6% and 14.7% acetylated

TABLE I
Effect of Varying Humidities and of Water on Laminates of Sheets of Acetylated Eucalypt Kraft Fibers and WNC-121 Polyethylene (30% w/w)

Fiber treatment	Modulus of elasticity in flexure, MPa				Flexural yield strength, MPa			
	32% R.H.		88% R.H.		32% R.H.		88% R.H.	
	65% R.H.	88% R.H.	65% R.H.	88% R.H.	65% R.H.	88% R.H.	65% R.H.	88% R.H.
Control	4400	4070	2980	420	33.2	29.1	23.1	4.0
Control sheeted from ethanol	1510	1370	1075	325	14.4	12.3	10.1	3.4
12.6% Acetylated (method II)	2850	2600	2000	515	24.1	21.0	17.8	4.5
12.6% Acetylated (method II) and sheeted from acetone	2010	2120	2020	665	18.3	17.1	16.0	5.5
11.3% Acetylated (method I)	2100	1860	1690	490	18.0	16.1	14.9	4.5
14.7% Acetylated (method I)	1870	1620	1330	640	15.7	14.0	12.7	5.9
14.7% Acetylated (method I) and sheeted from acetone	1580	1680	1410	830	13.9	14.4	13.3	7.2
LSD between two means 5% Level ^a		±170		±72		±1.00		±0.47

^a Taken over results in Tables I and II.

fibers were, on average, 9% and 6% thinner, respectively, than their counterparts based on water-laid acetylated fibers. The laminate prepared from untreated fibers which had been laid from ethanol instead of water showed an average increase in thickness of 8%. The remaining laminates in Tables I and II did not differ sensibly in thickness from the appropriate controls. These differences in the thickness of the laminates probably arose from changes in the degree of fiber swelling in the various sheeting media which were not removed in pressing the sheets into a laminate. However, since fiber swelling would change the size of the pores in the paper sheets, penetration of the polyolefin could also have been affected.

Acetylation Level

In laminates containing 30% or 40% low-density polyethylene the effect of 11% acetylation (method I) of the fiber prior to sheet formation from water is to reduce the mean modulus and flexural strength at all levels of R.H., with a diminishing effect at the higher levels of R.H. (Tables I and II). This parallels the marked reduction in burst factor and ring crush values which was observed for the paper sheets themselves.

Higher levels of acetylation, achieved by the same method, reduce still further the mean values of the flexural properties of the laminates at all levels of R.H., but the water-wet samples show significant improvements in their properties relative to those of the controls.

Method of Acetylation

Generally, the mean values of the flexural properties of the laminates made from fibers acetylated by method II are significantly higher than those for laminates based on fibers acetylated by method I. However, the level rather than the method of acetylation appears to determine the properties of the laminates in the water-wet condition.

The burst factor, breaking length, and ring crush values for sheets made from pulps acetylated by method II were also found to be higher than those for sheets comprising fibers acetylated by method I. The general reduction in the strength properties of sheets made from acetylated fibers has been attributed to a reduction in the number of hydroxyl groups available for hydrogen bonding⁵ and to attack on the fibers by the reagents, the latter effect being less for acetylation by method II.⁶

Sheeting Medium

The properties of the laminates made from acetylated fibers sheeted from acetone instead of water (Table I) show rather higher variability, probably because the difficulties of sheet making from acetone result in less uniform sheets. Nevertheless, the flexural properties of such laminates are less sensitive to increasing relative humidity and for water-wet samples have significantly higher values relative to those of the controls. Some of the improvement in flexural properties may be attributed to the reduced swelling of these laminates following exposure to moisture and the corresponding reduction in change of cross-sectional area in the wet state.

These results may be compared with those for the polyethylene laminate based on an untreated eucalypt pulp sheeted from ethanol instead of water (Table I). Over the range of 32%–88% R.H. both the modulus of elasticity and flexural strength are highly significantly decreased by the change in sheeting medium, although the proportions of the initial properties at 32% R.H. which are retained at 65% and 88% R.H. are independent of the sheeting medium.

Several factors could be responsible for the differences in properties of the laminates comprising sheets laid from acetone, ethanol, and water. The greater bulkiness of the ethanol-sheeted fibers should provide a larger surface for bonding to the polymer. However, any resulting improvement in the mechanical properties of the laminate must be outweighed by other factors. Since the ethanol-laid sheets themselves showed a marked reduction in mechanical properties one such factor might be the change in interfiber bonding brought about by the change in sheeting medium. In sheets laid from nonaqueous solvents there will be fewer hydrogen bonds between fibers and lower sheet densities. Photomicrographs show that a substantial part of the fiber network of water-laid sheets is not penetrated by the polymer during lamination¹ so that changes in bonding between the fibers would affect the mechanical properties of the laminates. The enhanced moisture stability of the laminates comprising acetylated fibers sheeted from acetone can be attributed to the formation in the sheets of cellulose acetate-type bonds⁵ which are water resistant and which protect some of the interfiber hydrogen bonds from the ingress of moisture by restriction of swelling.

Polyethylene Level

In the laminates based on 11% acetylated pulps, the polyethylene content appears to have a significant effect on both the modulus and flexural strength, with the mean values for laminates containing 40% polymer (Table II) being greater than those for 30% polymer (Table I) at all levels of R.H. but with the effect decreasing with increasing R.H. This result is somewhat surprising in that the laminate having the higher fiber content might have been expected to have the better mechanical properties. The result is explicable if at the higher polyethylene level the matrix is better able to infiltrate the fibers.¹⁶ However, the laminates are three- rather than two-phase systems (i.e., paper, polymer plus paper, and polymer), and thus an effect may arise from different thicknesses of each phase in the two systems.*

Change of Matrix

The mechanical properties of the laminates in which ethylene–vinyl acetate copolymer was substituted for polyethylene (Table II) are inferior to those of the control laminates at all levels of relative humidity irrespective of whether normal or 11% acetylated fibers are used, and generally the decline in properties with increasing R.H. is not greatly affected by the change in matrix. The flexural properties at 88% R.H. for the laminates based on the vinyl acetate copolymer were also found to be inferior to those of polyethylene-based systems regardless of the degree of acetylation of the fibers employed.

* We are indebted to a referee for this suggestion.

The loss of properties reflects the lower flexural modulus and yield strength of the copolymer as compared to polyethylene but is of lesser magnitude than the difference between the polymer properties.

Laminates from Treated Papers

Acetylated Papers

As with laminates based on papers made from acetylated pulps, the effect of acetylating preformed paper prior to lamination is generally to lower the mean values of the flexural modulus and yield strength of the composite (Table III). Most of these changes can be attributed to the increased thickness of the laminates containing acetylated papers. However, all these laminates show enhanced mechanical properties under water-wet conditions, the high modulus and strength of the polyethylene laminate based on 14.5% acetylated sack kraft being especially noteworthy. The water-wet laminates comprising the acetylated papers swell less than the controls but this reduction in swelling is too small to account for the observed improvements in their mechanical properties.

The properties of the acetylated papers themselves (Table IV) under dry conditions also show some decline, but under wet conditions the most highly acetylated paper retains about 40% of its dry breaking length and ring crush values compared to approximately 7% for the control, closely paralleling the flexural behavior of its laminate with polyethylene under similar conditions. The paper properties are consistent with expectations from the work of Stamm and Beasley,⁷ who showed that the acetylation conditions chosen give minimum embrittlement of paper and maximum reduction in its swelling when exposed to moisture.

As noted earlier for acetylated pulps, the change in matrix from polyethylene to ethylene-vinyl acetate copolymer results in inferior mechanical properties; but, in addition, a greater sensitivity to changes in relative humidity is evident.

Of all the combinations studied, the laminate of 6.3% acetylated paper with the copolymer should provide the highest degree of fiber/polymer compatibility, but its flexural modulus at the various relative humidities is lower than that of its counterpart containing untreated paper and, indeed, is less than the modulus for the laminates from either of these papers and polyethylene. Nevertheless, in the water-wet state the modulus of this acetylated laminate is higher than that for the control.

The greater susceptibility of the copolymer laminates to high humidities and to water probably arises from the more hydrophilic nature of the copolymer which allows water molecules to penetrate the surface more easily. These results suggest that if a more hydrophilic matrix is used to enhance polymer/fiber compatibility in the hope of achieving a stronger fiber/matrix bond and improved properties in the laminate, the effect will be offset by greater sensitivity to water.

TABLE III
Effect of Varying Humidities and of Water on Laminates of Acetylated Sack Kraft Paper and Polymers

% Acetylation	Modulus of elasticity in flexure, MPa			Flexural yield strength, MPa			Water soaked
	32% R.H.	65% R.H.	88% R.H.	32% R.H.	65% R.H.	88% R.H.	
31% w/w WNC-121 polyethylene							
Control	6860	6160	4610	56.2	50.1	36.8	6.0
6.3	6390	5670	4190	53.5	48.4	35.7	8.0
14.5	5510	5590	4550	50.1	47.4	41.0	16.4
33% w/w EVA copolymer							
Control	6600	5400	3560	50.9	39.2	28.8	4.4
6.3	5870	4960	3140	48.3	40.0	29.2	6.4
LSD between two means 5% level		±260			±1.56		±0.33

TABLE IV
Properties of Acetylated Sack Kraft Paper

Sample ^a	Burst factor, kPam ² /g	Breaking length, km			Ring crush, N		
		Dry	Wet	Wet/dry, %	Dry	Wet	Wet/dry, %
Sack kraft, control	3.8	7.8	0.5	6	81	7.0	9
Sack kraft, 6.3% acetyl (45)	4.1	b	b	b	57	9.0	16
Sack kraft, 14.5% acetyl (70)	2.9	6.7	2.9	43	60	25	42

^a Figure in parentheses is percent reduction in swelling effected by the treatment.

^b Insufficient sample to carry out test.

Formaldehyde-Crosslinked Papers

The results of mechanical tests on laminates of formaldehyde-crosslinked papers with low-density polyethylene are recorded in Table V. The thicknesses of the control and treated pairs of laminates were the same within experimental error except for the waxing kraft for which the treated samples were on average 15% thicker than the control. As the fiber contents of the two waxing kraft samples were the same, the improvement in mechanical properties brought about by the crosslinking is better on a fiber basis than on the material property basis indicated in the table.

Data from conventional tests on the crosslinked papers are shown in Table VI, in which all values except those for ring crush have been corrected for the varying weights of the paper sheets. All the treated papers show improved wet strength properties relative to those of the controls. Direct comparison between the test results for the papers and for the laminates made from them is difficult

TABLE V
Effect of Varying Humidities on Laminates from Formaldehyde-Crosslinked Papers and XJG-143 Polyethylene

Laminate	Modulus of elasticity in flexure, MPa			Flexural yield strength, MPa		
	32% R.H.	65% R.H.	88% R.H.	32% R.H.	65% R.H.	88% R.H.
Newsprint-35% polyethylene						
Control	5780	5420	3420 (1370) ^a	39.1	37.8	27.7 (9.3) ^a
Treated	5860	5510	3500 (1655) ^a	42.5	41.0	31.4 (13.2) ^a
Waxing kraft-48% polyethylene						
Control	6830	6000	4160	45.9	39.8	29.2
Treated	6290	6220	4360	49.7	45.5	35.5
Sack kraft-40% polyethylene						
Control	7630	6100	4050 (970) ^a	55.2	43.8	32.2 (9.8) ^a
Treated ^b						
1	6940	6020	3950	49.3	41.5	30.0
2	7680	7220	5010 (2220) ^a	62.1	54.2	39.4 (16.8) ^a
Corrugating paper-38% polyethylene						
Control	6070	4670	3180	41.8	38.2	23.2
Treated	6150	4900	3190	43.9	34.8	23.2
LSD between two means						
5% level		±320			±1.8	
1% level		±430			±2.4	

^a Figures in parentheses refer to samples soaked in water for 24 hr.

^b Fibers crosslinked to different extents (see Table VI).

TABLE VI
Properties of Papers Crosslinked with Formaldehyde with Formic Acid as Catalyst

Sample ^a	Burst factor, kPam ² /g	Tear factor, mNm ² /g	Breaking length, km			Ring crush, N		
			Dry	Wet	Wet/dry, %	Dry	Wet	Wet/dry, %
Newsprint								
Control	1.0	5.9	3.9	0.5	13	14	5.0	36
Treated (41)	0.9	3.0	4.2	2.1	50	17	7.5	44
Wax kraft								
Control	3.9	8.6	7.6	0.4	5	6.0	b	b
Treated (72)	2.3	3.5	7.2	2.3	32	6.5	3.5	54
Sack kraft								
Control	3.8	14.5	7.8	0.5	6	81	7.0	9
1. Treated (43)	3.6	8.5	7.6	2.9	38	79	21	26
2. Treated (56)	3.5	8.5	7.9	3.6	45	93	23	25
NSSC corr.								
Control	1.9	8.4	5.4	0.4	7	140	15	11
Treated (52)	2.0	6.7	5.8	1.8	31	165	40	24

^a Figure in parentheses is percent reduction in swelling effected by treatment.

^b Too small to be measured.

since the testing methods do not correspond. All the paper tests relate to failure so that any attempted comparison should be with the flexural yield strength rather than with the modulus of the laminates. Overall, the variation in the strength of the laminates is smaller than the variation between the test results for the papers from which they were made.

Though some of the paper properties reflect fiber embrittlement induced by the crosslinking treatment, the modulus and flexural yield strength of the laminates at 32% R.H. are little affected by the crosslinking. Only at the highest crosslinking level and in the water-wet state does crosslinking of the fibers significantly affect the loss of stiffness and strength exhibited by the laminates. The improvement in wet stiffness of a water-soaked sack kraft laminate brought about by crosslinking is most marked.

These results may be explained if it is remembered that the fibers in the papers are swollen to a certain degree, depending on their moisture content, prior to crosslinking. At moisture contents lower than those at the time of crosslinking the fibers will shrink and the small number of crosslinks introduced into the papers will not greatly affect the mechanical properties of the papers or of the laminates made from them. However, at higher moisture contents the papers and laminates will retain more of their modulus and strength because the crosslinks will resist the tendency of the paper to swell and to expose additional interfibrillar hydrogen bonds to the attack of water. Such crosslinks would affect the fiber-matrix interaction only if they enabled the formation of water-resistant bonds between the fibers and the matrix; this appears unlikely to be the case in the systems examined.

To avoid the embrittlement that occurs in paper when the cellulose moiety is crosslinked,¹² attempts were made with newsprint to crosslink only the lignin component via alkali-catalyzed reaction of formaldehyde with the free ortho positions of the lignin molecule. With ammonia, diethylamine, or sodium hydroxide as the catalyst, the treated papers when soaked in water swelled linearly

more than the controls, and for this reason they were not used to prepare laminates. When these sheets were subjected to a subsequent acid-catalyzed reaction with formaldehyde, the linear swelling of the papers returned to the control value. These observations could be rationalized if the initial alkaline treatment with formaldehyde resulted in the introduction of methylol groups which were subsequently converted into methylene bridges under acidic conditions. Alternatively, there may be insufficient active or suitably placed free ortho positions in the lignin in the newsprint to react with formaldehyde and form the crosslinks necessary for dimensional stabilization of the paper. Yet another explanation is that under the alkaline conditions used crosslinks were introduced while the fibers were more highly swollen than they would be in water alone so that, as discussed above, crosslinking would not have been detected by the test method employed.

Laminates from Sheets Containing Aligned or Glass Fibers

The flexural properties of laminates of low-density polyethylene with laboratory-made sheets of kraft fibers having an imposed orientation are shown in Table VII. The ratio of the tensile strengths in the machine and cross directions of a paper sheet is a measure of the degree of alignment of the fibers; this ratio was 4.0 for the sheets made in the laboratory on the Allimand machine compared to 1.5 for sack kraft paper. Fiber alignment also increases the stiffness of paper in the machine direction, and both these improvements in sheet properties are reflected in the directional differences in flexural properties shown by the laminates prepared from such sheets (Table VII). However, the orientation has little effect on the loss of modulus and strength when the humidity is increased from 32% to 88% R.H., the property retention being about 70% in each case; but in water-soaked samples flexural strength is retained somewhat better in the machine direction. The effects of orientation would perhaps have been more obvious had it been possible to achieve tensile strength ratios nearer to the 15:1 recently obtained by Prud'homme and Robertson¹⁷ using a new laboratory machine and special pulps.

The data in Table VII also show that there was no significant improvement in modulus or strength under wet conditions for the laminate formed from laboratory handsheets of eucalypt kraft paper containing 5% w/w glass fibers, although the sheets themselves when soaked in water showed a 47% reduction in linear swelling⁹ compared to that of a control.

Laminates with Other Polyolefins

The higher values of the flexural modulus and strength shown in Table VII for laminates of sack kraft with high-density polyethylene and with polypropylene probably reflect the enhanced moduli and yield strengths of the respective polymers. Again, however, the changes in laminate properties are much less than the changes in polymer properties, even though the proportion of polymer in the laminates is 50% instead of the 33% in the low-density polyethylene materials. This result suggests that the mechanical properties of the laminates are affected by, but are not closely related to, the intrinsic mechanical properties of the matrix polymers used.

TABLE VII
Effect of Varying Humidities and of Water on Laminates Made from Kraft Papers and Polyolefins

Laminate	Modulus of elasticity in flexure, MPa			Flexural yield strength, MPa		
	Water soaked			Water soaked		
	32% R.H.	65% R.H.	88% R.H.	32% R.H.	65% R.H.	88% R.H.
37% WNC-121 Polyethylene + lab. kraft comprising aligned fibers	9190	8570	6860	77.2	66.3	57.4
	3520	3250	2450	40.6	34.2	27.7
MD ^a						
CD ^a						
30% WNC-121 Polyethylene + lab. kraft	4400	4070	2980	33.2	29.1	23.1
30% WNC-121 Polyethylene + lab. kraft cont. 5% glass	4080	3830	3110	35.2	28.8	24.8
31% WNC-121 Polyethylene + sack kraft ^b	6860	6160	4610	56.2	50.1	36.8
50% HD Polyethylene + sack kraft ^b	9240	8490	6740	c	81.2	67.3
52% Polypropylene + sack kraft ^b	9340	8260	6520	c	83.4	69.2

^a MD = Machine direction, CD = cross direction.

^b Measured in the machine direction.

^c Not measured.

Fiber-Matrix Interactions Under Wet Conditions

It is noteworthy that under water-wet conditions the flexural modulus of every laminate examined in this study is greater than the modulus of the polymer from which the laminate was made. On the other hand, the flexural yield strength of a laminate under water-wet conditions is often less than that of its polymer constituent. This suggests that exposure of the laminates to water has a much greater effect on the strength of the fiber network than on the ability of that network to continue to share loads imposed on the system.

CONCLUSIONS

The severe decline in the flexural properties of paper/polyolefin laminates upon exposure to water can be markedly reduced by acetylation or crosslinking with formaldehyde of the fibrous component, especially when these treatments are applied to the paper rather than to the pulp from which it is made. Nevertheless, a considerable loss of properties still occurs. Higher levels of these treatments might impart additional water or humidity resistance but probably at the expense of other properties as the result of increased fiber degradation.

A new crosslinking process, announced after this work was completed, enables treated paper to retain 90% of its dry tensile modulus when wet.¹⁸ The application of this method to laminates of the types discussed above could result in wood fiber/synthetic polymer composites which retain almost all their modulus and strength under wet conditions.

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