Mechanical Properties of Polymer–Paper Laminates

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Synopsis

Tensile mechanical properties of synthetic polymer–paper laminates were measured. The laminates were constructed by hot pressing a sandwich made of a sheet of paper between polymer films. There is complete penetration of the polymer inside the paper; no voids are left. Two different polymer matrices were used: poly(methyl methacrylate) and polyethylene. Several paper samples were utilized: an unoriented holocellulose paper (a strong paper), a highly oriented holocellulose paper, and an unoriented Whatman filter paper (a weak paper). The laminates contain from 0% to 50% of paper. Young's moduli and breaking strengths of the unoriented holocellulose paper laminates can be theoretically predicted from the properties of their constituents using laws of mixtures. The mechanical properties of the Whatman paper laminates are significantly higher than those predicted from the laws of mixtures. This indicates that the polymer increases the strength of the fiber-to-fiber bonds of the weaker sheets, although it does not change the bond strength of a stronger paper such as the holocellulose paper. For the oriented paper laminates, changes in Young's modulus with angle of measurement are explained by the composite material theories if the angular variations in shear modulus are taken in to account. Changes in breaking strength with angle for the oriented laminates can be analyzed by Tsai and Azzi's theory for composite materials.

INTRODUCTION

Composite materials of various kinds have achieved a tremendous commercial success during the last two decades. These materials can be made of short fibers (2–10 mm in length) dispersed in a plastic matrix. Since the fibers are strong, they can carry important loads, assuming that there is good adhesion between the fibers and the matrix. In addition, the fibers can be oriented in particular directions where high strength is required, thereby optimizing the ratio of performance to material cost.

Cellulose fibers can be compared in many respects to the fibers used in such composites. Their length is about the same (2–5 mm). Their modulus and breaking strength are only slightly lower. They can be easily oriented. Consequently, these fibers are already commercially used in different composite products in two basic forms: (i) "real composites" where the oriented or unoriented cellulose fibers are dispersed in a plastic matrix; and (ii) laminates where oriented, or unoriented sheets of paper are sandwiched between polymer films.

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It is to be expected that composite theories will be as applicable to cellulose composites as they are for other sorts of composites. However, to our knowledge, no work has been reported in this direction. It is then the purpose of the present article to present some data indicating the behavior of paper–polymer laminates when using different kinds of paper. It will also be shown when the modulus and breaking strength of oriented and unoriented paper–polymer laminates can be predicted from the tensile mechanical properties of their constituents. It must be clear that our objective is not to reinforce sheets of paper by impregnating or polymerizing 10%, 20%, or 30% of polymer in the sheet. Our objective is to reinforce polymer films by laminating to them 10%, 20%, 30%, or at most 50% of paper.

The analysis of unoriented laminates will be essentially based on the following laws of mixtures:[1–4]

$$E = E_f V_f + E_m V_m \quad (1)$$

$$\sigma = \sigma'_f V_f + \sigma'_m V_m \quad (2)$$

where E and σ are the modulus and the breaking strength of the composite; V_f and V_m are the volume fractions of the paper and of the matrix; E_f and E_m are the Young's moduli of the paper and of the matrix; and σ'_f and σ'_m are the stresses borne by the fiber and the matrix at a strain equivalent to the elongation at break of the composite. Since the elongation at break of the composite can hardly be predicted, values of σ_f and σ_m at the elongation at break of the paper will be used. This procedure is justified because the elongation at break of the composite will always be close to that of the paper (Table I). For oriented laminates, eqs. (1) and (2) will also be used. The values E_f and σ_f will then be measured at the same angle of orientation that for the composite.

Variations in modulus and breaking strength of the paper constituent and of the laminate as a function of angle will be analyzed using the following three equations:[1–4]

TABLE I
Mechanical Characterization of the Unoriented Holocellulose Paper–PMMA Laminates

% Paper in laminate	Elongation at break, %	Experimental modulus, GPa	Theoretical modulus, GPa	Experimental breaking strength, MPa	Theoretical breaking strength, MPa
0 (PMMA)	2.56	2.36	—	38.0[b]	—
4.5	2.73	3.09	3.02	56.2	45.5
11.0	1.77	4.15	4.17[a]	52.8	56.3
14.0	2.28	4.23	4.41	60.8	61.2
18.0	2.69	4.72	4.99	68.2	67.9
25.0	2.33	6.12	6.00	90.6	79.5
30.0	1.87	7.21	6.72	92.7	87.8
36.0	2.08	7.96	7.62	105.0	97.8
100.0 (all paper)	1.96	16.9	—	204.0	—

[a] Computed using E_f = 18.8 MPa; a different holocellulose paper was used in that particular case.
[b] Value at an elongation at break of 1.96%.

$$\frac{1}{E(\alpha)} = \frac{\cos^4 \alpha}{E_l} + \left(\frac{1}{G_{lt}} - \frac{2\nu}{E_l}\right) \sin^2 \alpha \cos^2 \alpha + \frac{\sin^4 \alpha}{E_t} \quad (3)$$

$$\frac{1}{G(\alpha)} = \frac{1}{G_{lt}} + 4\left(\frac{(1+2\nu)}{E_l} + \frac{1}{E_t} - \frac{1}{G_{lt}}\right) \sin^2 \alpha \cos^2 \alpha \quad (4)$$

$$\frac{1}{\sigma^2(\alpha)} = \frac{\cos^4 \alpha}{X^2} + \left(\frac{1}{S^2} - \frac{1}{X^2}\right) \cos^2 \alpha \sin^2 \alpha + \frac{\sin^4 \alpha}{Y^2} \quad (5)$$

where $E(\alpha)$ and $\sigma(\alpha)$ are the modulus and the breaking strength of the material at an angle α relative to the machine direction; E_l and E_t are the moduli in the machine and cross directions; X and Y are the breaking strengths in the machine and cross directions; ν is Poisson's ratio; G_{lt} is the shear modulus for stresses applied in the l and t directions; $G(\alpha)$ is the shear modulus for stressed applied in the directions α and $\alpha \pm 90°$; and S is the shear strength. Equations (5) and (6) are derived from the orthotropic elasticity theory.[1–4] Equation (7) was originally derived by Azzi and Tsai.[5] It is a generalization of Hill's failure criterion[6] for the cases where the load is not applied in the principal directions of the orthotropic materials. We have previously shown[7] that eqs. (5) and (7) can be successfully used in the analysis of the oriented paper sheets from which the laminates are made. The same equations should also be applicable to the oriented laminates. These three equations assume that the stress is applied uniquely in the plane of the laminate.

EXPERIMENTAL

A black spruce wood sample was delignified using a holocellulose treatment (56% yield). The never-dried fibers were made into highly oriented sheets of paper on a laboratory machine previously described.[7] These sheets have a basis weight of 20 g/m^2, and ratios of modulus and tensile strength in the machine/cross directions of 12 and 22, respectively. Measurement of the distribution in fiber orientation of these sheets was made by an x-ray diffraction technique described elsewhere.[8] Unoriented paper sheets were made in a regular manner from the holocellulose pulp. Whatman filter paper No. 42 was also used.

Two different polymer matrices were used: a poly(methyl methacrylate) (PMMA) obtained from the Fisher Scientific Co. (M-215) and having a viscosity-average molecular weight of 110,000; and a low-density polyethylene (PE) having a melt index of 19. Both samples were originally in powder form and were made into films by heating and pressing on a Carver laboratory press between metal plates.

The laminates were made in a mold by heating and pressing a sandwich made of two or more layers of paper and polymer film in the Carver press. Typical temperature conditions were 135°C for the PE matrix and 165°C for the PMMA matrix. Typical pressure conditions were 3.0 MPa for the unoriented sheets of paper, and 0.20 MPa for the oriented sheets. The laminates were cooled in the mold for 30 min (out of the press, on the bench) and then taken out of the mold. Samples were cut from this 121 cm square laminate using a razor blade cutter. The distribution in fiber orientation was determined in the oriented laminate by the x-ray diffraction technique[8] and was found to be similar to that of the unlaminated sheet of paper.

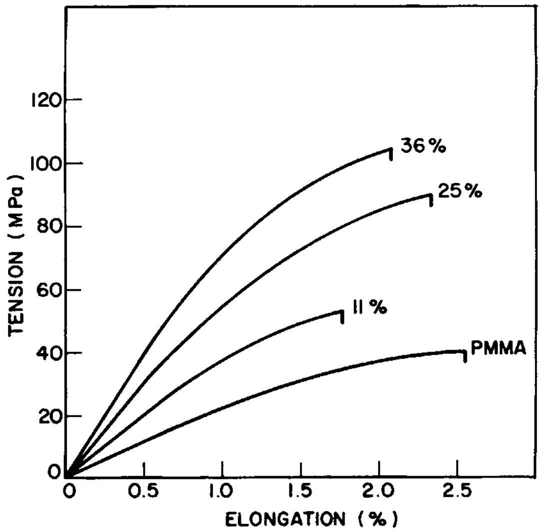

Fig. 1. Tension–elongation curves for the unoriented holocellulose paper–PMMA laminates at different paper volume per cent.

Mechanical measurements were made on an Instron tester, at room temperature, and at about 50% humidity. The rate of elongation was 0.83%/min in all cases. All samples were 7 mm wide and 9 cm long (6 cm between the grips). This ratio of length/width is sufficient to avoid the experimental imprecision often found in testing oriented samples because of the biaxial state of stress created.[3,9,10] The thickness of all samples was measured with a micrometer. In the case of sheets of paper, this is an apparent thickness. The equivalent thickness of the sheet of paper is calculated by correcting the apparent thickness for density. If we take the density of pure cellulose as being 1.54 g/cm^3, then the equivalent thickness is equal to the apparent thickness ÷ 1.54/density. All values of modulus and tensile strength of papers are reported on the basis of the equivalent thickness of the sheets. The volume fraction of paper in the laminate was taken as the ratio of the equivalent thickness of the sheet of paper after pressing at the temperature and for the time of fabrication of the laminate, over the thickness of the laminate. All experimental points reported are an average of at least six measurements, and in most cases of nine or ten measurements.

RESULTS AND DISCUSSION

Unoriented Holocellulose paper–PMMA

Tension–elongation curves for the unoriented holocellulose paper–PMMA laminates are presented in Figure 1 for different volume fractions of paper. A 60 g/m^2 basis weight paper was used in these materials. The tension–elongation curves are all characterized by an elastic region up to about 0.5% elongation, followed by an inelastic deformation before failure. The holocellulose paper alone exhibits the same sort of deformation behavior. One gets a reinforcement of the PMMA which seems to be proportional to the volume fraction of paper incorporated.

The modulus data can be predicted by using eq. (1). These are given in Table I. The agreement found between theory and experiment is satisfactory over the range investigated. The breaking strength data can be predicted by using eq. (2). These values are also included in Table I. These calculated data show more scatter around the experimental results than the modulus values. This reflects the greater experimental difficulties in measuring breaking strengths. Despite this scatter, eq. (2) still expresses the results satisfactorily.

The agreement found between the predictions of eqs. (1) and (2) and the experimental results is surprising since it is expected that the free paper containing about 50% of voids will deform differently than the paper layer in the laminate where all the voids have been replaced by a rigid PMMA matrix. In the latter case, it can be expected that the movement of the individual fibers, when subjected to a strain, will be severely reduced. But the experimental results clearly indicate that the modulus and breaking strength of the laminate can be predicted from the properties of its constituents. In particular, the elongation at break of the laminates is in most cases equal to or larger than that of the free sheet of paper, indicating that as much deformation takes place. This is a strong indication that the modes of deformation of the sheet of paper are the same in both cases. This can only mean that even if the free sheet of paper contains about 50% of voids, it forms a very rigid structure in which the movements of the fibers are very restricted. These movements contribute very little to the tensile deformation properties. Consequently, the elongation at break of the paper is small.

TABLE II
Mechanical Characterization of the Oriented Holocellulose Paper–PMMA Laminates Containing 20% per Volume of Paper at Various Angles of Measurement

	0°	5°	10°	20°	30°	45°	60°	90°
Paper								
Elongation at break, %	1.57	1.23	0.93	0.64	0.53	0.59	0.67	0.67
Experimental modulus, GPa	34.9	32.6	27.9	16.8	10.8	6.02	4.12	3.01
Experimental breaking strength, MPa	380.0	285.0	165.0	82.4	50.7	30.1	22.2	17.4
Laminate								
Elongation at break, %	1.22	1.29	1.38	1.49	1.44	1.60	1.18	1.19
Experimental modulus, GPa	8.79	7.47	7.49	5.92	4.77	3.88	3.20	2.73
Theoretical modulus, GPa; eq. (1)	8.72	8.28	7.35	5.18	4.01	3.08	2.70	2.49
Theoretical modulus, GPa, eqs. (1) and (4)	8.80	8.44	7.57	5.93	5.04	3.97	3.06	2.70
Theoretical shear modulus, GPa, eq. (4)	1.04	1.06	1.09	1.26	1.51	1.69	1.51	1.04
Experimental breaking strength, MPa	92.3	82.6	88.4	73.0	56.7	49.0	33.3	29.3
Theoretical breaking strength, MPa, eq. (2)	95.0	78.0	55.8	41.0	34.1	31.8	25.0	24.1

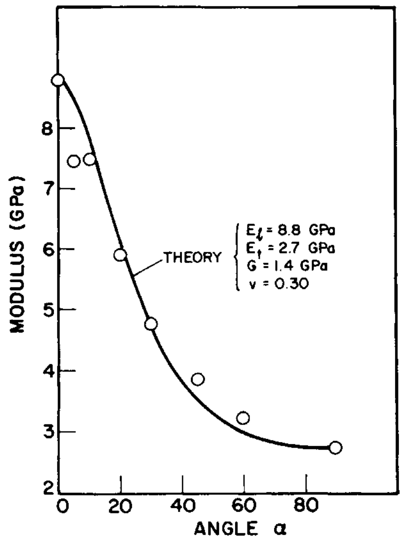

Fig. 2. Modulus for the oriented holocellulose paper–PMMA laminates as a function of the angle of measurement relative to the machine direction. The laminates contain 19.5% paper.

Similar measurements were made for an holocellulose paper–PE laminate. Again, modulus and breaking strength values can be predicted using eqs. (1) and (2).

Oriented Holocellulose paper–PMMA

All oriented laminates analyzed in this study have a paper volume fraction of 0.19_5. Other smaller volume fractions were studied, but are not reported here since the same conclusions were reached in all cases. These laminates were all made from the highly oriented 20 g/m^2 sheets of paper fully analyzed in a previous report.[7] Some of the experimental results obtained from these papers and necessary in the analysis of the laminates are presented in Table II. The variations in modulus and breaking strength with angles for the oriented laminate can be seen in Figures 2 and 3 and in Table II. These values decrease very rapidly in the angular range of 0–45 degrees, while little change is observed in the range of 60–90 degrees.

Equation (3) can be applied to the results presented in Figure 2. Values of E_l and E_t are read from the measured moduli at 0 and 90 degrees. Poisson's ratio ν must be assumed since we did not measure it experimentally. For PMMA, reported values are in the range of 0.30–0.33. For an oriented paper, Poisson's ratio is probably[7,11,12] lower than 0.30. The composite must have an intermediate value. We have arbitrarily chosen a value of 0.30. However, this choice will not influence our analysis very much since in eq. (3) the term $2\nu/E_l$ is smaller than the $1/G_{lt}$ term and, consequently, values of ν in the range of 0.20–0.30 will only change the analysis by a few per cent. The value of G_{lt} is chosen to give the best fit with the experimental data. Agreement is obtained between the experimental and calculated data for G_{lt} = 1.4 GPa. It can be mentioned that the value of G_{lt} obtained in this manner is intermediate between the value deduced for the oriented paper, 3.01 GPa, and the one deduced for PMMA, 0.90 GPa. Laminates

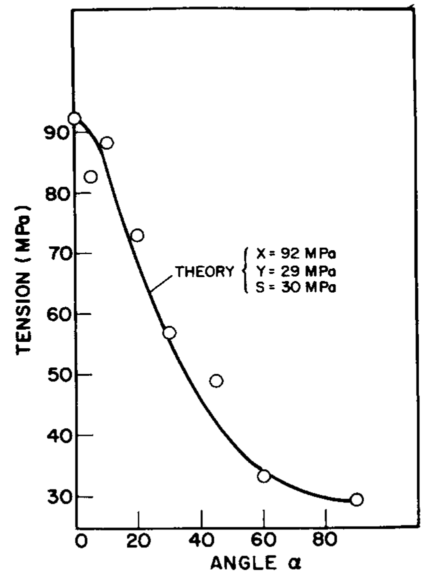

Fig. 3. Breaking strength for the oriented holocellulose paper–PMMA laminates as a function of the angle of measurement relative to the machine direction. The laminates contain 19.5% paper.

with lower paper content give values of G_{lt} smaller than the one found here, but larger than that of PMMA.

Similarly, eq. (4) has been applied to the results presented in Figure 3. Values of X and Y are read from the measured breaking strengths at 0 and 90 degrees. The value of S is chosen to give the best fit with the experimental data. Agreement between calculated and experimental values is found when using $S = 30$ MPa.

Figure 4 presents a picture of the broken laminate samples when stretched at different angles. At 0 and 5 degrees, the broken ends are irregular; at all other angles, the broken ends are quite regular. In addition, the breakage line always occurs close to the machine direction of the laminate (for $\alpha \geq 10$ degrees). A similar behavior was found for the sheets of paper.[7] This is consistent with the interpretation that the paper acts as a reinforcing medium in the laminates. It carries most of the load placed on the sample. But when it breaks, the matrix cannot support the load put on it and the whole sample fails. Since the paper tends to break by a fiber breakage mode of failure at small angles ($\alpha \geq 5$ degrees), the breakage line will be irregular in these cases and perpendicular to the machine direction; since the paper tends to break by a fiber-to-fiber shear and strain mode of failure in their bonding areas at larger angles, the breakage line will be regular in these cases and along the machine direction. These modes of failure are implicit in eq. (5). But as previously discussed,[7] even for oriented paper, these modes of failure are to a certain extent mixed at all angles. It is expected that it will be the same in the laminates.

Combining the oriented paper tensile properties (Table II) and the PMMA properties (Table I), it is possible to use eqs. (1) and (2) to predict the modulus and breaking strength properties of the laminates. The result of this calculation is presented in Table II. It is seen that the moduli are reasonably well predicted

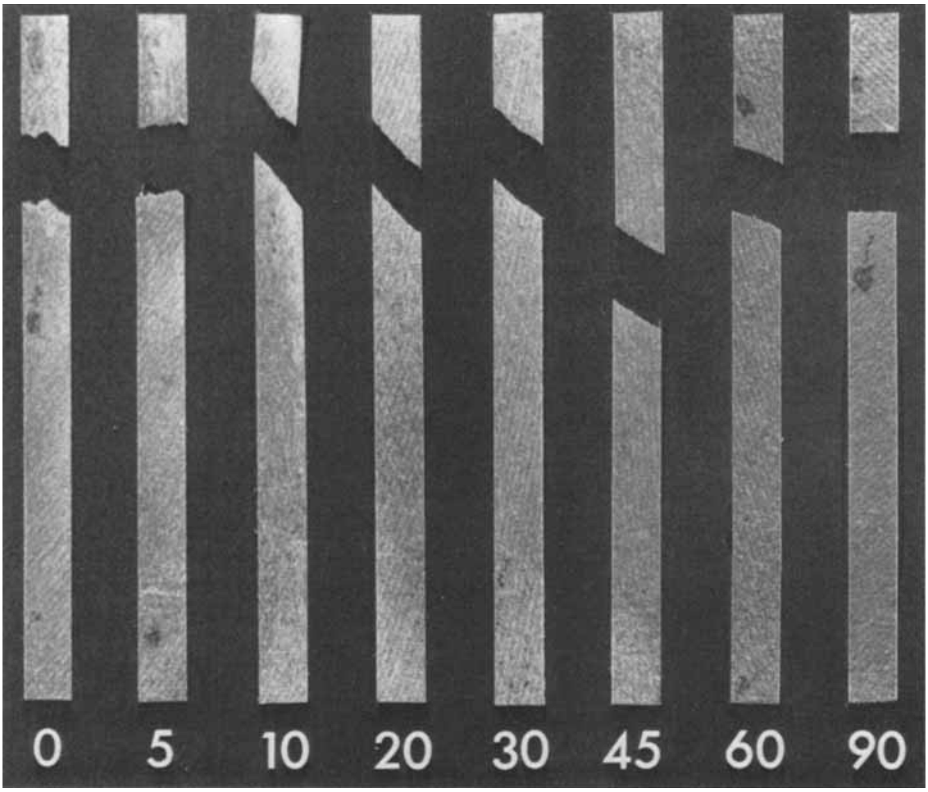

Fig. 4. Broken ends of laminate specimens tested at various angles relative to the machine direction.

at angles of 0, 10, and 90 degrees. The breaking strengths are reasonably predicted at 0, 5, and 90 degrees. The predictions are too low for all intermediate angles. This is especially true for the breaking strength. This may be due to additional contributions from the shearing modes of deformation which occur when the strain is not imposed along the machine or perpendicular directions of the laminate. This has been demonstrated theoretically and experimentally on numerous occasions.[1-4] Assuming that this is the major reason for the discrepancy observed above, one can calculate a theoretical value for the shear modulus G_{lt} of the laminate by using the formula[2]

$$G_{lt} = \frac{G_f G_m}{G_f V_m + G_m V_f} \tag{6}$$

Since $G_f = 3.01$ GPa and $G_m = 0.90$ GPa (PMMA), one gets $G_{lt} = 1.04$ GPa. This value can be introduced in eq. (4) to calculate $G(\alpha)$. The calculated values of $G(\alpha)$ are tabulated in Table II. These values can now be used in the place of G_{lt} in eq. (3), and values of $E(\alpha)$ can be calculated. These are also reported in Table II. These values are in excellent agreement with the experimental values. In fact, it is surprising to find such a good accord considering the approximate nature of the different equations used. However, this treatment was found appropriate for all the oriented paper–polymer laminates that we have tested so far.

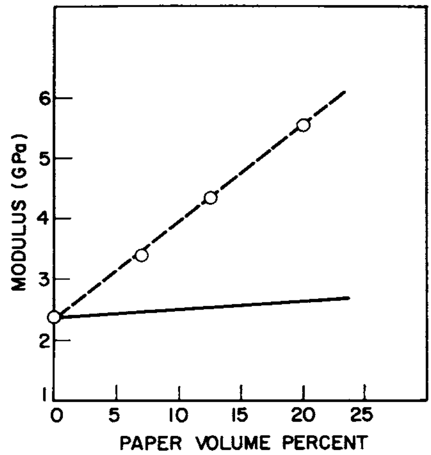

Fig. 5. Modulus vs. paper volume per cent for the unoriented Whatman filter paper–PMMA laminates.

It must be noted that eq. (4) predicts values of $G(\alpha)$ in the range of 1.04–1.69 GPa. The experimental value of G_{lt} determined earlier using eq. (3) was 1.40 GPa. This is an intermediate value which is much higher than the value of G_{lt} determined from eq. (6). This indicates that eq. (3) does not generate the true value of G_{lt} unless one uses it in combination with eq. (4), which takes into account the variation of the shear contribution with angle. Equation (6) seems to be satisfactory for predicting G_{lt}. It then seems that the discrepancy noticed between the experimental values of modulus and those calculated from eq. (1) is due to contributions from the shearing modes of deformation of the sample. These can be accounted for using eqs. (3), (4), and (6). The same phenomenon must be responsible for the discrepancy observed between the experimental values of breaking strength and those predicted by eq. (2). Unfortunately, no appropriate equations have been derived yet in that case. But for the modulus, it suffices to know the shear and Young's moduli in the machine and in the perpendicular directions of the matrix and of the paper sheet and the volume fraction of paper in the laminate to be able to predict the modulus of the laminate at all angles using eqs. (1), (3), (4), and (6). For the tensile strength, eq. (2) will predict values which can be considered as "lower bounds," the experimental values being larger.

Whatman Paper–PMMA

All laminates reported so far were made from a strong holocellulose paper. This paper is, in fact, significantly stronger than most commercial papers. At this point, it would be interesting to see if eqs. (1) and (2) do apply to a laminate made from a weaker paper. The system Whatman filter paper–PMMA seemed to be particularly interesting in this respect since the modulus of the paper is only slightly larger than that of PMMA, and its breaking strength is even smaller.

Laminates were then fabricated from this system. Their tension–elongation curves are quite similar to those reported in Figure 1. Changes in modulus and breaking strength with paper volume per cent are presented in Figures 5 and 6. It is seen that the reinforcement effect of the paper on the polymer is much larger

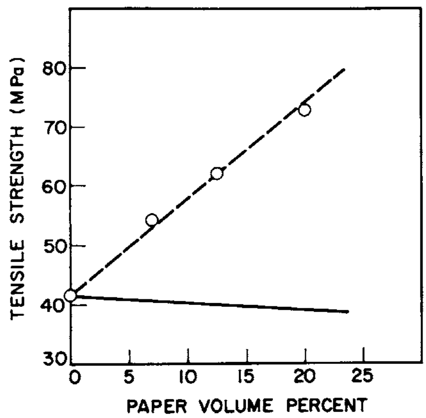

Fig. 6. Breaking strength vs. paper volume per cent for the unoriented Whatman filter paper–PMMA laminates.

than that expected from the laws of mixtures, eqs. (1) and (2). These equations are also plotted in Figures 5 and 6 as continuous lines. This reinforcement effect is quite interesting. It is similar to that reported by Marchessault and Fisa[13] on sheets of paper encapsulated by PE, and by Robertson[14] on sheets of paper impregnated with polymer. These authors have noticed that the mechanical properties of weak sheets of paper are upgraded by the incorporation of a polymer by a value which is larger than predicted from the laws of mixtures. Similarly, we observed that weak sheets of paper can be used in the reinforcement of polymer laminates in a much more effective way than expected. In all these cases, it seems that the polymer improves the fiber-to-fiber bond strength by some mechanism which is not well understood. This improvement is, however, not present when the paper, such as holocellulose paper, is strong and already has good fiber-to-fiber bond strength.

These results can be empirically described by modifying eqs. (1) and (2) to

$$E = KE_f V_f + E_m V_m \tag{7}$$

$$\sigma = K\sigma_f' V_f + \sigma_m' V_m \tag{8}$$

where K in an efficiency factor. When K is equal to unity, eqs. (7) and (8) reduce to the laws of mixtures, eqs. (1) and (2). In composites where imperfect adhesion plays a role, K is found smaller than unity.[5,6,15] In the present case, K will be larger than unity. Using $K = 3.4$, the broken lines shown in Figures 5 and 6 through the experimental results are generated. These results demonstrate that it is highly desirable to make a laminate where the polymer penetrates the paper as compared to side-by-side layer laminates since the latter will certainly not show the upgrading in the tensile mechanical properties observed in Figures 5 and 6. Similar results were found for PE–Whatman paper laminates with $K = 2.0$.

CONCLUSIONS

A series of tensile mechanical measurements have been made on oriented and unoriented paper–polymer laminates. The results indicate that the equations used in composite material analysis can be in general applied to paper–polymer laminates. Adhesion is often a problem in the composite field, but it is not a necessary requirement in these laminates since both phases are continuous and because they share directly the load from the loading system.

In the case of oriented laminates, it has been shown that the variations in modulus with angle can be predicted from a few basic properties of their constituents. However, the variations in breaking strength with angle cannot be accurately predicted. The theories give values which are too low because they do not account for additional shearing forces acting on these materials.

For unoriented composites, it was found that Young's modulus and breaking strength of the polymer–paper laminates can be predicted by the laws of mixtures if the original paper is strong. If the original paper is weak, the effective reinforcement observed is larger than predicted by these laws. It seems that the polymer increases the fiber-to-fiber bond strength of the paper. Work is now in progress in our laboratories to determine if this additional reinforcement is uniquely a function of the strength of the original sheet of paper and to determine the minimum strength of the sheet of paper above which the laws of mixtures apply.

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More complete data on the system PMMA–paper and also on the system PE–paper may be obtained upon request from the author.

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