Institute of Paper Science and Technology
Atlanta, Georgia

## IPST TECHNICAL PAPER SERIES

NUMBER 453

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SEPTEMBER 1992

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Submitted to
Nordic Pulp and Paper Research Journal

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SUMMARY: The strength of individual fiber/fiber bonds and the resulting damage during rupture to the fiber walls was measured under a variety of conditions. The major variables were degree of refining, relative humidity, and the absence or presence of chemical strength additives. In general, the degree of fiber wall damage, as estimated from scanning electron micrographs, was found to increase with increasing bond strength. Use of a strength additive provided about a twofold increase in bond strength with concomitant increase in the amount of fiber wall damage. Elevated relative humidities during bond rupture reduced the bond strength but did not change the relative amount of fiber wall damage.

Torn S1 material, found with some ruptured bonds along the edges of the bonded area, was interpreted to be evidence of Nanko and Ohsawa's "skirt" effect. The presence of such material correlated with greater bond strength thereby supporting the suggestion of those authors that the skirt should reduce the stress concentration present at the periphery of the bonded area.

Weak bonds tended to fail at the interface between the two fibers. Stronger bonds and particularly those that were enhanced with a polymeric strength aid shifted the locus of failure to between the S1 and S2 layers of one (or both) fibers.

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Paper strength is a function of both individual fiber strength and the strength of the bond between the fibers (1, 2). Previous work (3-13) has provided direct measurements of the latter including the effect of chemical strength additives (6, 13). In the absence of additives, the interactions between fibers are thought to be hydrogen bonds plus the ubiquitous van der Waals bonds. Chemical additives can supplement these interactions to produce improved wet or dry strength. If the fiber/fiber interactions are strong enough, the locus of failure may be shifted from between the two fibers to between the S1 and S2 layers of one of the fibers. It is important that we know the location of the failure so that we may direct the chemical additives to this weak spot (i.e., between or within the fibers).

Previous workers have presented photomicrographs (optical, SEM, or TEM) of formerly-bonded fibers. In some (3, 7) the magnification was too low to reveal much detail. In other studies (14-16),"picking" of microfibrils was found. Skowronski and Bichard (17) found different types of bond failure when a delamination test was carried out at a slow strain rate compared with "impact" conditions. Although showing no examples, Thorpe et al. (11) described SEM results that showed fracture at the fiber/shive interface for a holocellulose . For bonds formed from TMP at 110 or 210$^{o}$ C, they found failure within the fiber wall. In all of these studies, only single examples were given, and no systematic study of the relationship between bond strength and fiber damage was undertaken. The present study seeks to fill this gap.

## Experimental

Details of pulp preparation, fiber/fiber bond preparation, and bond strength measurement have been given elsewhere (13). Abbreviated descriptions of these and details of the SEM analysis follow.

### Materials

Southern pine chips were pulped using a conventional kraft cook to a yield of 47.5% (kappa number of 34.2), refined to either 570 or 345 mL CSF, and classified to remove the fines. Earlywood and latewood portions of loblolly pine were separately pulped using conventional kraft cooks with no subsequent refining.

Chemical strength aids, when used, were combinations of a cationic polymer followed by an anionic polymer. Polyamide polyamine epichlorohydrin (1% by weight based on the pulp) followed by carboxymethylcellulose (0.4%) was designated A/C. The second combination was polydiallyldimethyl ammonium chloride (0.5%) followed by sodium polystyrene sulfonate (0.5%) and was designated D/S. The combination A/C can form covalent, ionic, and hydrogen bonds with the fibers (18), while D/S can only form ionic bonds.

**Techniques**

Individual fiber/fiber bonds were prepared by positioning a pair of wet fibers at right angles to each other on a teflon-faced rubber disc. The pair was dried at 105°C for one hour under a nominal pressure of 0.12 MPa. The bonded fiber/fiber pair was cemented at the ends of the fibers to a special mylar mount (*fig. 1*). Bonded area was measured using Page's polarized light technique with vertical illumation (19). The "tongue" area of the mount was painted with black ink before the fibers were attached to it to reduce reflection and enhance contrast between bonded and nonbonded regions. The breaking load of the bond was determined using the FLER II (20), a second generation fiber load elongation recorder (21). This instrument was located in a room with the atmosphere controlled at 23° C and 50% RH, and the tests were made at those conditions except as noted below. To obtain representative mean values, 40 to 50 bonds for each pulp were prepared and tested.

After bond failure the two parts of the mylar mount, each with its attached fiber, were removed from the clamps of the FLER II, coated with gold-palladium *in vacuo,* and installed in a scanning electron microscope. Formerly-bonded areas were easily recognized, and the locus of failure could be seen.

For comparison purposes, a (subjective) rating of the degree of damage in the formerly-bonded area was devised and is shown in *fig. 2*. The failure surface of each of the formerly-bonded fibers (axial and cross) was compared with those in *fig. 2* and assigned a ranking of 1 to 6. Briefly, the relative amounts of damage for the six archetypes in *fig. 2* can be described as follows.

1. No damage.
2. Slight "picking" of the surface.
3. Moderate "picking."
4. Significant "picking," some tearing of surface layer.
5. Moderate tearing.
6. Extreme tearing.

Note that the background in archetypes 2, 4, and 6 (which are axial or "tongue" specimens) is the inked surface of the mylar mount.

For those fibers that had been refined, additional damage to their surfaces was sometimes evident and took the form of external fibrillation and peeling of wall material at the edges of the fibers. This type of damage is exhibited by the prototypes in *fig. 2* and was assigned a "Damage Type" of unity. The unrefined fibers and some of the refined fibers showed no such damage and were given a value of zero for this parameter. The presence or absence of this material along the edges of the fiber appeared to be independent of the amount of damage in the central portion of the bond.

## Results and Discussion

### Degree of Damage

The SEM observations provided us a great deal of information concerning how and where bonds fail. Two extremes are shown in *figs. 3* and *4*. The former was found most frequently with unrefined fibers untreated with strength aids, the latter with refined, treated fibers. However, a variety of degrees of damage were found for a given pulp. For the fibers in *figs. 3* and *4*, the degree of damage was 1 and 6, respectively. The damage type (see EXPERIMENTAL section for definition) for both these fibers was zero in contrast to those in *fig. 2* which was one.

The average values and standard deviations for the "rank" and "type" of damage for both axial (T) and cross (C) fibers for the several pulps are listed in *table 1* along with values for the bond strength which is the ratio of the breaking load (from FLER II) to the bond area (Page technique).

Because the geometry of the loading experiment is nonsymmetrical (that is, the load is applied axially to one fiber and transversely to the other), it was of interest to determine the effect of this geometry on the damage produced during bond failure. The average damage ranking in the C (cross) direction for the nine different pulps was plotted against the corresponding average ranking for the T (axial) fiber. The individual values were averages of about 40 fibers. A line through the origin with slope one fit the data with an $r^2$ of 0.83. There was no systematic dependence of damage on the experimental geometry.

There was, however, usually a wide variety of degrees of damage for a given pulp. It would be expected that greater amounts of damage would be correlated with larger bond strengths, and there is some evidence that this is so. In *fig. 5* the bond strength is plotted against the sum of the damage ratings of the mating fibers for the lightly beaten pulp (A5). Fiber pairs with like total damage values were grouped together, and their average bond strength and its standard error are shown. The line shown is a least squares fit to the data. Greater damage is associated with stronger bonds.

For comparison, the bond strength values for the same pulp treated with the "ionic only" strength aid (ADS) are also given in *fig. 5*. The lines drawn are least squares fits to the data. The tips of the arrows indicate the overall average bond strength and damage ranking for each pulp. Obviously, the strength aid increases both the bond strength and the severity of damage to the fibers.

This is apparently a general result as shown by the values in *table 1*. For two different pulps, the presence of either A/C or D/S produces greater damage when the fiber/fiber bond is ruptured. For the earlywood pulp, the locus of failure is shifted from the interface between the fibers to within the fiber wall. Addition of A/C to this pulp reduces the amount of rank 1 damage (i.e., no damage, see *fig.* 2) from about 10% to less than 2% of the samples. Since the amount of strength aid added is equivalent to less than a monolayer of the polymer (22), there is no continuous "film" of adhesive between the two fibers. Instead, the strength aid is providing additional individual bonds within the bonded area.

Examining the results in *table 1,* we find that relative humidity has no statistically significant effect on the amount of damage occurring during bond failure. There is a small increase in the amount of damage when the A5 pulp (570 mL CSF) is further refined to the A3 (345 mL CSF) condition. However, it is not possible to differentiate between the additional damage produced by the refining operation from that which might be caused by the more intimate contact available to the A3 fibers. The bond strength is not increased by refining.

Finally, we can say with greater than 99% certainty that more damage occurs when the bond between two latewood fibers fails than the corresponding case for two earlywood fibers. This result parallels the greater strength of the latewood bond as listed in *table 1.*

**Evidence for the "Skirt" Effect**

As mentioned above, some of the formerly-bonded fibers possessed additional fibrillated or wall material along their edges. As it happens, all of the fibers chosen as archetypes for the damage ranking (*fig.* 2) were of this type, while those shown in *figs. 3* and *4* were not. The two types were assigned ratings of 0 (material absent) or 1 (material present) without regard for the amount of material. At the time we were puzzled by these fragments whose presence seemed independent of the amount of damage in the central regions of the bond. We now believe that they are a result of and further evidence for the "skirt" effect recently discovered by Nanko and Ohsawa (23). This phenomenon is shown in *fig. 6* taken from their paper. The skirt is formed by the adhesion of the S1 layer, which has swollen and separated from the S2 layer of the same fiber, to the surface of the mating fiber. Nanko and Ohsawa found this separation in both refined and unrefined fibers and suggested it occurred in the latter as a result of the pressing operation. We only found type 1 behavior for refined pulps. Significantly, we did not find it for unrefined, earlywood fibers treated with a strength aid which showed large amounts of damage in the central regions of the bonds. Apparently, for this pulp, S1-S2 separation did not occur during bond formation. The different species of pulp used in Nanko and Ohsawa's and our work, Japanese beech and loblolly pine, respectively, may account for the presence or absence of S1-S2 separation for unrefined pulp.

Additional evidence for the skirt effect is adduced in *figs. 7-9*. The fibers in *figs. 7* and *8* were mates from a single bond, and both show the effect. Considerable tearing (peeling) of S1 material is also exhibited in *fig. 8*. Such tearing was most commonly found when strength aids were used (cf. *fig. 4*) but was also observed for other well-bonded samples. Apparently, the bond strength between the mating S1 layers of the two fibers is greater than that between the S1 and S2 layers of one or the other of the fibers.

The rupture of the skirt material is perhaps most clearly shown in *fig. 9*. Here, the peeled-back skirt material and its locus of fracture are obvious. The locus is shown schematically in *fig. 10* which can be viewed as a close-up of the interface region of the dried state in the Nanko and Ohsawa schematic (*fig. 6*). Those authors suggest that the presence of the skirts is important for increasing the strength of fiber/fiber bonds. More important than the additional bond area that the skirts provide is their role in distributing the stress at the periphery of the bond. The stress concentrations that are expected to be large here are reduced and redistributed by the skirts, and a higher load can be sustained. As the applied load is increased further, stress concentrations eventually lead to bond failure. The evidence from our SEM photos suggests the locus of failure of the S1 layer to be in the vicinity of the arrow drawn in *fig. 10;* that is, the peak stress is not at the outer edge of the bond but is slightly inside it. To improve bond strength further would require strengthening the material in the S1 layer.

The reduction of stress concentration by the skirt material is supported by our strength data. Bond strength is plotted in *fig. 11* against the rating for the evidence of this skirt material on the mating fibers. Thus, values of 0, 2, or 1 on the abscissa indicate that neither, both, or only one of the fibers showed this material. For both the untreated (A5) and treated (ADS) pulps, the trend is clear: bond strength increases when the skirt material is present. The error bars show the standard error, while the tips of the arrows indicate the overall average values for the bond strength and (CType + TType) parameter. Note that the average value for this latter parameter is approximately the same for both pulps even though the strength aid increases the bond strength substantially. Apparently, the skirt effect is little influenced by additives.

Based on these results, one could argue that one of the ways by which refining enhances bond strength (and, hence, sheet strength) is by loosening the attachment between the S1 and S2 layers of a fiber. The "skirt" effect then becomes possible leading to reduced stress concentrations and higher bond strength.

## Conclusions

Weak bonds fail at the fiber/fiber interface with little or no damage to the fiber surface. Stronger bonds tend to produce "picking" of microfibrils from the surface of one or both fibers. The strongest bonds produce failure at the S1-S2 interface of one or both fibers with substantial tearing of the S1 layer. Nanko and Ohsawa's "skirt" effect enhances bond strength, apparently by reducing stress concentrations at the periphery of the bond.

## Acknowledgments

The authors are indebted to Mr. Keith W. Hardacker for advice and help in measuring the bond breaking load. The expertise and patience of Mrs. Mary Block and Ms. Ellen Foxgrover in obtaining the SEM photographs is gratefully acknowledged.

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Table 1. Mean Fiber Bond Properties

| Pulp | Code | Add.[a] | R.H., % | Bond Strength, MPa | CRank | TRank | CType | TType |
|---|---|---|---|---|---|---|---|---|
| Earlywood | E0 | - - | 50 | 2.1 (2.1)[b] | 2.08 (0.50) | 2.00 (0.45) | 0.00 (0.00) | 0.00 (0.00) |
| Latewood | L0 | - - | 50 | 6.4 (4.2) | 2.46 (0.88) | 2.50 (0.78) | 0.00 (0.00) | 0.00 (0.00) |
| Earlywood | EAC | A/C | 50 | 3.9 (1.7) | 3.67 (1.04) | 3.62 (1.59) | 0.00 (0.00) | 0.00 (0.00) |
| 570 mL CSF | A5 | - - | 50 | 3.5 (2.8) | 3.82 (0.96) | 3.40 (1.04) | 0.82 (0.38) | 0.81 (0.40) |
| 570 mL CSF | A75 | - - | 75 | 2.9 (2.4) | 3.90 (1.23) | 3.71 (1.02) | 0.74 (0.44) | 0.69 (0.47) |
| 570 mL CSF | A88 | - - | 88 | 2.1 (1.9) | 3.80 (1.14) | 3.41 (0.86) | 0.71 (0.46) | 0.73 (0.45) |
| 570 mL CSF | AAC | A/C | 50 | 7.5 (6.7) | 4.34 (1.15) | 4.38 (1.17) | 0.58 (0.50) | 0.66 (0.48) |
| 570 mL CSF | ADS | D/S | 50 | 9.3 (5.7) | 4.07 (1.01) | 4.67 (0.87) | 0.77 (0.43) | 0.70 (0.47) |
| 345 mL CSF | A3 | - - | 50 | 3.7 (4.4) | 4.41 (0.91) | 3.98 (0.80) | 0.92 (0.27) | 0.81 (0.39) |

a) Additive. Fibers treated with A/C (see text) or D/S polymers.

b) Values in parentheses are standard deviations.

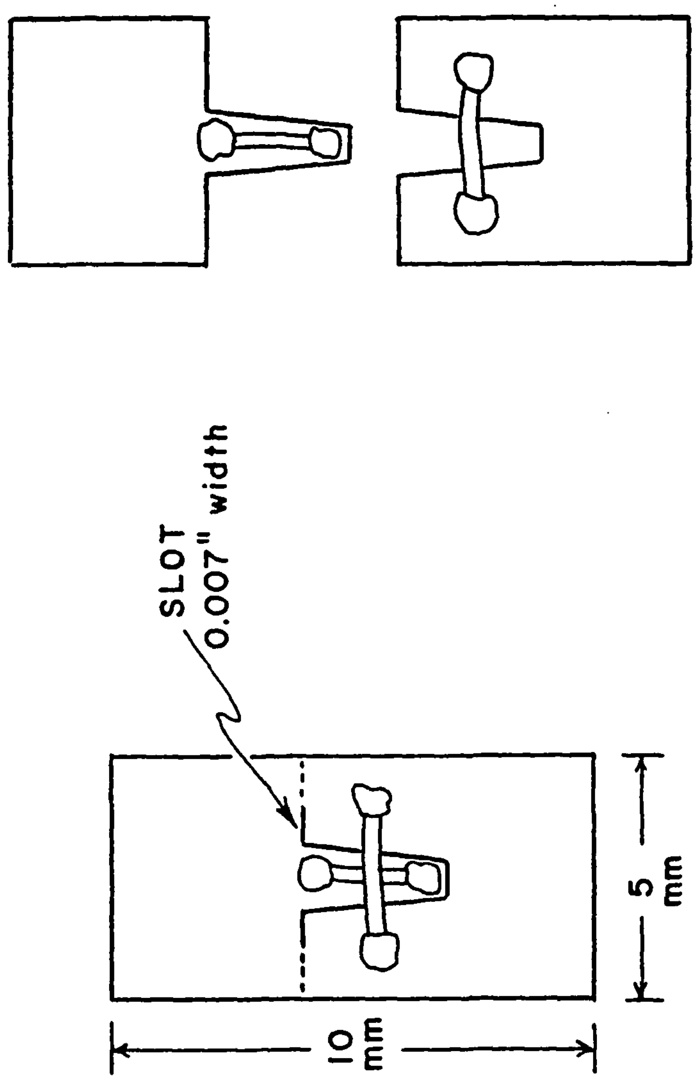
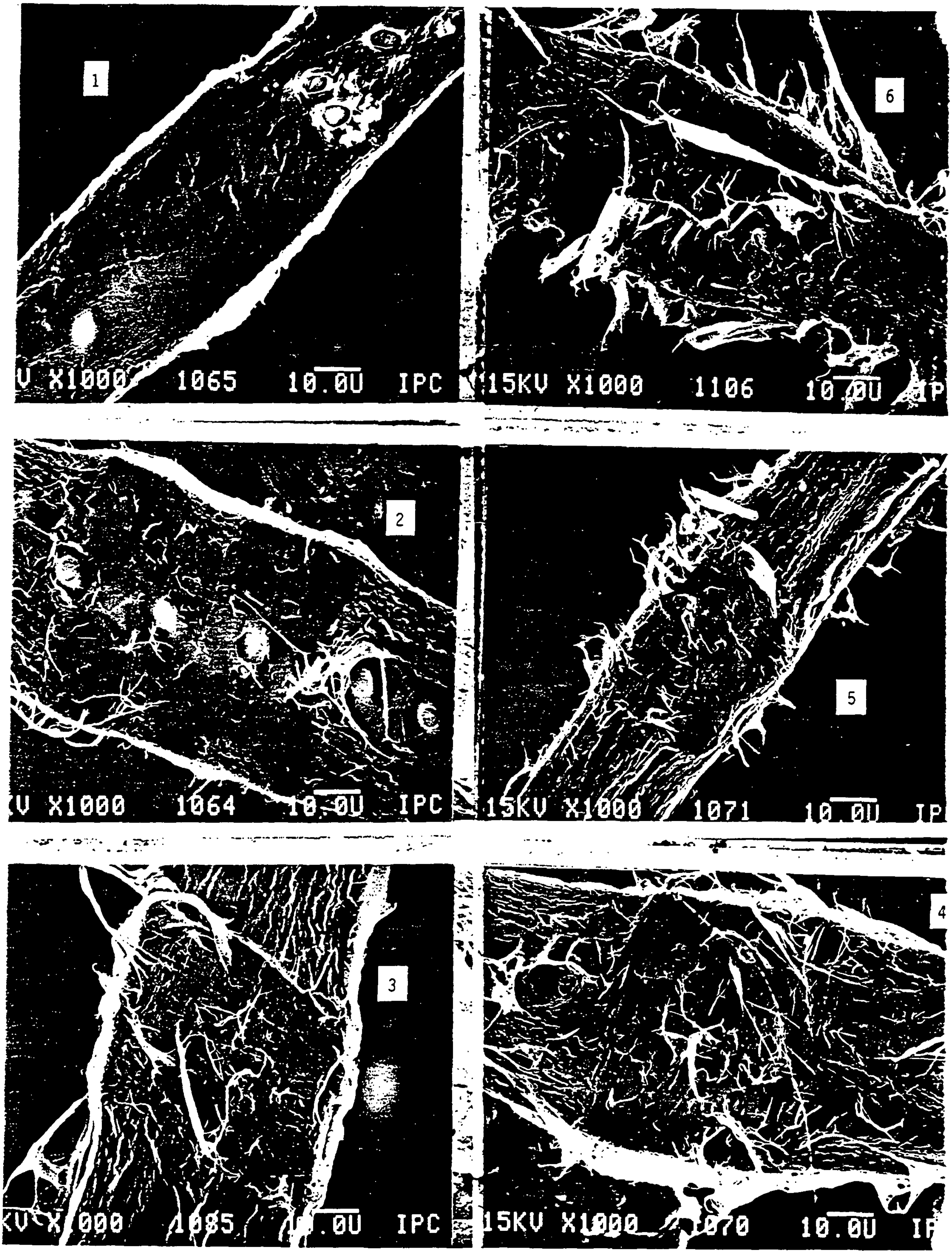



Fig. 1 Mylar tab for holding bonded fibers. a) Before bond fracture. b) After fracture. (Fibers shown not to scale.)

Fig. 2 Archetypes of fiber damage resulting from bond rupture. Increasing rank from 1 to 6 anticlockwise starting in upper left-hand corner.



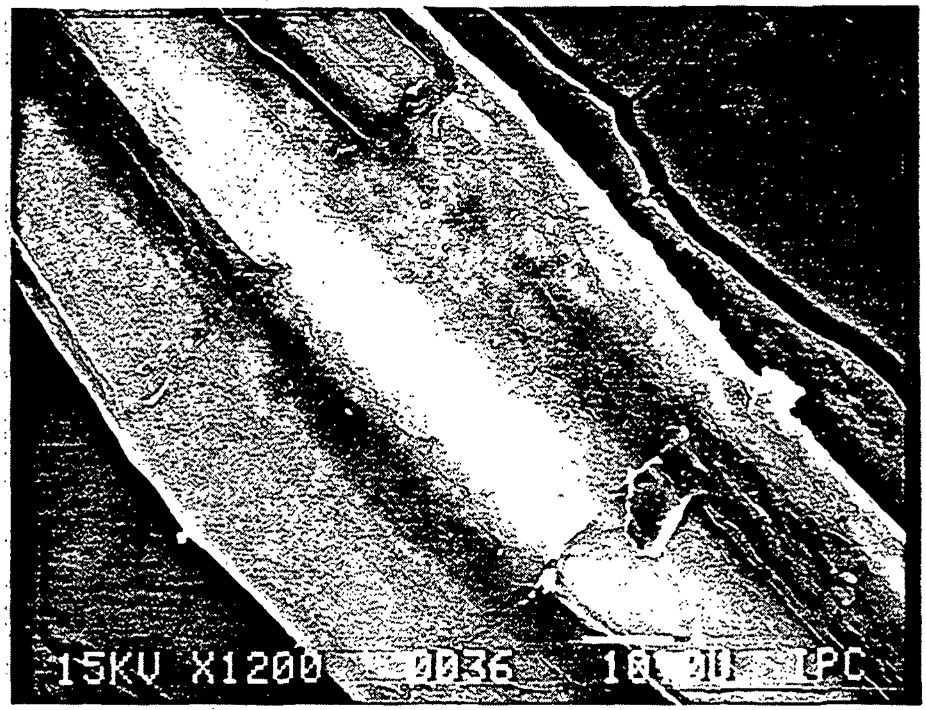



Fig. 3  SEM of formerly-bonded fiber. Pulp: E0, TRank: 1, TType: 0.

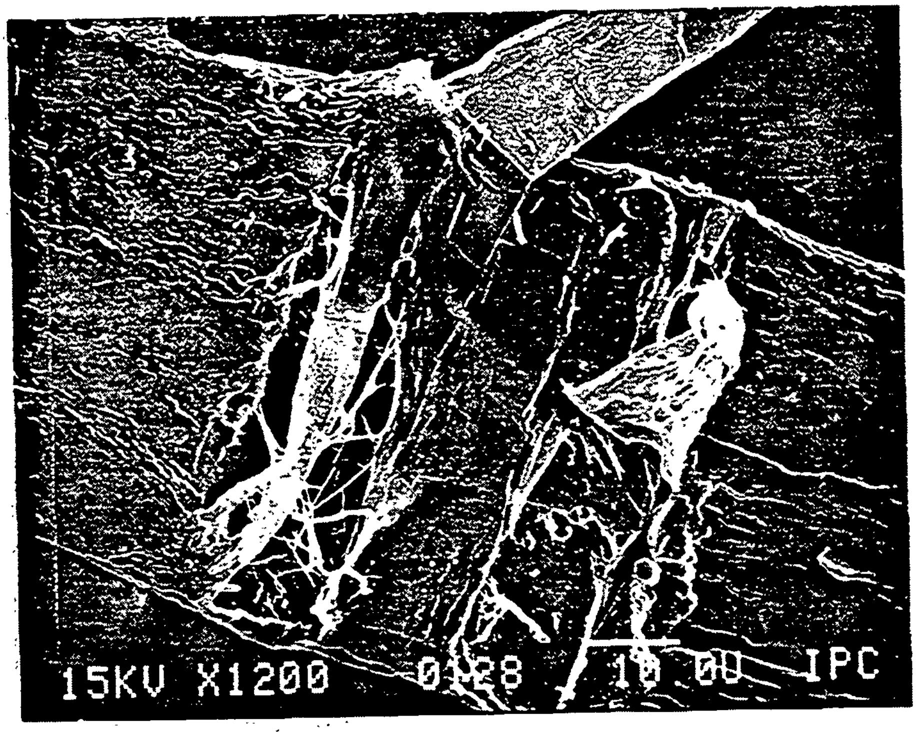



Fig. 4  SEM of formerly-bonded fiber. Pulp: EAC, TRank: 6, TType: 0.

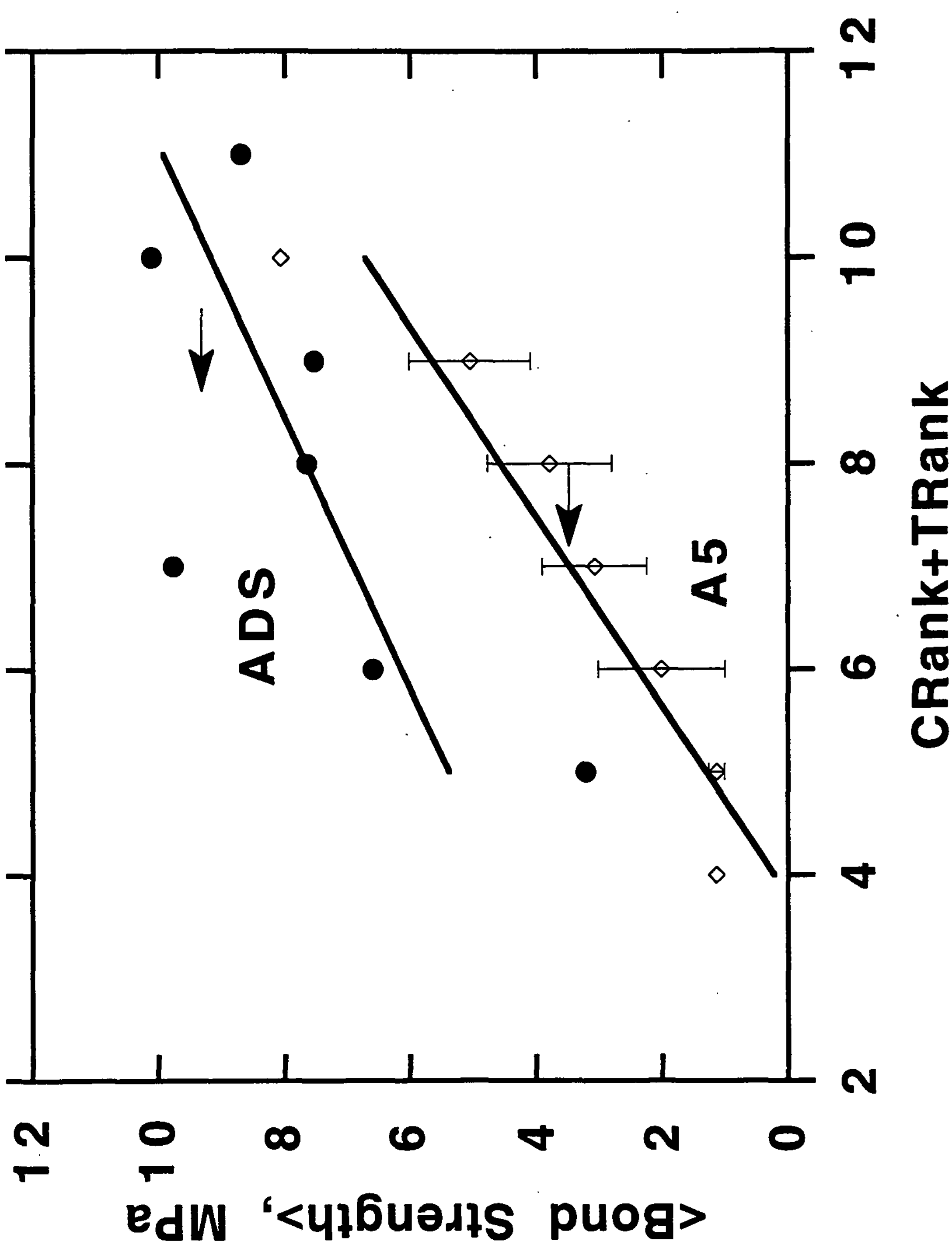



Fig. 5 Effect of strength aid on damage rating for the lightly refined pulp. Tips of arrows indicate overall average values for strength and damage rating for each pulp.

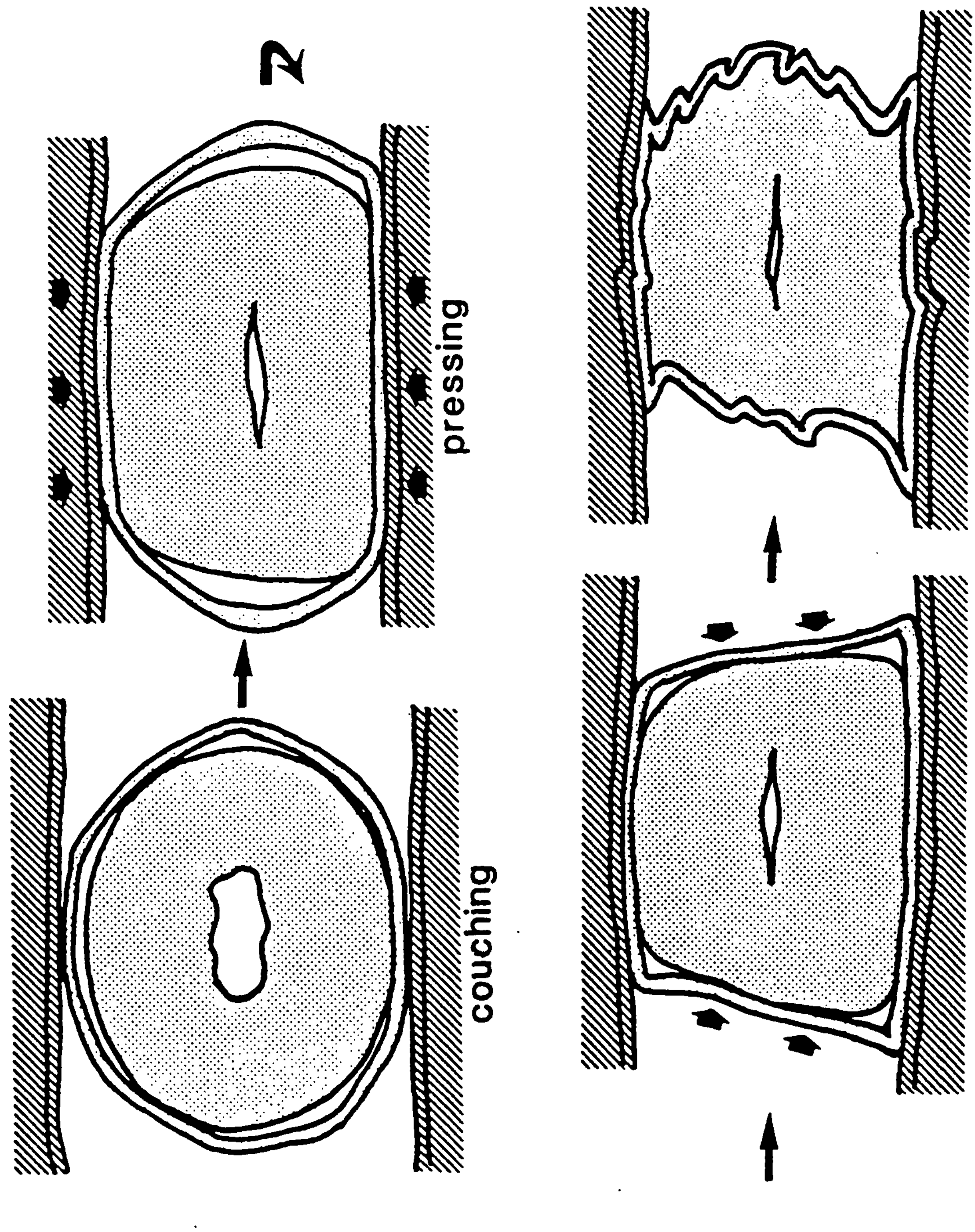



Fig. 6 Schematic representation of the changes occurring during fiber bond formation. Taken from Nanko and Ohsawa (23).

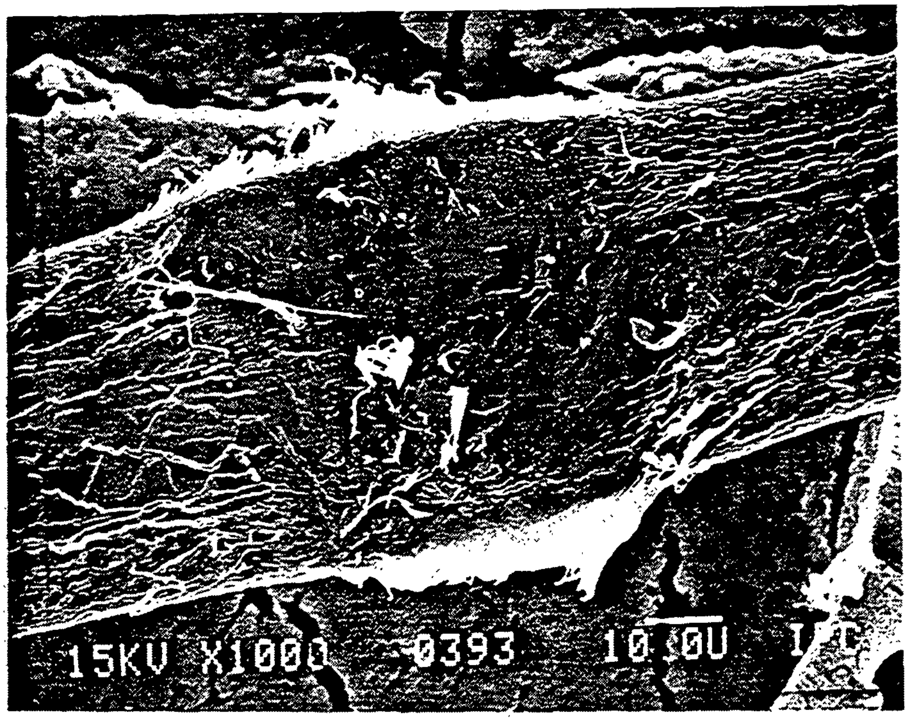



Fig. 7 SEM of formerly-bonded fiber showing skirt material. Pulp: A5.

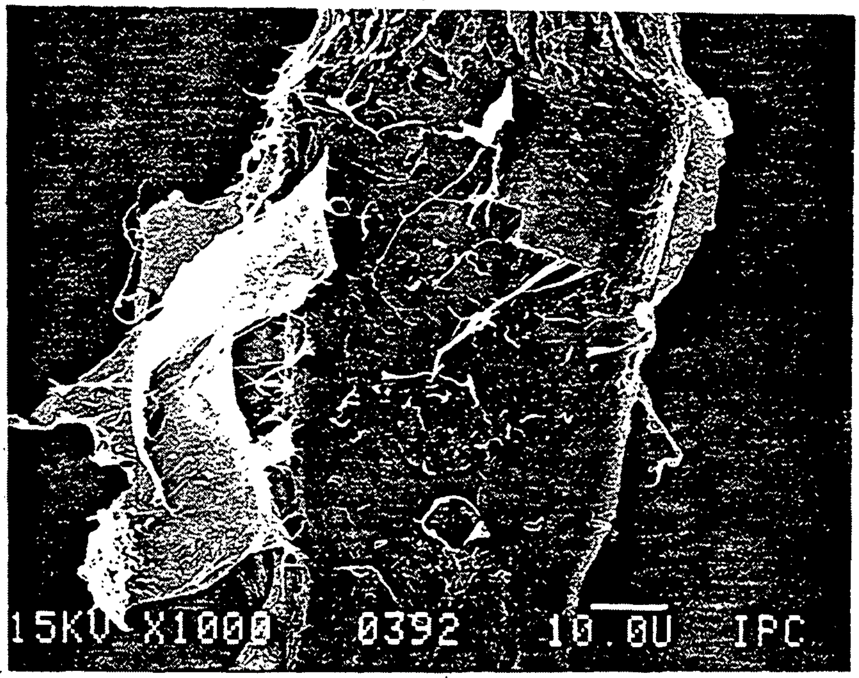



Fig. 8 SEM of formerly-bonded fiber showing skirt material. Pulp: A5, (Mate to fiber in Fig. 7).

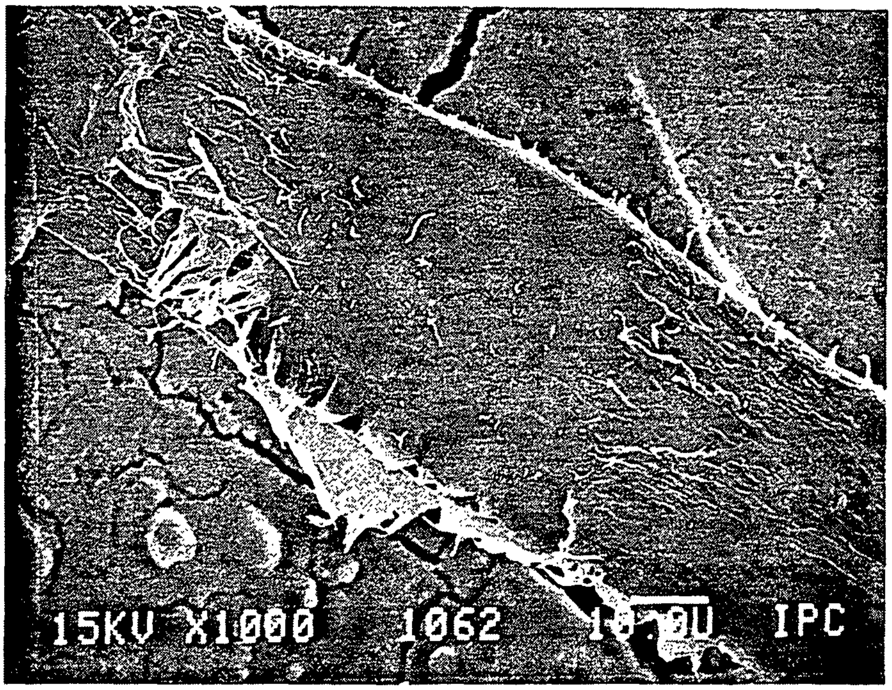



Fig. 9 SEM of formerly-bonded fiber showing fracture zone of skirt material.
Pulp: A75.

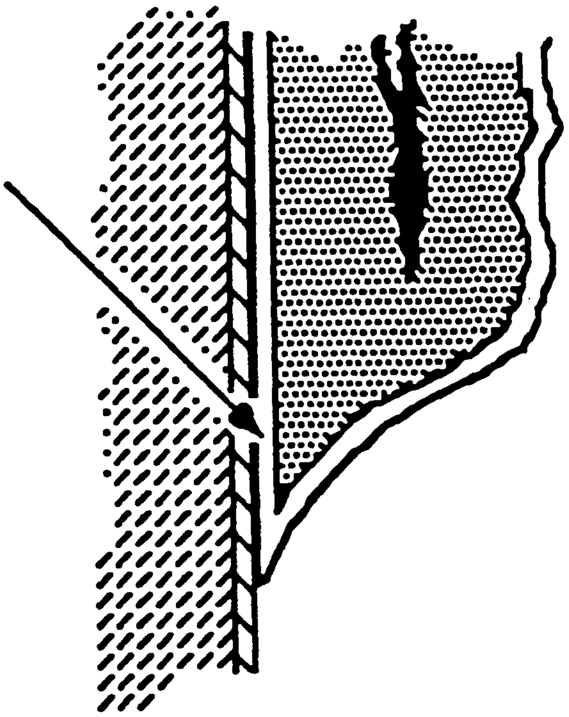


Fig. 10 Schematic representation of the location of fracture of the S1 layer.

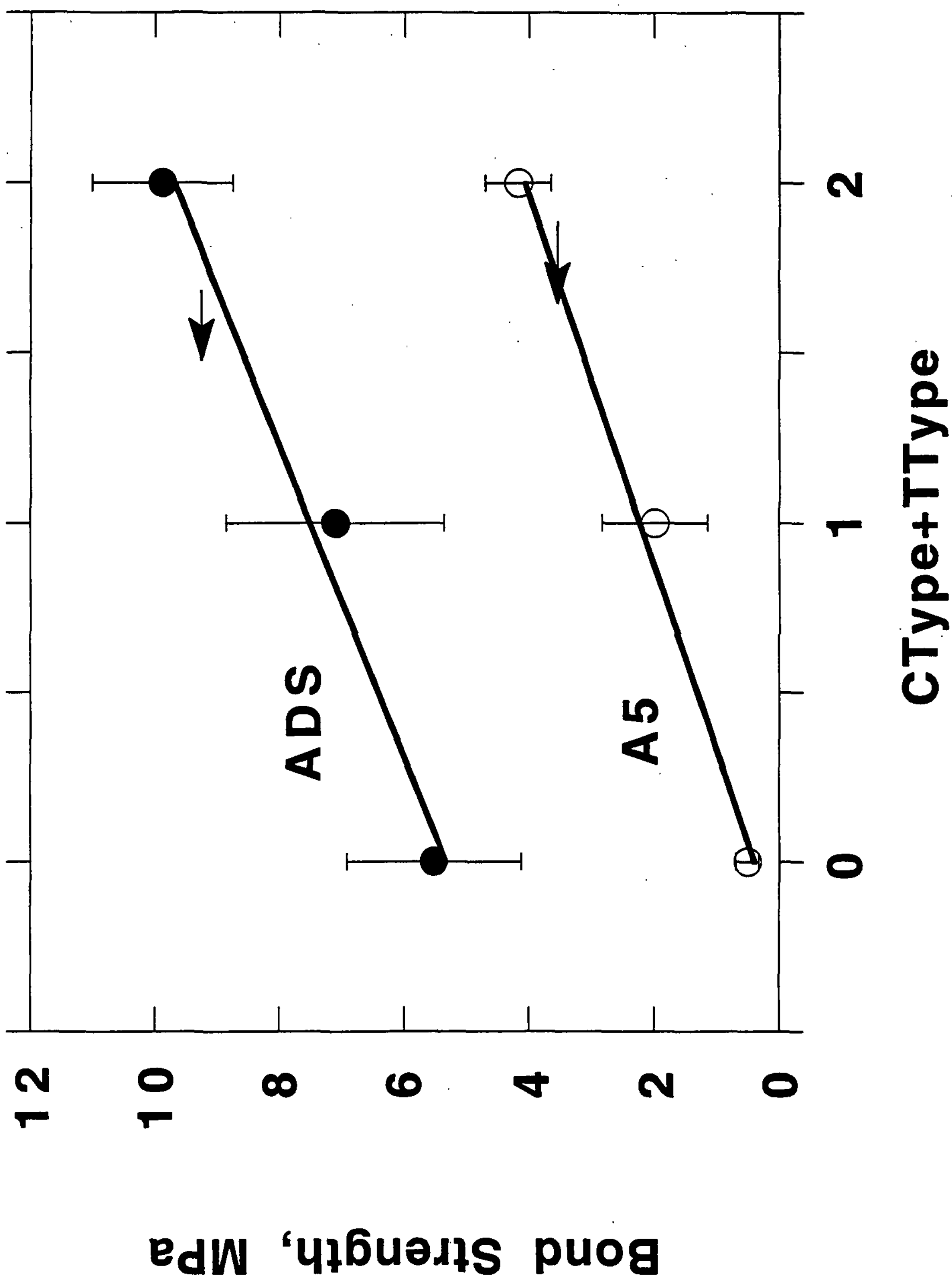



Fig. 11 Dependence of bond strength on the presence of "skirt" material. Tips of arrows indicate overall average values for strength and amount of skirt material for each pulp.