

Mechanical interlocking in coating adhesion to paper

ROBERT J. DICKSON AND PIERRE LEPOUTRE

SEVERAL INDUSTRIAL APPLICATIONS use aqueous pigmented coatings applied on porous substrates. As an example, pigmented latex paints are applied on wallboard, particle board, cement block, and wood for protective or purely aesthetic reasons. In the manufacturing of printing papers, paperboard for packaging, and many specialty paper grades, there is often a pigmented coating on the base sheet to improve its optical and printing properties. The coating consists of an aqueous suspension of a pigment such as titanium dioxide, clay, or calcium carbonate and a binder such as latex, starch, protein and other additives to control rheology.

The main difference between common paints and paper coatings is the binder level. Most paper coatings do not have to meet the stringent requirements of protective paints. For economical reasons, their formulation is usually above the critical pigment volume concentration (CPVC). This means they contain low binder levels and are porous. Coated paper or paperboard must still withstand significant in-plane and out-of-plane stresses in printing with tacky inks or in the creasing, folding, and gluing operations during converting. Factors influencing adhesion and cohesion of a porous pigmented coating on a porous substrate like paper therefore have considerable scientific interest. The goal of this research is to separate the physical and physicochemical factors influencing the adhesion between coating and paper.

BACKGROUND

A review of adhesion literature and various adhesion theories provides a basis for understanding bond formation between two surfaces. For the cases examined here—bonding pigment particles and fibers with a polymeric binder, the requirements of formation of an interface through wetting and spreading processes (1) and of the development of strong bonds through Lifshitz-van der Waals (LW) and acid-base (AB) interactions (2) appear essential. Much current work is trying to characterize these types of interactions and assess their importance in quantitative terms (2-21). Equation 1 describes an approach using the work of adhesion:

$$W_a = W_a^{LW} + W_a^{AB} \quad (1)$$

where

W_a = work of adhesion

W_a^{LW} = LW contribution to work of adhesion

W_a^{AB} = AB contribution to work of adhesion.

The question of adhesion, bond formation, and ultimate bond strength between porous surfaces has received little attention. The porous surface of the substrate provides more area for potential sites for LW and AB interactions. Not all surfaces are porous, but all surfaces do have roughness albeit only at a microscopic level. This roughness can provide more surface area for bonding. Porosity and roughness may

ABSTRACT

Experiments measured the level of mechanical interlocking by pretreating handsheets with a fluorocarbon to remove the physicochemical interactions. Peel test and a z-direction test measured adhesion. Results indicated that mechanical interlocking increases as the surface roughness increases by providing sites for such interlocking. Coating weight nonuniformity influences the failure mechanism so that the peel force and the z-direction strength appear to decrease with increasing coating weight. Measurements of single fiber coating adhesion showed that the fiber's microroughness can contribute up to 20% of the fiber coating adhesion.

Application: Mechanical interlocking influences adhesion between coating and paper at both macroscopic and microscopic levels.

also allow the adhesive to anchor physically into the substrate causing mechanical interlocking (MI). MI results from the purely physical anchoring of one adherent into the structure of the other as **Fig. 1** shows.

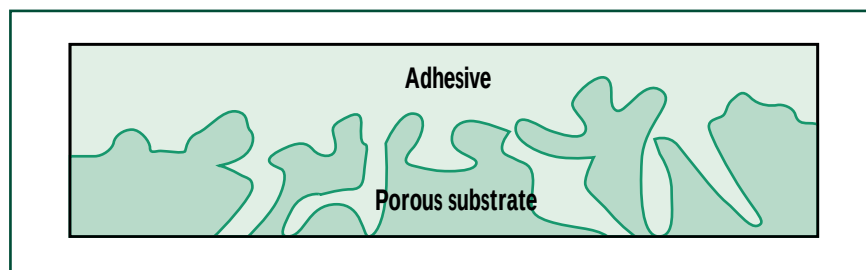
MI therefore depends on a combination of the topography, roughness, and porosity of a substrate. Since MI means that extra energy is necessary to remove the adhesive, it can enhance the work of adhesion. An additional term is therefore necessary in Eq. 1:

$$W_a = W_a^{LW} + W_a^{AB} + W_a^{MI} \quad (2)$$

where

W_a^{MI} = MI contribution to work of adhesion.

McBain and Hopkins (22) studied the effect of roughness and porosity on bricks, wood, metal, etc., using adhesives like gelatin, glue, cement,



1. Adhesive applied to a porous and rough substrate where MI could contribute to adhesion

	Air permeability, mL/s	Roughness, μm	Void fraction, vol./vol.
Basestock: Wood-containing*	2.1	4.5–5.0	0.59
Basestock: wood-free*	4.8	5.7–6.0	0.48
Calendered basestock: wood-containing*	1.6	2.8–3.6	0.54
Calendered basestock: wood-free*	3.7	3.4–4.0	0.42
Paper bag	6.8	7.8–8.6	0.58
Copy paper	5.8	5.6–6.5	0.49
Fax paper	3.3	2.8–3.4	0.36

*The basestock papers will be coated. Wood-free paper is paper made from lignin-free fibers. Wood-containing does contain undelignified fibers.

1. Typical values for different types of paper

etc. They found that surface roughening—while not causing pores—did not contribute to adhesion. An increase in porosity did increase the adhesion level. Gent *et al.* (23) found that surface roughness increased the relative bonding area with a concomitant increase in adhesion level for natural rubber and styrene butadiene polymer on a treated aluminum substrate. These workers also found that pores in the substrate increased the bonding area. Of greater significance was the fact that adhesive penetration into the pores increased the adhesion level. This was because the adhesive would have to break for removal from the substrate.

Most investigations of adhesion phenomena in paper have concerned gluing of paperboard or extrusion coating of paper with polyolefins. Concerns raised with the gluing of paperboard include the rate of bond formation and the failure location (24, 25). Bond formation rate is very important. If the bond does not form quickly, the paper or board could easily rip in subsequent converting steps. Location of failure after application and drying of the glue is important. In commercial use, an operator relies on the simple test of tearing the bond apart. If the failure occurs in the basestock, the product is acceptable. If the failure is in the glue or at

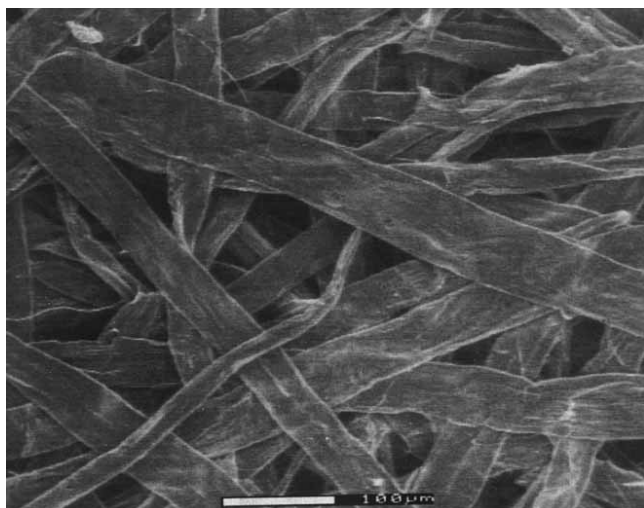
the interface between glue and paper or board, the product is not acceptable (24). The bond should be stronger than the basestock.

In extrusion coating, it is important that the polymer film applied to the paper basestock adheres strongly during the converting processes. This is because extrusion coated products find frequent use to keep moisture in—juice cartons—or out—cereal boxes. Swanson and Becher (24) studied the effect of surface energy of the paper substrate on the adhesion of polyethylene. They found that a decrease in surface energy of the paper gave an expected decrease in adhesion. They did not investigate the contribution of roughness. Gervason *et al.* (25) examined the effect of paper roughness on adhesion between polyethylene and sized paper. They found that roughness did not affect the adhesion level except at coating weights below 10 g/m², where smoother surfaces had higher adhesion levels.

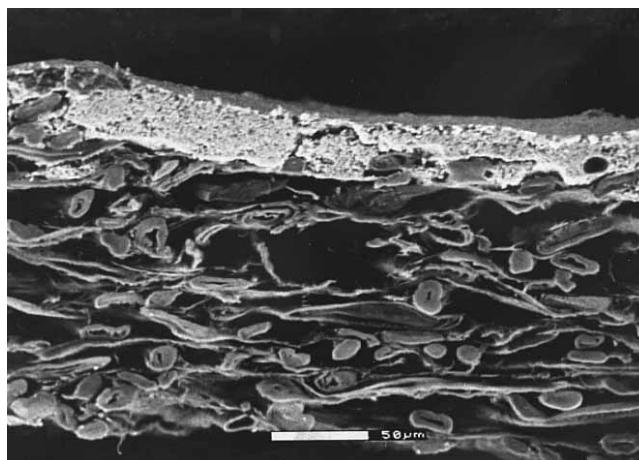
PIGMENTED PAPER COATINGS

Studies of adhesion in pigmented coated papers have only concerned the parameters affecting the cohesion of the coating such as binder type and content, pigment size and shape, etc. (26–31). There has been no critical examination of adhesion of such coatings to paper, although it is important.

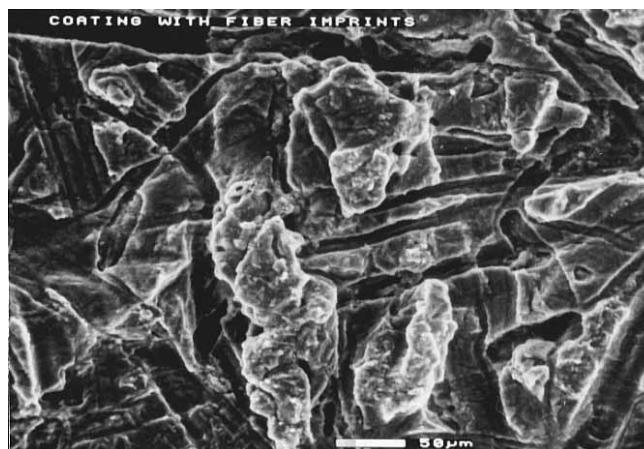
Coating are applied as an aqueous suspension of a pigment, binder, and additives as noted above. These pigments are approximately 0.1–2.0 μm equivalent spherical diameter in size. They are in the shape of plates, rhombs, spheres, needles, etc. After coating application, water is absorbed into the paper and evaporates from the surface of the coating causing the coating to consolidate and dry. The dry coating layer is porous because there is an insufficient amount of binder to fill the spaces between the pigment particles. Air voids therefore form. During drying, the binder forms a film



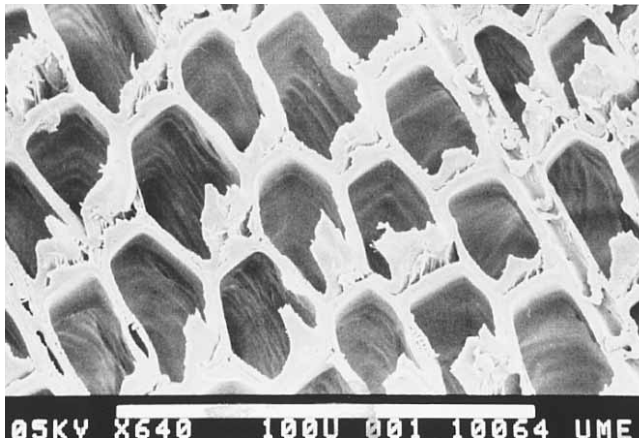
2. Example of the porous nature of a paper surface made with chemical fibers



3. Example of the pores in the cross section of coated paper



4. The paper coating interface with the paper fibers removed leaving the fiber imprint on the coating

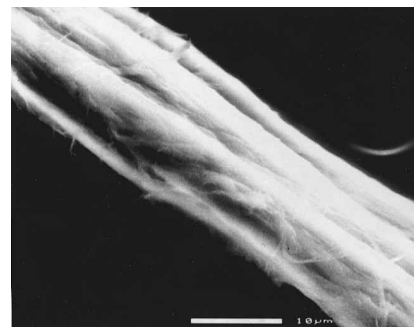


5. Cross section view of wood

which bonds the pigment particles together and to the fibers. These bonds involve dispersive and acid-base interactions. **Figures 2 and 3** show that paper substrates are porous and rough. During setting of the coating, the aqueous dispersion of binder and pigment particles can penetrate into the surface pores. Here they set and physically anchor into the substrate causing MI that contributes to adhesion.

Measurement of porosity and roughness of paper basestock uses standard techniques described in TAPPI Test Methods. Measuring the air leaking along the surface of paper as it undergoes loading provides an

estimate of roughness. An estimate of porosity as void fraction or pore volume comes from thickness measurement for known compositions or from mercury intrusion. Measurement of air permeability can also characterize porosity in terms of pore size and connectivity. Air permeability is the measure of air flow through the thickness of paper under a pressure gradient. While air permeability does not measure pore size, one may conclude that there is a higher flow rate with larger pores for a given total pore volume. **Table I** shows typical values of roughness, air permeability, and void fraction for a range of papers.

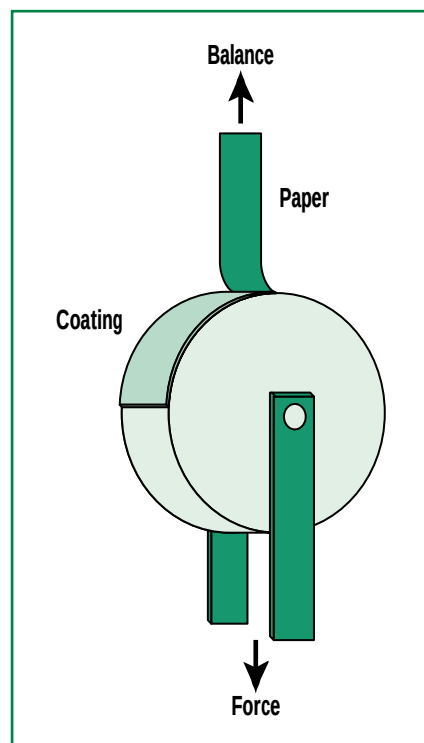


6. Example of microroughness of a fiber surface

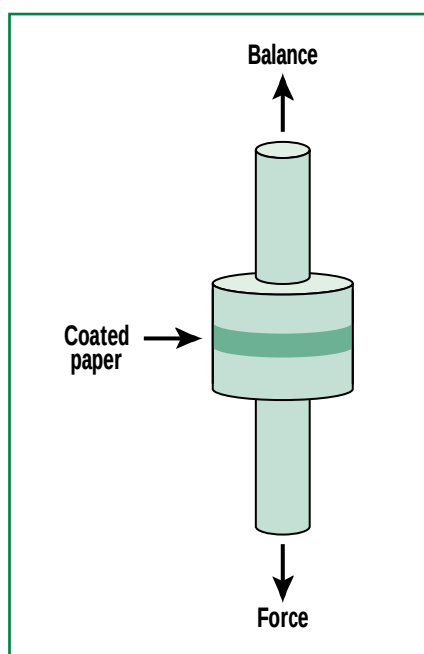
To demonstrate that MI is possible with coated paper, **Fig. 4** shows a scanning electron micrograph of the rear of a clay coating with the paper fibers dissolved away. This

Ingredient	Parts based on pigment
Calcium carbonate	100
Carboxymethyl Cellulose	1
Polyacrylate dispersant	0.2
Styrene butadiene latex	10

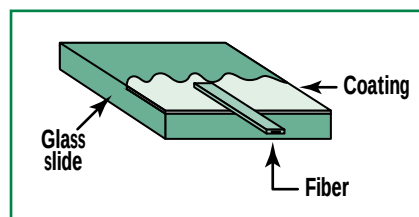
II. Coating formulation



7. Wheel used for the peel test



8. Attachment used for the z-direction test



9. Diagram illustrating the apparatus containing the fiber for peeling from the coating

figure shows there are zones where the coating penetrated into the surface pores of the paper and underneath the fibers. At these locations, either the fiber or the coating must break or pull out for failure to occur.

Figure 5 indicates that fibers in wood are hollow tubes with thin walls. In well-bonded papers, the fibers have collapsed into the ribbons of Fig. 2. While dry paper fibers are nonporous, they do have a degree of roughness on a microscopic level that Fig. 6 shows. This microscopic roughness can also provide sites for MI.

APPROACH

Paper

Our approach was to pretreat handsheets to suppress physicochemical interactions between coating and paper without changing the roughness or porosity. After we determined the level of pretreatment, it was possible to vary the roughness and porosity of softwood handsheets to determine their effect on MI. The porosity was varied by changing the wet pressing pressure. The roughness was varied by wet pressing against sandpaper of different grit. After preparing the handsheets, we coated and dried them. MI measurement used two different tests—a peel test and a z-direction

Roughness, μm	Permeability, cc/s	Peel force, N/meter
9.6	0.51	26
9.6	0.05	11

III. Effect of porosity on MI

bond strength test. A peel wheel attachment made to fit in a mechanical tester determined the peel force, and a z-direction attachment in a mechanical tester determined the z-direction bond strength. After all tests, we examined the failed specimens in a scanning electron microscope (SEM) to detect whether failure was adhesive or cohesive.

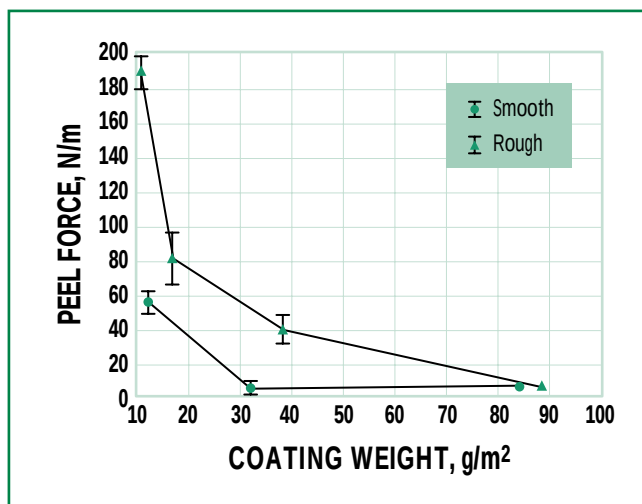
Fiber

We used the same approach as in the handsheets to pretreat individual, never dried, kraft, loblolly pine fibers with a fluorocarbon emulsion. After pretreatment, we laid the dry fibers on a wet pigmented coating. After the coating was dry, we peeled the fibers off the surface of the coating. Measurement of the peeling force combined with SEM examination of the failed areas provided an estimate of the extent of MI on a micro-scale.

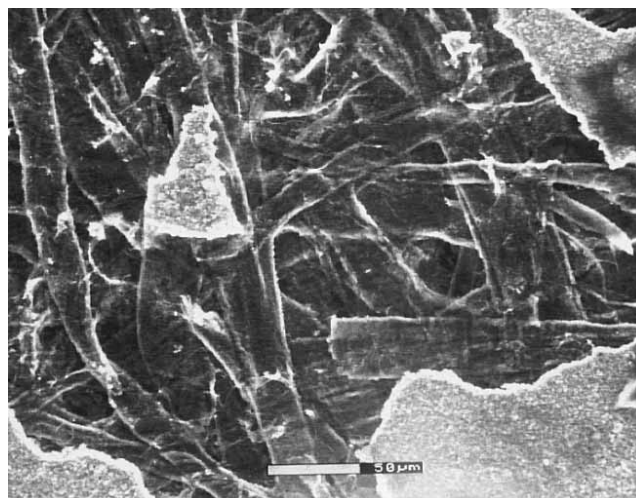
Experimental procedure

Handsheet preparation We formed northeastern U.S. pine kraft pulp into 1.2 g handsheets according to TAPPI Test Method T 205 om-88 except a change in the wet pressing process for the handsheets. Wet pressing causes handsheets to become denser and changes the porosity of the sheet. Our wet pressing pressure varied at 400 psi, 500 psi, and 600 psi compared to the TAPPI standard of 50 psi. Air permeability provided a measure of porosity. Higher air flow in TAPPI Test Method T 460 om-88 indicates a larger size or amount of pores.

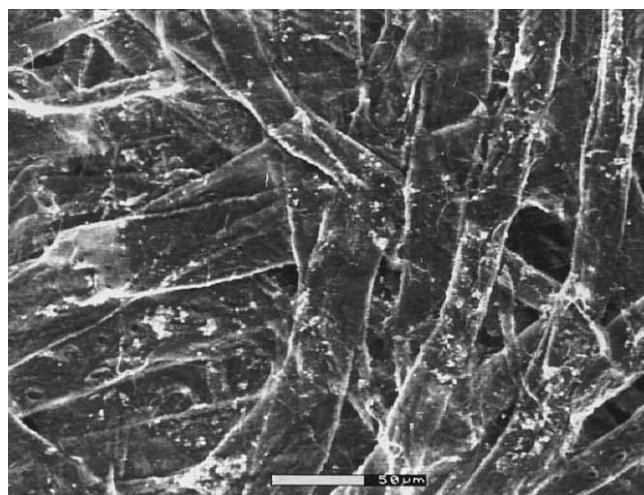
To obtain different degrees of roughness, we wet pressed the sheets against sandpapers of different grit number—150, 240, 320, and 600—and a smooth surface polyester film. A diamond tip stylus profilometer gave roughness measurements.



10. Peel force vs. coating weight for two different base sheet degrees of roughness using the peel wheel



11. Surface of a low coating weight paper after peeling



12. Surface of a high coating weight paper after peeling

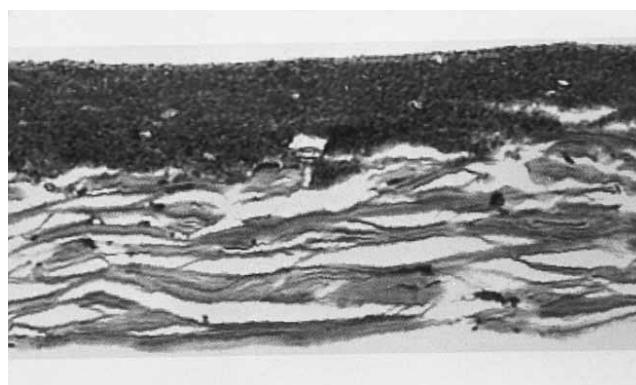
Pretreatment. Pretreatment involved dipping the handsheets in a fluorocarbon emulsion in ethanol of known concentration, pressing between two blotters to remove excess fluorocarbon, and air drying for 1 h. Placing in an oven at 105°C for 15 min provided curing.

Coating. We coated the handsheets with a pigmented coating using a draw down coater. Table II gives the details of the coating formulation applied at 60% solids. Ashing the sample provided a determination of the final coating weight applied to the sheet. After applying the coating to the handsheets, we dried them at room temperature for 1 h followed by heating in an oven at 105°C for 15 minutes to ensure filming of the latex.

Peel test. We cut the handsheets into 0.5 in. by 6 in. samples, applied double sided tape to the coating side, and then adhered samples to the peel wheel as Fig. 7 shows. Measuring the force necessary to remove the paper from the coating with the peel wheel apparatus in



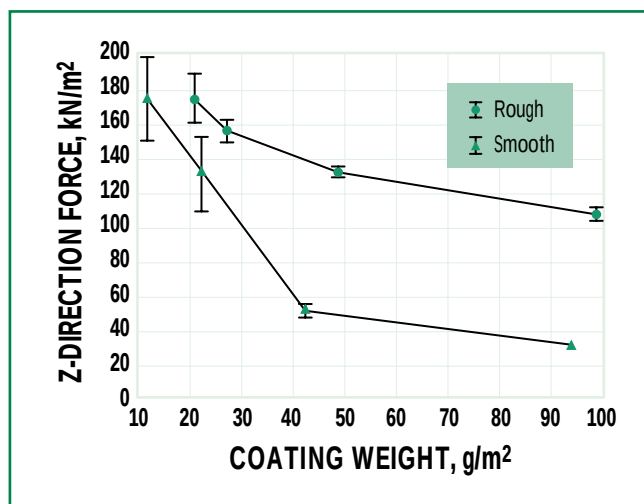
13. Low coating weight cross section at 18 g/m²



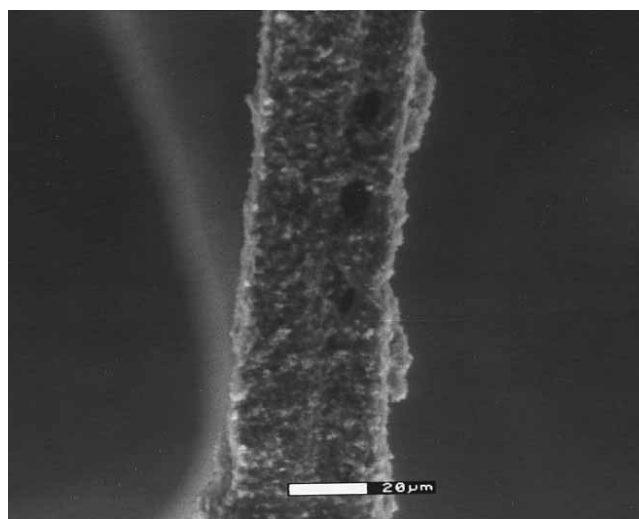
14. High coating weight cross section at 78 g/m²

a tensile tester provided the peel strength. Note that the peel strength measured was due not only to MI but also to bending and plastic deformation of the layer peeled.

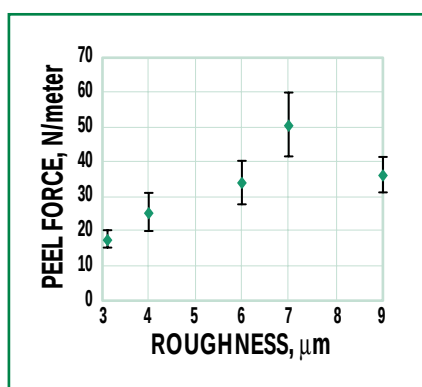
Z-direction test. For this test, we cut coated paper into 1 in. diameter samples and applied them to two discs with double sided tape. We attached the discs and sample to a mechanical tester, Fig. 8.



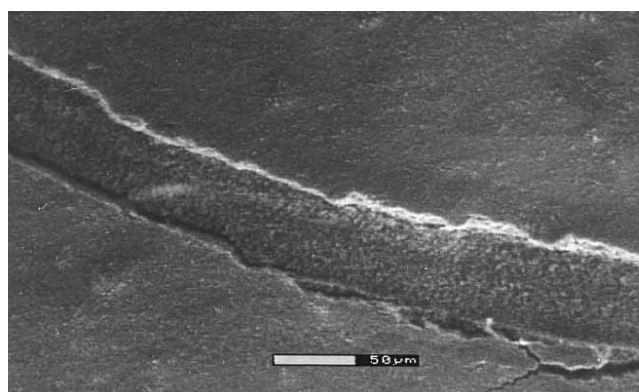
15. Z-direction force vs. coating weight



17. Untreated peeled fiber



16. Peel force vs. roughness with error bars calculated from 95% confidence interval



18. Coating after peeling

Original roughness, μm	Roughness after pretreatment, μm	Roughness after water treatment, μm
3.2 ± 0.3	3.4 ± 0.4	4 ± 0.6
3.9 ± 0.3	4.6 ± 0.7	4.9 ± 0.8
4.7 ± 0.5	5 ± 0.6	5.5 ± 0.9
6.1 ± 0.7	6.4 ± 0.5	7.2 ± 0.8
8.3 ± 0.5	8.7 ± 0.4	9.4 ± 0.4

IV. Effect of pretreatment and water to the roughness

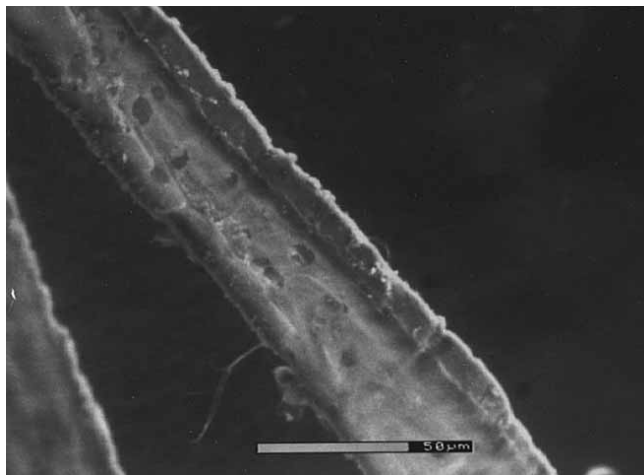
Preparation of individual fibers. We prepared two sets of individual, never dried, kraft, loblolly pine fibers—treated and untreated. Treating meant placing the fibers in an emulsion of a fluorocarbon in ethanol. Untreated fibers were in water. The pretreatment level was the same as in the handsheet experiments. We removed the treated and

untreated fibers from their solutions and placed them on separate glass slides with 20 fibers on each slide. We covered the untreated and the treated fibers with another slide to ensure they would not curl during drying. All fibers underwent an initial drying at room temperature for 24 h followed by curing for 15 min in an oven at 105°C.

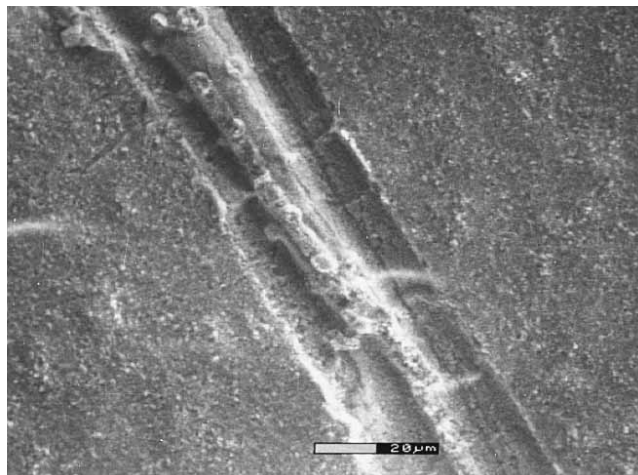
Fiber coating. After pretreatment, we gently laid the fibers on a film of wet pigmented coating—10 pph calcium carbonate in a styrene butadiene latex—applied to a glass slide with one end hanging over the edge as in Fig. 9.

The coating was dried for 1 h at room temperature followed by curing for 15 min. at 105°C. Then we examined all specimens under a light microscope to determine if the fibers were laying on the surface of the coating or if there was a layer of coating covering the fibers. If the coating covered the fiber, we discarded the sample.

Fiber peel. We tested the MI at the microscopic scale level by performing a 90° peel test with an electrobalance. The apparatus allowed attachment of the fiber to the



19. Treated fiber after peeling



20. Coating after peeling

microbalance with a small hook and attachment of the glass slide to the moving platform. A computer recorded force, distance, and time data. After peeling the fiber off the coating, we examined the coating using an SEM to determine the type of failure—adhesive for coating removing from the fiber or cohesive for internal failure in the coating or fiber—and to measure the fiber width.

Base sheet dissolution. After removal of the base sheet, the coating is fragile. For added strength, we placed a piece of packing tape on the coated side of the coated base sheet before removal.

The dissolving agent used for clay coatings was 72% sulfuric acid. We soaked the sample in the acid 1–5 min (the cellulose turned dark), removed the sample from the acid solution, thoroughly washed it with water, and allowed it to dry.

The dissolving agent used for calcium carbonate coatings was cupriethylenediamine (CED). We soaked the sample in CED for 10–30 min. The cellulose turned into a blue gel. Then we removed the sample, washed it thoroughly, and allowed it to dry.

RESULTS

Effect of treatment level

We established a pretreatment level that was sufficiently high to reduce

the chemical interactions without changing the porosity or the roughness of the sheet or the microroughness of the fiber. We determined the efficiency of the pretreatment from measurements of the surface energy, porosity, and roughness before and after treatment. SEM examination also verified that the pretreatment did not change the paper surface morphology. A level of 3% by weight of fluorocarbon polymer on paper was sufficient to meet the criteria.

From sessile drop measurements, we found that the fluorocarbon polymer on paper gave an LW component of 18.2 mJ/m^2 and an AB component of approximately 0 mJ/m^2 using water, formamide, and methylene iodide as liquid probes using the Van Oss approach (30). This indicates a reduction of the surface energy, almost total removal of the AB component, and an assumption by the surface of the paper of the chemical properties of the fluorocarbon polymer. As an example, polytetrafluoroethylene has an LW component of 18.5 mJ/m^2 and an AB component of 0 mJ/m^2 (32).

Effect of coating thickness

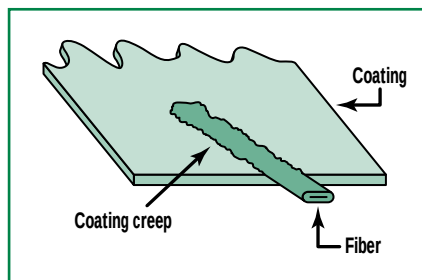
Figure 10 shows the effect of coating weight thickness on MI. As the coating weight increased, the measured peel force decreased with both rough and smooth sheets. Observation of the failed specimens in the SEM such as Fig. 11 indicated

that there were more chunks of coating remaining on the surface at low coating weight. Figure 12 shows no such chunks at higher coating weight. We believe that the nonuniformity in coating weight shown in Fig. 13 affects the stress propagation and therefore the failure mechanism. More failures in the coating could lead to higher peel force values because energy would be expended in breaking the coating chunks off the bulk coating. At a high coating weight of 78 g/m^2 , the coating thickness is essentially uniform as Fig. 14 shows. At higher coating weights, the coating layer has enough integrity, and the failure is less sensitive to thickness variations.

Figure 15 shows that the results of the z-direction tensile strength measurements agreed with the peel force data by showing the same trend of a decrease in tensile strength with increasing coating weight. The same explanation would therefore seem to apply for the z-direction test.

Effect of porosity

As the porosity increased, Table III shows that the measured peel force also increased. This effect is normal because at higher porosities the pores in the sample are larger, more numerous, or both. They therefore would give the coating more opportunity to anchor into the base sheet.



21. Illustration showing the coating creeping up and over the edge of the fiber

Effect of roughness

Water causes the base sheet to become rougher and bulkier from the addition of water (31). We therefore measured the roughness before and after application of the pretreatment. Table IV shows that the sheets roughened by approximately 6% from their original roughness. Since coating contains water that is in contact with the sheet for a time, we performed an experiment to simulate the coating operation. We pressed a wet paper towel on the surface of the treated sheets and left it on the surface to dry. (This experiment is preferable to applying water to the surface because the surface is hydrophobic. Water would not stay on the surface of the base sheet.) Table IV shows that the base sheet roughness increased after the water treatment.

Figure 16 shows that the peel force increased as the roughness of the base sheet increased. Sometimes the peel force was as high as 60% of the delamination energy of the paper base sheet. Even in the coating weight experiments using two different degrees of roughness, the rougher sheet gave higher values than the smooth sheet as Fig. 16 shows. The results of the z-direction test in Fig. 15 agree with the trends of the peel test.

MI at the fiber level

The force required to peel untreated fibers averaged 65 ± 16 N/meter over 12 fibers. The force measured is not only MI but also bending and stretching of the fiber. The SEM observation of Fig. 17 showed that the fibers had a layer of coating attached. Approximately 90% of the fiber surface retained coating. This means that the force measured was almost totally cohesive failure of the coating rather than adhesive failure.

The treated fibers had an average peel force of 27 ± 5 N/meter using 20 fibers. Inspection in the SEM showed that failure was at the coating-to-fiber interface. The fibers had 5–20% of their surface area covered with the coating. Using Fig. 18, we can assume MI on a microscopic scale. Figure 19 shows a clean impression of the fibers in the coating after peeling compared to the undefined pattern in Fig. 20 for the untreated system. Because of the pattern remaining from the fiber where the coating penetrated into the pores and the roughness, we conclude that there was good contact between the coating and the treated fiber.

Most of the coating remaining on the treated fibers appears attached on the edge of the fiber. The explanation is that during placement of the fiber on the surface of the wet coating it sank some into the coating. The coating then covered the edge of the fiber as Fig. 21 shows.

SUMMARY AND CONCLUSION

MI may play an important role in adhesion between coating and paper at both macroscopic and microscopic levels. The contribution of MI is even higher for untreated surfaces because of greater penetration.

As the roughness, porosity, or both of a base sheet increased, the peel force or bond strength increased because more potential sites for MI become available. Sometimes, the peel force represented up to 60% of the delamination strength of the paper.

Both peel force and z-direction bond strengths appear to decrease with increasing coating weight. Data obtained at low coating weights probably incorporate failure processes unrelated to pure MI.

MI also occurs at the microscopic level. Experiments with single fibers showed that up to 20% of the coating to fiber adhesion comes from microscopic MI of the coating into the fiber surface crevices.

Wherever MI occurred either on a microscopic or macroscopic scale, the coating failed in the interlocked areas. This means MI depends on coating cohesion. **TJ**

Dickson is a graduate student, and LePoutre is a professor of chemical engineering and ober chair at the University of Maine, 5737 Jenness Hall, Orono, ME 04469.

The authors thank the industrial sponsors of the Paper Surface Science Program at the University of Maine.

Received for review March 6, 1996.

Accepted Oct. 9, 1996

Presented at the TAPPI 1996 Coating Conference.

KEYWORDS

Adhesion, bibliographies, chemical properties, coatings, paper, paper boards, peel strength, physical properties, surface properties.

LITERATURE CITED

1. Zisman, W.A., *Ind. and Eng. Chem.* 55(10): 19(1963).
2. Fowkes, F. M., *J. of Adhesion* 4: 155(1972).
3. Allen, K.W., *J. of Adhesion* 21: 261(1987).
4. Allen, K.W., *Int. J. of Adhesion and Adhesives* 13(2): 67(1993).
5. Berg, J. C., *Nordic Pulp and Paper Research J.* Vol. 8 (1): 75(1993).
6. Chibowski, E., *J. Adhesion Sci. Tech.* 6(9): 1069(1992).
7. Fawcett, W. R., Fedurco, M., and Kovacova, Z., *Langmuir* 10(7): 2403(1994).
8. Fowkes, F. M., *J. of Physical Chemistry* 66: 382(1962).
9. Fowkes, F. M., *J. of Physical Chemistry* 67: 2538(1963).
10. Fowkes, F. M., *Ind. and Eng. Chem.* 56(12): 40(1964).
11. Fowkes, F. M., *J. of Colloid and Interface Science* 28(3/4): 493(1968).
12. Fowkes, F. M., *J. of Adhesion Sci. Tech.* 1(1): 7(1987).
13. Good, R. J., *J. of Adhesion Sci. and Tech.* 6(12): 1269(1992).
14. Hayes, R. A., Robinson, A. C., and Ralston, J., *Langmuir* 10(7): 2850(1994).
15. Huttinger, K. J., Hohmann-Wien, S., Krekel, G., *J. of Adhesion Sci. and Tech.* 6(3): 317(1992).
16. Israelachvili, J. N. and Ninham, B.W., *J. of Colloid and Interface Science* 58(1): 14(1977).
17. Lee, L-H., *J. of Adhesion Sci. and Tech.* 7(6): 583(1993).
18. Ryley, D. J. and Khoshaim, B. H., *J. of Colloid and Interface Science* 59(): 243(1977).
19. van Oss, C. J., Good, R. J., and Chaudbury, M. K., *J. of Colloid and Interface Science* 111(2): 378(1986).
20. Wu, S., *Polymer Interface and Adhesion*, Marcel Dekker, New York, 1982, pp. 29-60.
21. Yasuda, T. and Okuno, T., *Langmuir* 10(7): 2435(1994).
22. McBain, J.W. and Hopkins, D. G., *J. of Physical Chemistry* 25: 188(1925).
23. Gent, A. N. and Lin, C.W., *J. of Adhesion* 32: 113(1990).
24. Swanson, J. W. and Becher, J. J., *Tappi* 31(5): 198(1948).
25. Gervason, G., Cheradame, H., Ducom, J., et al., *Cellulose Chem. and Tech.* 21: 431(1987).
26. Parpaillon, M., Engstrom, G., Pettersson, I., et al., *J. Appl. Polym. Sci.* 30: 581(1985).
27. LePoutre, P. and Hiraharu, T., *J. Appl. Polym. Sci.* 37: 2077(1989).
28. LePoutre, P. and Rigdahl, M., *J. Mat. Sci.* (24): 2971(1989).
29. Inoue, M. and LePoutre, P., *J. Adhesion Sci. and Tech.* 6(7): 851(1992).
30. van Oss, C. J., Giese, R. F., Li, Z., et al., *J. Adhesion Sci. and Tech.* 6(4): 413(1992).
31. Skowronski, J. and Lepoutre, P., *Tappi J.* 68(11): 98(1985).
32. Owens, D. K. and Wendt, R. C., *J. Appl. Polym. Sci.* (13): 1741(1969).