SURFACE STRUCTURE OF THERMOMECHANICAL PULP FIBERS STUDIED BY ELECTRON MICROSCOPY¹

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ABSTRACT

Pulp samples were obtained from the Bauer pressurized refiner and from the Masonite process. The surface structure of these fibers was studied by light and electron microscopy and related to the defibering temperature.

It was found that refiner pulp produced at 110 C consists mainly of individual fibers and fiber bundles. These units expose mainly cellulosic S_1 microfibrillar structure with intermittent areas of S_2 and display rough surface structure with numerous surface "fibrillation."

The Masonite pulp produced at 254–298 C consists of about 60% fiber bundles and 40% fully separated fibers and fragments of fibers. In contrast to refiner pulp, Masonite pulp exposes smooth surface structure that consists of a continuous and intact envelope of primary wall. In addition, these fibers are coated with a thick layer of amorphous middle lamella substance over part of their surface and possess vertical ridges of middle lamella at the cell corners. The pulp is dark in color and is considerably degraded.

INTRODUCTION

The physical structure and chemical nature of the fiber² surface effect many of the pulp properties important in paper making. These include the drainage properties of pulp; the wet strength of paper; the development of fiber to fiber bond in paper; the retention of fillers, dyes, and additives; and the adsorption of sizing, mineral products, and organic substances over the fiber surface. For this reason it is of considerable interest to have a detailed knowledge of the physical structure and chemical nature of the external fiber surface.

First, it is important to learn about the type of surface that is formed at the time wood is broken down into its basic components into fibers by a particular pulping process. Second, it is necessary to follow, step by step, the physical and chemical changes that take place in the external fiber surface during the various stages of the manufacturing process. Only then is it possible to control these changes and produce the type of surface that leads to optimum paper properties, i.e., maximum bond strength and good printability. The objective of this study was to evaluate in detail the external surfaces of some thermomechanical pulp fibers in terms of the defibering temperature.

MATERIALS AND METHODS

The pulps used in this study included refiner pulp produced at 110 C and Masonite pulp defiberated between 254–298 C.

Refiner pulp

This was made of 30% spruce and 70%balsam fir, and the pulp was produced by a Bauer pressurized refiner at Anglo Paper Products, Ltd. In this process wood chips are fed into the Bauer digester, where the stock is steamed at 10 psig pressure (115 C) for several minutes. Then the chips are transported to the center of the double disc refiner, which rotates at 1,200 rpm. From here the chips proceed towards the periphery of the discs, while being rubbed against one another, as well as against the grooves of the refiner plates. By the time the chips reach the periphery of the discs, they are broken down into the so called "refiner pulp."

Masonite pulp

This pulp was made of jack pine, which was obtained from the Canadian International Paper Company, Gatineau, P. Q.

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² The terms "fibers" and "tracheids" are used interchangeably in this paper.

In the Masonite process, wood chips are treated with saturated steam, which is gradually increased to some 600 psig (254 C) in 30 to 60 sec. Then the steam pressure is rapidly increased from 600 to 1200 psig (298.2 C) and immediately after the superheated chips are blown out of the gun through restricted orifices into atmospheric pressure, where the chips explode into pulp (Atchison et al. 1962).

Light and electron microscopy

Both types of pulp were studied by light and electron microscopy. For light microscopy the fibers were stained with an aqueous solution of Chlorozol Black E (Strelis and Green 1961) and subsequently mounted on slides in Canada balsam. A light microscope was employed to study the overall morphology of pulp constituents, the degree of fiber separation, and the extent of fiber damage.

For electron microscopy, fibers were extracted in a Soxhlet apparatus with alcoholbenzene (1:2) for 5 hr to remove from the fiber surface coatings of deposited resins, waxes, and other extractives. For scanning electron microscopy, the extracted fibers were mounted onto aluminum stubs with double-coated tape. The specimen was then coated with a 200-Å-thick laver of gold-palladium alloy in a high vacuum evaporator, and the edges were painted with silver to provide contact with the aluminum stub. Finally, the specimens were examined in the Cambridge scanning electron microscope (Smith 1959). This technique provided excellent three-dimensional views of the surface morphology and topography of fibers.

The fine structure of the fiber surface was best observed by transmission electron microscopy, utilizing the ultrathin sectioning method and the direct carbon replica technique (Côté, Koran, and Day 1964).

RESULTS

I. Refiner pulp

Light and electron microscopic observations revealed that refiner pulp produced at 110 C consists of fiber bundles, fully separated fibers, and fragments of fibers (Fig. 1A). In many cases, the individual fibers are cut up into tubelike segments ranging from short pieces to the full fiber length. These elements appear to maintain their tubular structure without undergoing a significant amount of collapse.

The fiber fragments that constitute the "fines" portion of the pulp include such units as wall ribbons originating from the S_2 layer, wall lamellae of various shapes and sizes (S_1) , fragments of ray cells, round discs of pit borders, microfibril bundles, and even short pieces of individual microfibrils.

Overall surface structure

Scanning electron microscopic observations revealed various types of modifications on the external surfaces of refiner pulp fibers. These include short and narrow strips running across the fibers, relatively long ribbons of wall layers, thin lamellae, microfibril bundles, and even individual microfibrils. These surface modifications are formed as a result of the rubbing action of fibers against one another and against the grooves of the refiner plates.

The various parts of the fiber surface, such as the pit-free tangential wall, the pitted radial wall, and the ray contact areas, resist surface modifications to various degrees. Of all portions of the fiber wall, the pit-free tangential walls are the least resistant to surface loosening, while the ray contact areas proved to be the most resistant to surface modifications.

Pit-free walls

Electron microscopic observations reveal that in pressurized refining, fiber separation occurs within the S_1 layer of the secondary wall. Consequently, any surface loosening produced by additional refining starts with the gradual delamillation of the S_1 layer, which results in the formation of short cross strips over the fiber surface (Fig. 2A). Many of these strips become further loosened as the refining action progresses and eventually become completely detached from the fiber (Figs. 2A and 3C). At the same time, new cross strips are formed that again may be removed from the fiber sur-



FIG. 1. Scanning electron micrographs of refiner pulp fibers (110 C). A. Low magnification view showing a loose sheet made up of fiber bundles, individual fibers, and fragments of fibers in between. B. Long ribbons of fibrillation (r) originating from S_2 and arching across adjacent fibers in a sheet. C. A thin perforated sheet (PS) of microfibrillar material formed of surface loosenings that arch across the gap between adjacent fibers. D. Ray contact area of a tracheid exposing ray middle lamella (RML) and ray-tracheid pitting.

face. In many instances, this process continues until the entire S_1 layer is peeled away from portions of a fiber, as a result exposing the S_2 layer of the secondary wall.

Representative examples of S_2 structure are seen in Figs. 2B, 2C, and 2D. Often portions of the S_2 layer are also peeled away, which results in the formation of long ribbons (Figs. 1B, 2C, and 2D). In most

LIST OF ILLUSTRATIONS

Note that in all micrographs:

 $V = vertical direction; S_1 = outer \\ML = middle lamella; S_2 = middle \\P = primary wall; S_3 = inner \\ary wall$

Magnification is in diameter; Scale is in microns;

^oC = refining temperature, or the prevailing temperature in the Masonite gun.



FIG. 2. Scanning electron micrographs of refiner pulp fibers (110 C). A. A tracheid exposing S_1 surface with pitting, surface fibrillation (F) and cross strip attached (CS_1) to the fiber and detached (CS_2) from the surface. B. A tracheid exposing S_2 surface in the tangential wall (T) and almost undisturbed intertracheid pitting in the radial wall (R). C. A tracheid exposing S_2 structure that started to peel away in forms of thin ribbons (r). Note also that the pit border remains intact at X, becomes partially removed at Y, and completely detached at Z. D. A tracheid exposing S_2 surface and a thin ring of the residual pit border (PB) after the S_1 layer has been peeled away completely. Note the long ribbon (r), which originates from the S_2 layer.

cases these remain attached to the fiber surface and produce what is called "fibrillation" in the literature.

As refining progresses, many of these long strips become completely detached from the fiber surface and scattered among the fibers throughout the sheet. Figure 1B is an example of such strips arching across fibers and thus providing additional bond strength to paper. In other instances, wall lamellae and strips form sheetlike networks between fibers that possess perforations of various sizes and shapes (Fig. 1C). These networks partially bridge the relatively



FIG. 3. Direct carbon replicas of refiner pulp (110 C) fibers. A. Pitted radial walls exposing S_1 surface structure, the pit membranes, tori and the inner pit border. B. Ray contact area displaying secondary wall (S), primary wall (P), and ray middle lamella structure (*RML*). C. Tracheid surface exposing S_1 surface, amorphous *ML* region and a cross strip (*CS*₂) detached from the tracheid. D. Secondary wall (S₁) structure with surface fibrillation (F).

large openings between fibers in a sheet, as a result producing paper with smoother surface, greater bond strength, and generally improved properties.

Pitted walls

A transmission electron micrograph of a pitted radial wall is shown in Fig. 3A, exposing S_1 surface structure around the pits, and in the pit region the radial strands of the pit membrane with the torus in the center and the circularly oriented micro-fibrillar structure on the inner surfaces of pit borders.

It was observed that the pitted walls of the radial faces of tracheids react differently from the nonpitted wall during the abrasive action of refining. Figure 2B shows that the S_1 layer is almost completely removed from the pit-free tangential wall, while the radial wall containing the bordered pits remains almost completely intact. This and other observations suggest that the circularly oriented microfibrils in the pit borders, and the general deviation of the microfibrils around the pits seem to reinforce the pitted wall.

However, if the refining action continues long enough, the pit borders become partially detached (Fig. 2C and 2D) or completely removed (Fig. 2C) from the fiber wall along with the S_1 layer of the secondary wall. In this process, the pit borders become separated from the S_1 layer and appear in the "fines" fraction of the pulp as thin circular units with the apertures in their centers.

Ray contact area

Figure 1D is an example of a ray contact area exposing horizontal ridges of ray middle lamellae (RML) and numerous ray tracheid pitting. A transmission electron micrograph of a similar ray crossing area is seen in Fig. 3B. This clearly shows the two horizontal ridges of middle lamella (RML) running across the tracheid. These ridges possess amorphous lignin structure, while the ray wall in between exposes secondary wall (S) and primary wall (P)structure. Because of the presence of the horizontal ridges of RML regions, and the numerous ray-tracheid pitting, the ray contact areas of fibers expose a topographically different surface structure, with higher lignin content, than other parts of the fiber surface. This is the reason why the ray contact areas resist surface modifications to a greater extent than other parts of the fiber surface, thus resulting in a relatively undisturbed surface structure.

Microfibrillar surface

Direct carbon replicas produced of refiner pulp fibers (110 C) revealed that the fibers expose predominately the microfibrillar structure of the S_1 layer. A representative example is seen in Fig. 3C, where the microfibrillar orientation is nearly perpendicular to the tracheid axis. It is further seen that a thin lamella of cross strip has been torn out of the fiber surface, as a result exposing another lamella of the S_1 layer that is nearer to the S_2 layer. This type of delamillation is commonly observed on refiner pulp fibers (110 C) [see also Fig. 2A].

Figure 3D is an example of S_1 structure showing surface fibrillation. Note that individual microfibrils are pulled out of the secondary wall, which extend away from the fiber surface in suspension and dry onto the fiber surface in paper.

In the advanced stages of refining, all of the S_1 layer may be peeled away from portions of the fiber wall, as a result exposing microfibrillar structure of the S_2 layer, which is nearly parallel with the tracheid axis (Fig. 2D). Primary wall surface is rarely observed on refiner pulp fibers (110 C). When present, it occurs mostly in the ray contact areas, as seen in Fig. 6B, or in occasional areas. Similarly, amorphous *ML* structure occurs only at the vertical ridges that corresponds to the cell corners (Fig. 3A) and at the ray crossings (Fig. 3B).

II. Masonite pulp

This pulp is dark in color and the fibers appear to be highly degraded. Degradation can be traced back to the treatments of stock in the manufacturing process. In the Mason gun, the stock is subjected to high



FIG. 4. Scanning electron micrographs of Masonite pulp fibers (254–298 C). A. Overall view of Masonite pulp consisting of fiber bundles and individual fibers, both occurring broken and intact. B. A fiber bundle consisting of 3 fibers, exposing smooth and undisturbed surface structure with axial shrinkage folds. C. Fibers exposing smooth surface structure with axial shrinkage folds and vertical ridges of middle lamella (ML). D. A fiber exposing horizontal ridges of ray middle lamella (RML).

steam pressure, reaching a maximum of 1200 psig in the final stage. At this high pressure and temperature (298 C), acetic and formic acids are released from the fibers, which lower the pH of the stock to 3.9. This relatively strong acid medium causes a rapid hydrolysis in the stock. The hemicellulose fraction of wood is affected to the greatest degree, part of which is reduced to water-soluble hexose and pen-

tose, which are later separated from the fiber by washing. Some degree of depolymerization of the lignin also occurs; its extent depends on the degree of hydrolysis (Atchison et al. 1962).

Microscopic examinations revealed that the pulp consists of: 1) fiber bundles, 2) fully separated fibers, and 3) fragments of fibers. It was estimated that about 60% of Masonite pulp consists of fiber bundles and



FIG. 5. Masonite pulp fibers. A. A fiber bundle consisting of a radial row of tracheids held together by rays. Note that the separation of the bundle in the middle has been stopped by the rays. B. Ultrathin cross sections of two fibers showing the site of fiber separation at the interface of ML and P. Fiber II contains the entire layer of the middle lamella, while fiber I exposes the P wall. Note also the vertical ridge of middle lamella (VRML) at the cell corner. C. Enlarged view of Fig. 5B.

the remaining 40% is made up partly of individual fibers and partly of fiber fragments.

Fiber bundles are pulp units consisting of two or more fibers that remain joined together after pulping. Typical examples of fiber bundles are seen in Figs. 4A and 5A. Such bundles may reach 20 mm in length and may contain up to 25 fibers. In most instances, these bundles are broken at both ends (Figs. 4A and 5A). Most fiber bundles occur in the form of radial rows of fibers that appear to be held together by horizontal rows of ray cells. An example of this is seen in Fig. 5A, where there is a separation in the middle of the bundle parallel with the fiber axis, but further splitting is stopped at the ray crossings (B). This micrograph, along with other observations, suggest that rays aid the breakdown of



FIG. 6. Masonite pulp fibers. A. Cross-sectional view of a portion of fiber showing a degraded fiber wall with a thick layer of ML on the outside including two vertical ridges of ML (VRML). B. Transmission electron micrograph of jack pine tracheid surface, an enlarged area like E in Fig. 4B, showing a smooth surface structure with numerous axial shrinkage folds. C. Enlarged view of an area like A in Fig. 6B showing the random microfibrillar structure of P embedded in an amorphous matrix of substances. D. A similar surface as in Fig. 6C, after a 5-hr NaClO₂ treatment. Note that the random microfibrillar structure of the P wall becomes clearly evident.

wood chips into radial rows of fiber bundles along the radial plane, but resist the separation of these bundles into individual fibers by acting as reinforcing elements over the surfaces of fiber bundles (Fig. 5A).

The fully separated fibers appear as relatively straight and partially collapsed elements (Fig. 4A). Many are broken at their ends, or into shorter pieces, but on the whole these fibers seem to maintain their tubular structure.

The smaller pieces, referred to as "fines," include a variety of fiber units, including wall fragments of variable shapes and sizes, ray cells, pit borders, microfibril bundles, and even short pieces of individual fibers.

Surface structure of masonite pulp fibers

Figures 4A, 4B, 4C, and 4D are typical scanning electron micrographs of Masonite pulp fibers. It is apparent that these fibers expose relatively smooth, coherent, and undisturbed surface structure, in contrast to the surfaces of refiner pulp fibers (110 C; Figs. 1, 2, and 3). Cross-sectional views of Masonite pulp fibers are seen in Figures 5B, 5C, and 6A. These electron micrographs and similar observations reveal that separation of Masonite fibers occurs predominately in the region of the interface of the primary wall and ML. Similar results were observed by Wardrop, Dadswell, and Davies 1961, using light microscopy. They observed that high temperature treatment results in fiber separation within the middle lamella region.

Interface separation (P and ML) is seen in Figs. 5B and 5C. Fiber II contains a thick layer of ML, while fiber I exposes the primary wall. This was confirmed by direct carbon replicas prepared of similar fibers. A representative example is seen in Fig. 6C, which reveals the random microfibrillar structure of the primary wall encrusted with an abundant supply of amorphous ML substance. Although, in many areas, primary wall structure can be identified, other areas of the fiber surface are coated and encrusted with a thick layer of amorphous ML substance.

A 5-hr NaClO₂ treatment of a fiber surface, such as seen in Fig. 6C, results in a surface observed in Fig. 6D. It is apparent that during this treatment, the amorphous surface layer is dissolved away and the random microfibrillar structure of the primary wall becomes evident over the fiber surface (Fig. 6D). The fact that NaClO₂ is a lignin solvent and that a treatment with this solution removes the amorphous encrusting layer confirms the finding that Masonite pulp fiber surface is lignin-rich in nature. Note also that the microfibril structure of Figs. 6B, 6C, and 6D is not disturbed in any way, which again confirms an interface separation between P and ML in the Masonite process.

Shrinkage folds

It has been observed that the surfaces of Masonite fibers exhibit numerous shrinkage folds that are densely spaced and uniformly distributed over the entire fiber surface. Representative examples are shown in Figs. 4B, 4C, and 6B. The origin of these folds can be traced back to the excessive shrinkage of fibers as a result of the loss of hemicelluloses from the fiber wall. This in turn is indicated by the yield, which was reported to be about 70% in the Masonite process.

It was observed that the larger percentage of the shrinkage folds appear to be parallel with the microfibrillar orientation in the S_2 layer (Figs. 4B, 4C, and 6B). This would suggest that these shrinkage folds are caused by a greater shrinkage in the S_2 layer, than in the outer layers (S_1 and P) in which the shrinkage folds occur. This in turn would suggest that during hydrolysis the greater part of hemicelluloses are lost from the S_2 layer.

Excessive weight loss from Masonite pulp (S_2) is also indicated by the development of numerous splits in the fiber wall, such as seen on the cross sections of Figs. 5B, 5C, and 6A. These splits indicate considerable weakening of the fiber wall. It is important to note that such splits do not occur in the untreated fiber wall, which eliminates the possibility of these being artifacts produced during ultrathin sectioning.

Axial ridges of middle lamella

These are characteristic features of Masonite pulp fibers. Figure 4C exhibits representative examples of vertical ridges on the surfaces of Masonite fibers. These run parallel with the fiber axis and originate from the ML substance at the cell corners.

Cross-sectional views of vertical ridges of ML are seen in Figs. 5B and 6A. Note that the ML substance possesses a higher electron density than the fiber wall (Fig. 6A). There are several such ridges on a fiber surface, each corresponding to a cell corner. These ridges possess variable heights, widths, and forms, but in all cases consist

chiefly of lignin. This is confirmed by the fact that these ridges are dissolved away during the NaClO₂ treatment.

Horizontal ridges of middle lamella

The radial faces of fibers expose numerous horizontal ridges of ML at the ray crossings. A representative example is seen in Fig. 4D. These ridges correspond to the ML between adjacent ray cells (RML), and are similar to the vertical ridges of MLbetween adjacent tracheids. After NaClO₂ treatment, the RML ridges disappear from the fiber surface like the VRML, which indicates that these too consist chiefly of lignin.

DISCUSSION

It is known that heat has a plasticizing effect on wood, which becomes more plastic with increasing temperature, especially in the presence of moisture. The wood constituents that are most affected are the hemicellulose and lignin. Goring (1963) reported that the hemicelluloses begin to soften already at 50 to 60 C, and the lignin transition occurs at 90 to 100 C, in contrast to cellulose, which softens only around 231 to 253 C. Because the hemicellulose and lignin components of wood, which bind fibers together in the wood, and the microfibrils in the cell wall soften much before the cellulose skeleton of the fiber walls, it is easier to defiber wood at higher temperatures than under normal conditions. The higher the temperature, the more plastic lignin and hemicellulose become; therefore, the easier it is to separate fibers from one another, rather than breaking the fibers into pieces across their axes—that is, across the cellulosic microfibrils.

Several industrial processes, such as the Masonite, Boehm (1944) and the Asplund (1953) processes, operate at elevated temperatures in order to improve fiber separation and reduce energy consumption through the plasticization effect of heat on wood. More recently, the same principle has led to the development of the pressurized refiner, which at the present time operates on commercial scale at 110 C.

Refiner pulp

The pulp consists of fiber bundles, individual fibers, and a high percentage of fiber fragments in the form of ribbons, lamellae, and microfibril bundles. Transmission electron microscopy reveals that these fibers are enveloped by the S_1 layer of the secondary wall on the greater part of the fiber surface. However, in the advanced stages of refining, the entire S_1 layer may be removed from portions of the fiber, as a result exposing the S_2 layer of the secondary wall. In either case, these fibers expose the parallel microfibrillar structure of the secondary wall. Therefore, this type of fiber surface is cellulosic in nature.

In addition, refiner pulp fibers (110 C) contain numerous extensions in the form of cross strips partially detached from the S_1 layer and long ribbons extending away from the S_2 layer. These extensions are called "fibrillation" in the literature and are considered to be important elements in improving the bond strength of paper. Furthermore, refiner pulp (110 C) possesses the type of fiber surface that can be further fibrillated in second pass refining in order to increase the bond strength of paper. Commercial practice has proven that pressurized refiner pulp (110 C) is suitable for the production of newsprint without the addition of chemical pulp.

Masonite pulp

These fibers appear relatively stiff and little collapsed; and the pulp contains a high percentage (60%) of fiber bundles. Electron microscopic observations revealed that Masonite pulp fibers produced between 254–298 C possess a very smooth surface structure with practically no surface modifications, such as the type observed on refiner pulp (110 C). The Masonite fibers are enveloped by a continuous network of primary wall, which is heavily encrusted by lignin and in many areas covered by thick layers of ML substance. Therefore, this is a lignin-rich surface, possessing no surface fibrillation. In most respects, this is similar to the tracheid surfaces that were produced in tensile failure at 250 C (Koran 1967, 1968).

In addition, Masonite fiber is highly degraded. The degradation is indicated by: 1) the dark color of fiber, 2) by the considerable amount of weight loss (70% yield), and 3) by the weakening of the fiber wall as indicated by the development of checks in the ultrathin sections of fibers (Figs. 5B, 5C, and 6A). The hygroscopicity of fibers is also affected, which in turn leads to the reduction of fiber swelling.

It has been found that further refining of Masonite pulp produces little change in the surface structure of Masonite pulp fibers. This is expected because the Masonite fibers are enveloped by an intact and continuous layer of primary wall that possess random microfibrillar structure. This in turn is heavily encrusted and in many cases coated with a thick layer of amorphous ML substance. Such a surface would resist surface loosening as a result of mechanical action. In further refining, instead of producing external fibrillation, the fibers tend to be cut up into shorter pieces, which results in an overall decrease of average fiber length.

Because of its overall characteristics—1) dark color, 2) degradation in the fiber wall, and 3) smooth and lignin-rich surface with no surface fibrillation, 4) difficulty involved in further refining—Masonite pulp is not suitable for paper making.

CONCLUSIONS

The above results suggest that in thermomechanical pulping the physiochemical structure of the fiber surface depends mainly on the temperature of defibering. An increase in defibering temperature from 110 C to 254-298 C results in the change of fiber surface from a rough, "fibrillated" and cellulosic S_1 surface to a smooth fiber surface enveloped by a continuous layer of primary wall, which in addition is encrusted and coated by a layer of amorphous lignin. Such changes in the surface structure of fibers affect many of the surface properties of fibers, such as beatability, bonding potential in paper, surface absorption, etc., and determine the final utilization of the pulp. Because of the above properties, refiner pulp produced at 110 C is suitable for the

production of newsprint, while Masonite pulp produced at 254–298 C is suitable only for hardboard production.

Finally, it is interesting to note that the surfaces of refiner pulp fibers (110 C) are similar to the tracheid surfaces exposed in tensile failure at 100 C. Similarly, the surfaces of Masonite fibers (254-298 C) are almost identical to the tracheid surfaces that were exposed in tensile failure at 250 C (Koran 1967, 1968). These findings suggest that the physical structure and chemical nature of the exposed fiber surface are governed by the temperature of the wood at the time of fiber separation, rather than by the type of manufacturing process.

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