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The Effect of Fiber Length and Degree of Fibrillation on Water Removal by Wet Pressing

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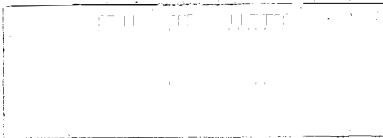
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The Effect of Fiber Length and Degree of Fibrillation
on
Water Removal by Wet Pressing |

by
John C. Walkush

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Abstract

The amount of water in paper determines indirectly the strength of it by dictating what type of bonds are formed between fibers. The less water in paper the stronger it is. Wet pressing is considered in detail as one method of water removal to determine what factors affect the amount of water removal since this would indirectly affect the development of paper strength. Specifically the effect of fiber length and the degree of fibrillation was studied. It was found that as fiber length decreases the amount of water that can be removed decreases and that as the degree of fibrillation increases the extent of water removal decreases in a linear fashion.

Objective

The objective of this investigation is to determine the effect of fibrillation and fiber length on the extent of water removal by wet pressing and to correlate paper strength with the percentage of water that can be removed by pressing.

Historical Review

The strength of a sheet of paper is dependent on the strength and number of interfiber bonds formed between the individual fibers of the mat. There are many factors which directly affect the bonding and determine the overall strength. According to Campbell the three main factors are (a) the surfaces that are to be bonded, (b) the type of forces holding these surfaces together, and (c) the means used to bring these surfaces together.¹

Surfaces

A fiber used in papermaking is made up mainly of cellulose in the form of fibrils. Frey-Wyssling define them as being small cellulose chains containing about 100 cellulose molecules in cross section with a length of about 100 angstrom units.¹ The cellulose molecules are arranged side by side in a crystalline type lattice.

Another theory suggested is that of Colvin who has shown that a fibril can be grown to any length by the addition of a cellulose molecule to the end of a growing chain. This has been accomplished using glucose, enzymes, and ATP (Adenosine triphosphate). It has been concluded from these and other studies that the basic structural element in a fiber is the fibril.

These fibrils are held together by three different types of bonds, i.e., the primary covalent bond, the hydrogen bond and van der Waal's forces.² The primary covalent bond is the strongest of the three, about 60 K cal/mole, which hold the individual cellulose molecules together in a chain. They are formed by the sharing of an electron by two atoms.³ The bonding distance between the two atoms is about 1-2 angstrom units.

The hydrogen bond is formed by the sharing of a proton by two electronegative atoms like oxygen.³ The bonding energy of about 4.5 K cal/ mole is considerably less than covalent bond energy and the bonding distance, 2.5-3.5 angstrom units, is longer. A cellulose molecule contains hydroxyl groups that are able to bond in this manner. The hydrogen bonds hold the cellulose chains in the same relative position and contribute a considerable amount of strength to the fiber by virtue of their large numbers.

The van der Waal's forces are the weakest bonding forces and are due to the electrostatic forces developed by the moving atoms in a molecule.³ They have a bonding energy of only 1-2 K cal/mole and they act over a bonding distance of 3-5 angstrom units. They contribute little to the overall strength of the fiber, but their presence should not be overlooked as a source of strength in it.

The basic structural element of a fiber has been defined as the fibril. A fiber can then be defined as a large aggregate of fibrils in a specific pattern held together by hydrogen bonds and van der Waal's forces.

The total area of fibrils using Frey-Wyssling data would be 400-500 m²/g cellulose.¹ Purves and associates have found the total surface area between 300-400 m²/g cellulose.¹ These figures are for the total area of all fibrils including those in the fiber wall so they are of little value in practical paper-making. Mechanical and chemical action is used to develop and to free some of this area for bonding to increase strength.

Chemical action in the various pulping methods destroys the primary wall and removes extraneous material from the fiber. The primary wall is made up of a tangled mass of fibrils that cannot easily be brushed from the parent fiber. It acts as a cellophane cover over the fiber which makes it difficult to free the fibrils from the inner wall where they are easily removed by mechanical action.

Mechanical action in the form of beating or refining loosens the closely packed fibrils, freeing them from the main fiber so that they can bond to other fibers. The internal fibrils are loosened so that water can penetrate into the fiber wall causing it to swell. It should be noted here that mechanical action does not increase the overall fibril surface area of 400 m²/g cellulose. This has been proven by the studies of Russell and Campbell.²

The specific surface of a fiber has been shown by Robertson and Ingmanson to be about 0.8 m²/g cellulose by the permeability method.⁴ On beating the specific surface area is increased substantially as shown in one study with an increase of about 80%. It is the belief of Campbell that the increase in area is due to internal swelling of the fiber and not the fibrillation of it since fibrils, on drying, rebond to the parent fiber.

Thus far only the overall available surfaces to be bonded have been considered. In particular there are three general ways in which fibers can bond. There are: (1) the primary wall of one to the primary wall of another, (2) the primary wall of one to the secondary wall of another and (3) the secondary wall of one to the secondary wall of another.⁵ The latter one would form the stronger bonds because of the fibril orientation.

Another area of bonding, especially found in refined pulp, is that between the lumen area in the internal portion of the fiber when it is split axially. If this area were included as specific surface available for bonding, the overall area would be increased to about 1.5 m²/g cellulose instead of only 0.8 m²/g cellulose.¹

The orientation of fibers in the mat affect a great deal the bonding area between fibers. One should realize that the actual bonding area of fibers arranged side by side would be much greater than that due to random orientation of the fibers. For two fibers arranged side by side the available bonding area has been estimated to be 100 sq. microns.⁵

Many methods have been used to determine the actual bonded area in paper. The basic idea of most methods has been one of adsorption of a molecule on the unbonded surface area. Some of these methods include the geometric method, optical method, silvering method, chemical adsorption, and liquid permeability methods.⁶

Much work has been done in trying to correlate the effect of bonded area on paper properties since it is believed that the greater the area, the more the interaction between surface

forces, and the greater the paper strength. Swanson and Steber have been able to correlate tensile strength with the bonded area of the paper using nitrogen gas adsorption.⁶

Ingmanson and Thode using a nitrogen gas adsorption method of determining bonded area have found that the total dry fiber area available for fiber bonding which is effective in developing paper strength remains constant with refining time and is unaffected by production of fines or the degree of fibrillation.⁷ In essence this would be true because as surface tension increases on evaporation of free water the fibrils that had been brushed off are forced back on to the parent fiber. There they rebond to it keeping the overall surface area constant.

Van Der Akker has suggested another explanation of how beating increases the bonding strength independent of surface area.⁵ He presents a theory based on two different types of bonding forces, an adhesive and a cohesive force. The adhesive force is due to the actual chemical bonding at the intersection of two fibril surfaces. The cohesive force is due to the mechanical entanglement of the fibrils while free water is present. Then as the water is removed the entanglement is left intact in a woven fashion of high strength.

He suggests that the cohesive bond is the predominate force which determines the overall strength of the paper as developed by beating. This fact has been proven by determining the relative thickness of the bonds in paper. They are relatively thick which is indicative of the cohesive bond.

Two theories of what actually determines the strength of paper prepared from beaten stock have been presented. One,

a chemical view in which strength is dependent on area, and the other a mechanical view in which strength is dependent on the type of surface. The exact reason for increased strength need not be resolved for this study, suffice it to say the actual mechanism is probably a complicated combination of the two. It would seem that the increased area would allow more bonds to be formed, increasing the overall strength.

Bonding

A quick coverage of the surfaces to be bonded has been presented with passing mention of bonding forces and energies but with no mention of the exact nature of these interfiber bonds. Thus far all of the experimented work and the theoretical studies have led to the same conclusion that the hydrogen bond is the main source of interfiber strength. The hydrogen bond as was mentioned before is a bond formed by the sharing of a proton by two electronegative atoms like oxygen with a bonding energy of 4.5 K cal/mole.³ The average bond length is between 2.5-3.5 angstrom units.

Cellulose with its many hydroxyl groups is in a good position to under go extensive hydrogen bonding. It is known from spectroscopic work that in papermaking fibers almost all of the hydroxyls are involved in hydrogen bridges. However, dueteration experiments by Corte, Schaschek, and Broens showed that only about 0.5-2.0 per cent of all hydroxyls present were really involved in interfiber bonding.⁵ If these results are true, it would mean that the majority of

hydroxyls are really involved in interfibril bonding within a fiber and not with interfiber bonding which determines the paper strength.

The overall strength of paper is not due to the individual strength of the hydrogen bond, but it is due to the overall strength produced by many bonds taken together. The more bonds that are developed the stronger is the paper. On paper formed on a moving wire, the majority of bonds are formed in the xy plane with relatively few found in the y plane. Those few are due only to chance contact between adjacent fibers. The greater strength of paper in the machine direction can be explained by the shrinkage which occurs in the xy plane across the web. As the paper shrinks the adjacent fibers are forced together increasing the bonding.

The importance of water in the formation of hydrogen bonds has long been known. Water being a polar compound penetrates the fibers and replaces the cellulose to cellulose bonds with cellulose to water bonds. The opposite happens when water is evaporated or pressed from the fiber at which time the cellulose to water bonds are replaced by the cellulose to cellulose bonds.

The strength of paper has been shown to be due to hydrogen bonds, but in order for these to form, it is necessary to have the bondable areas within about 5 angstrom units and the right amount of free water is present. The next section presents the various methods used to obtain optimum bonding conditions.

Methods to Obtain Bonding

Fibers are made more susceptible to bonding by increasing the probability of two fibers or fibrils coming into a mutual bonding distance of 5 angstrom units. This is accomplished by delignification, refining, wet pressing, and drying.⁴

Delignification at both the pulping and bleaching operations improves the probability of cellulose bonding by removing lignin and other extraneous matter which might interfere in bonding. Lignin by nature coats and impregnates the fibers with a plastic, water-repellent covering. Most of the pulping processes dissolve some of it away so that water can easily penetrate the fiber to form cellulose to cellulose bonds on evaporation.

The pulping processes do one other important service and that is the removal of the primary wall. This is especially true of the sulphite process. As was mentioned before this wall is a tangled group of fibrils that do not bond well because they cannot be brushed easily from the fiber to act as cohesive bonding agents. In general then, one could say that the more primary wall that can be removed by cooking, the higher will be the probability of two fibers bonding.

Another delignification process that improves bonding is bleaching. In this process lignin and other extraneous matter not removed in the pulping operation is removed by oxidation or reduction. When these materials are removed the cellulose portion of the fibers are able to come into closer contact. Water is more easily able to penetrate the fiber wall and swell it which increases surface area. This swelling action

as stated before by Campbell is most important in interfiber bonding.

Marton has shown that as lignin content goes down in high yield pulps the degree of swelling increases.⁸ This would mean that lignin and extraneous matter hinders swelling which decreases the probability of fibers bonding.

In general, from this discussion one could conclude that the more lignin and extraneous matter that can be removed from a fiber the more liable it is to bond because water can penetrate the wall and cause swelling. Swelling increases bonding surface which increases the probability that two fibers will come within 5 angstrom units to bond.

Another process which increases the bonding probability of fibers is refining. Here a purely mechanical action brushes the fibrils from the fiber and loosens the internal fibrils so that hydration can occur. The latter two results together increase the overall surface area which as in the case of delignification increases the probability of bonding surfaces being within 5 angstrom units.

Another means used to bring fibers and fibrils into a bonding region is by removing the free water through evaporation and drying. This is an intricate mechanism thoroughly studied by many men. In general the main idea on which the mechanism is based is that as water is removed from a system it tends to shrink. This shrinkage in paper pulls the fibers closer together where they might bond more easily. It should be mentioned here that the cellulose itself does not shrink since it is crystalline, but it is the overall fiber mass that is pulled together.

The exact force that shrinks the paper is the tension due to water leaving the small interstices between fibers. In molecular form there is intermolecular bonding in free water due to hydrogen bonding and van der Waal's forces. These forces hold the water to the fibers as bound water. Now as this bound water is forced from its position either by heat or a difference in vapor pressure, it being bonded to two cellulose chains, pulls on both of them. As it does this it pulls them both into the mutual bonding region of 5 angstrom units where bonding can take place.

This particular mechanism is in operation when the fibrils or cellulose chains are free to move relative to one another small distances with less force than that from the surface tension. This method is quite important in determining overall paper strength since it is the only method known today which can increase strength after the press section irregardless of surface treatment.

The final means of increasing contact area is by wet pressing. In essence this method operates by removing the water and forcing the fibers together by application of an external force to the surface of the mat.

When an external force is applied to paper, some of it is transmitted to the free water and some to the compression of the cellulose fibers. The force applied to the water pushes it from the system and, as this is happening, the fibers are being forced together into the bonding region. However, when the force is released, the fibers would probably leave the bonding region because either there is too much free water present or because the fibers are too elastic.⁴ If there is

too much free water the fibrils will tend to "float back" away from another in it. If the fibers are too elastic they will "spring" back to the position they occupied before pressing, out of the bonding region.

It can be concluded from this then that the more flexible the fiber the more bonds will be formed and the stronger will be the paper. It can also be concluded that the less free water present after pressing the more bonds will be formed and the stronger will be the paper.

From the latter conclusion it could be theorized that as the amount of water being removed is increasing, the overall paper strength would be increasing also. Going one step further then the factors which determine the amount of water that could be pressed from a sheet would indirectly determine the overall paper strength.

It will be necessary to go into the theory of wet pressing. to determine what these factors are.^{9, 10} Campbell in 1933 theorized that the rate of flow through a porous mat was directly proportional to the area of the mass and to the applied pressure. It is inversly proportional to viscosity of the liquid and to the depth of the mass. This could be represented by the following equation.

$$\frac{Q}{A} = \frac{P}{RW\eta} \quad (1)$$

where Q = rate of flow
A = area of mat
P = pressure applied
R = specific resistance
 η = viscosity of liquid
W = basis wt.

Equation (1) is valid if the mass is compressed uniformly and if all of the pressure applied is effective as hydraulic pressure on the water and not in compressing the fibers.⁹

However, in paper due to the hollow nature of the fiber much of the applied pressure is used to crush and compact the individual fibers. In order to compensate for this it is necessary to add an empirical constant the equation (1) and square R and W so that

$$\frac{Q}{W} = \frac{KP}{R^2 W^2} \eta \quad (2)$$

Since equation (2) gives the rate of flow through the mass the amount of water that could be removed by pressing could be determined by multiplying by (t) time to give.

$$M = \text{Mass of water} = \frac{KPtA}{R^2 W^2} \eta \quad (3)$$

Now all of these terms in equation (3) are real and can be measured exactly except the empirical value for specific resistance R. Since one term is empirical the whole equation is, but still it is useful in giving some idea of what determines the mass of water that can be removed from paper.

As the specific resistance R increases the amount of water that can be removed decreases and if R decreases the amount of water that can be removed increases. No information was found in the literature survey indicating some attempt to determine exactly what factors affect R.

It can be hypothesized that the specific resistance R to water removal by wet pressing is dependent on the degree of fibrillation, of swelling, of delignification, the amount of fines and the fiber geometry.

As the fibers are fibrillated the macro-and microfibrils will intermesh to form a compact porous mat. Therefore, as the number of these are increased by refining the more resistant would be the pad to water flow because of the smaller capillaries and higher density.

As the fiber geometry or shape is changed by cutting, it would seem that the small pieces would fill in the large openings between the large fibers. This would increase the density of the pad and make the capillaries smaller so it would be more resistant to water flow. The effect of increased fines could probably be explained in like manner.

When a fiber swells in an aqueous solvent, the overall surface area increases many times. Now as this area increases, it would seem that the adjacent fibers when formed in a mat would have less area between them. As this area decreases, the resistance to flow would increase because of the smaller capillaries present for the water to flow through.

As a fiber becomes more flexible it is more easily forced into the large areas between adjacent fibers. As the number and size or volume of these open areas are decreased, the resistance would be increased because of the smaller capillaries again.

The degree of delignification of a fiber determines for one thing how flexible it is so the effect on resistance could be explained as above. The more lignin that is removed the more flexible would the fiber be so its resistance would be greater.

This has been a rather broad survey of the obvious factors which determine the specific resistance of a pulp pad to water removal by wet pressing. Some of these are interrelated with one another making it difficult to determine the exact effect of each on R. It would seem then if those factors which could be separated were studied a clearer picture of water removal by wet pressing would be obtained and it might be beneficial in determining what affects the overall strength of paper.

An attempt has been made in this study to separate two of these and determine their specific effect on resistance. They are fiber length and the degree of fibrillation.

Experimental Procedure

Softwood bleached kraft pulp was subjected to two different operations of cutting and fibrillation. The cutting was carried out on wet handsheets of ca. 25 g. by slicing them into 1/8 inch strips using an ordinary paper cutter. The strips were repulped, handsheets reformed, and the cutting repeated 0, 5, and 10 times respectively. The exact fiber length was determined by measuring about 150 fibers using a fiber slide projector and a map measurer.

Fibrillation was developed using a lab ball mill containing 25 g. of pulp at 0.75% consistency and 150 - 3/4 inch porcelain cylinders. The different degrees of fibrillation were obtained by varying the time intervals 0, 1, 2, and 4 hours, of rotation. The amount of fibrillation was determined

by freeness measurements.

Handsheets were then made from each pulp on the Noble and Wood sheet mold. The sheets were drained for two minutes and the moisture content determined. The handsheets were then pressed at 100 psi. pressure three times for five minutes changing blotters after each pressing. This would give a moisture content that would be in equilibrium with the pulp. It was assumed that this moisture content would be a direct indication of water removal at the higher levels encountered in actual papermaking.

The actual amount of water that could be removed by wet pressing was determined by calculating the per cent difference in moisture content after drainage and wet pressing.

Tensile strength of the handsheets was determined according to Tappi standard T-404 because it is indicative of overall interfiber bonding. The breaking length was then calculated and correlated against the amount of water removed.

All of the variables in equation (3) were kept constant to determine the effect of R on M.

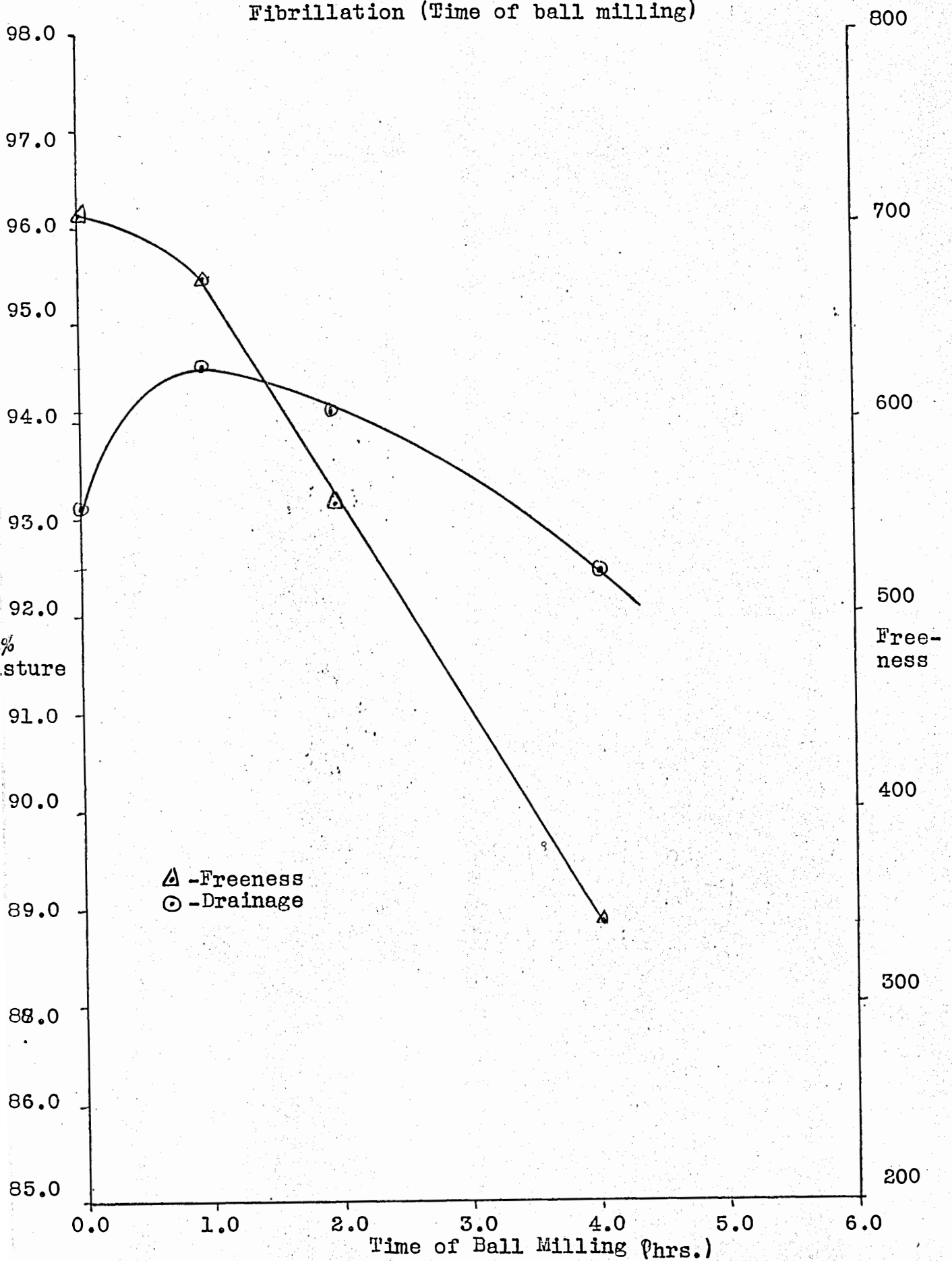
Data

Fiber Length mm.	FIBER LENGTH					Breaking Length Meters
	Freeness cc.	% Moisture Drainage	% Moisture Pressing	% Water Removed	Tensile Kg/15 mm.	
2.50	700	93.2	8.1	91.8	4.8	6,520
1.50	660	92.5	8.8	90.5	4.7	6,300
.86	630	91.7	10.2	88.9	5.4	5,350

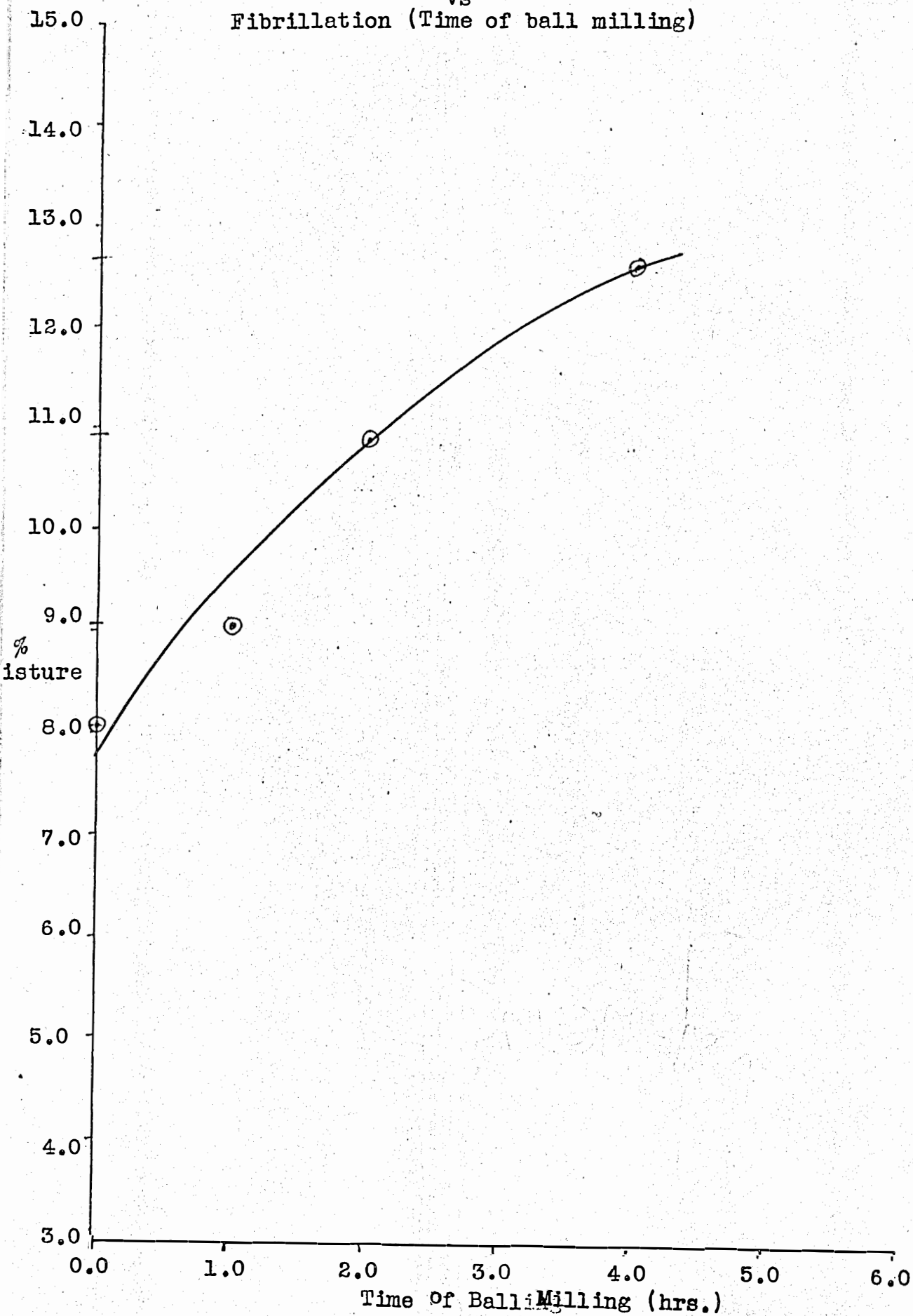
Add data averages of at least six trials.

FIBRILLATION							
Time B.M. Hours	Freeness cc.	Fiber Length mm.	% Moisture Drainage	% Moisture Pressing	% Water Removal	Tensile Kg/15 mm.	Breaking Length Meters
0	700	2.50	93.2	8.1	91.8	4.8	6,520
1	670	2.20	94.6	9.1	90.2	7.0	8,300
2	550	2.00	94.2	10.9	88.5	9.3	10,600
4	340	1.80	92.5	12.7	85.3	9.8	10,100

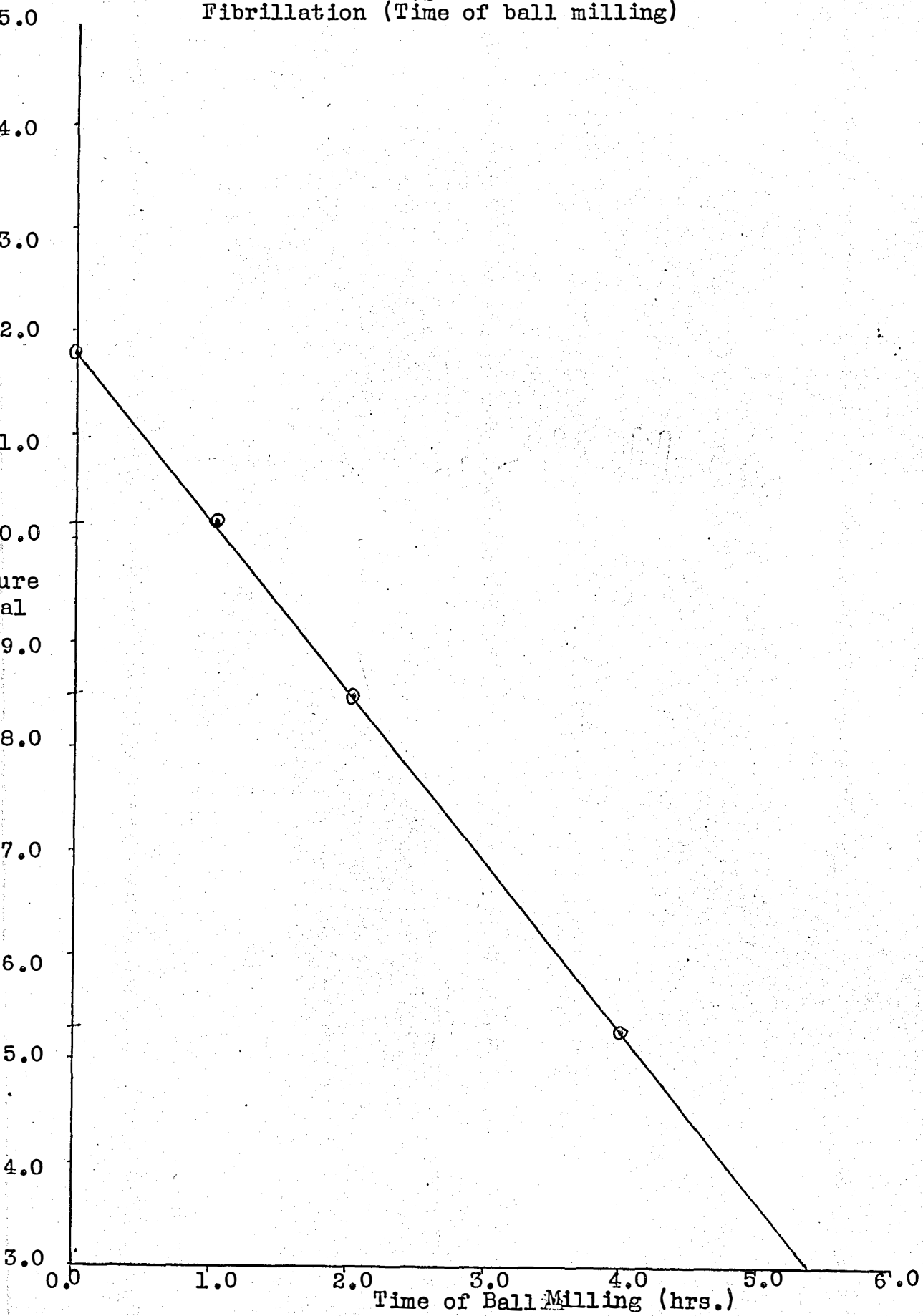
Drainage Moisture Content
vs
Fibrillation (Time of ball milling)



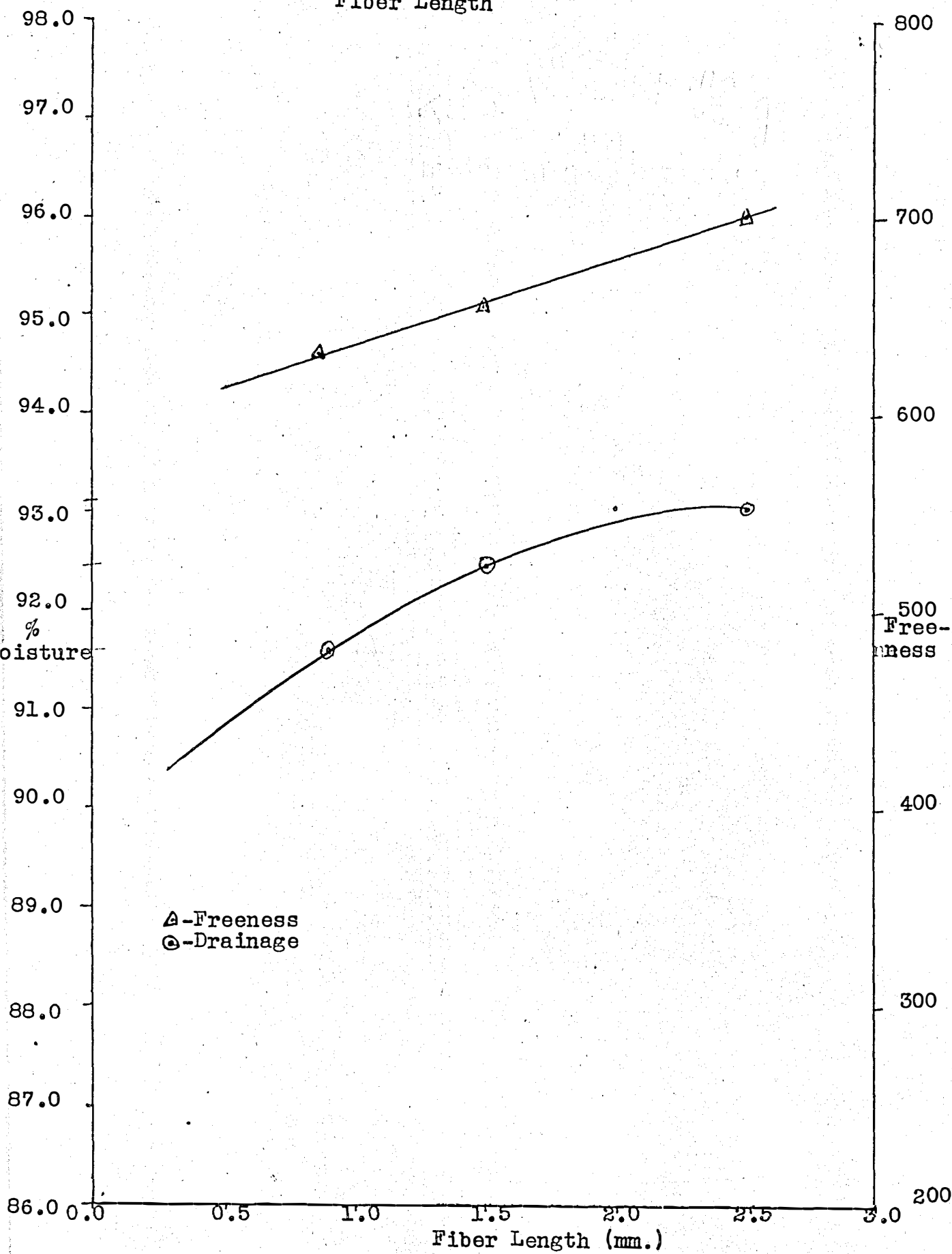
Pressing Moisture Content
vs
Fibrillation (Time of ball milling)



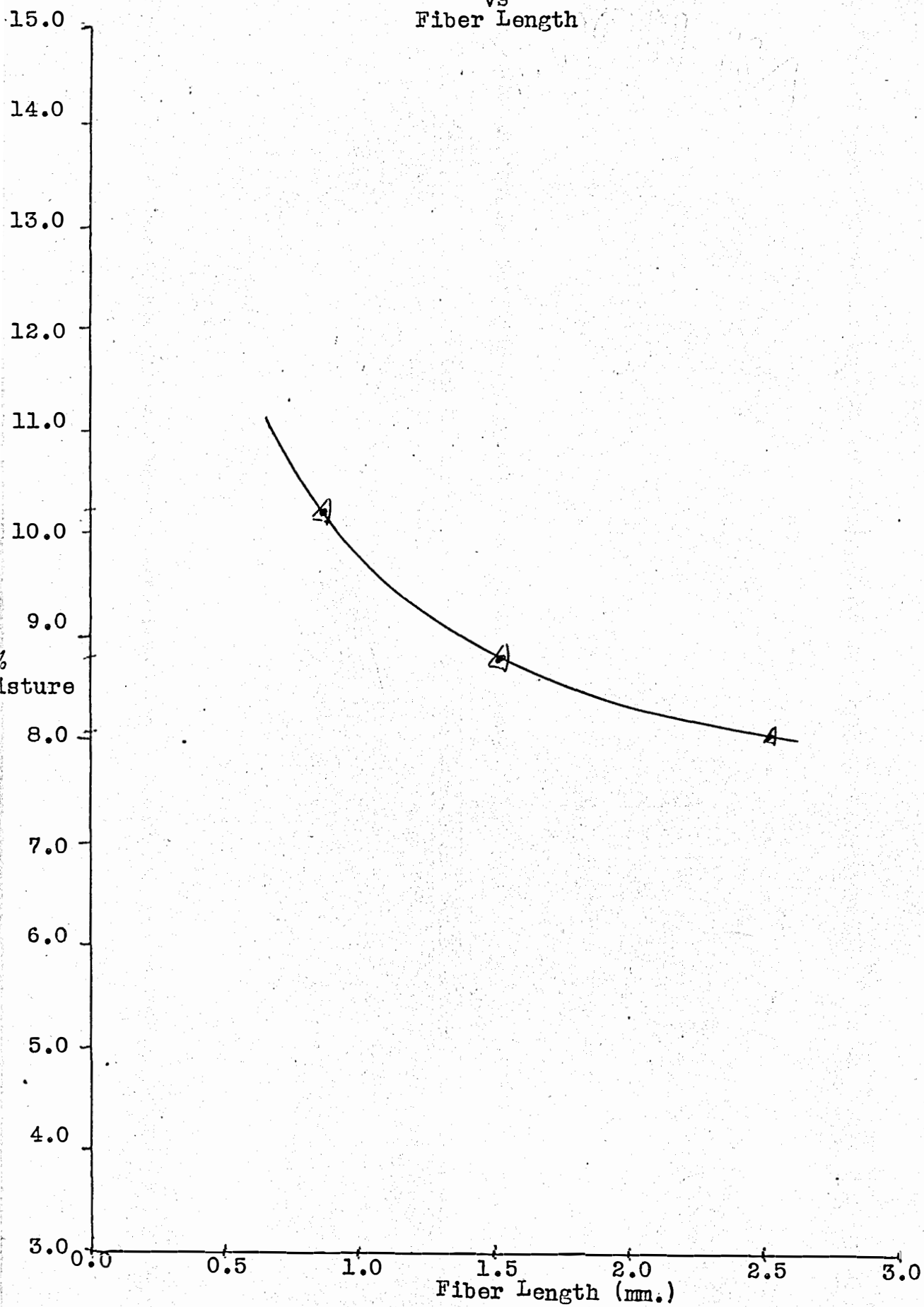
% Water Removal
vs
Fibrillation (Time of ball milling)



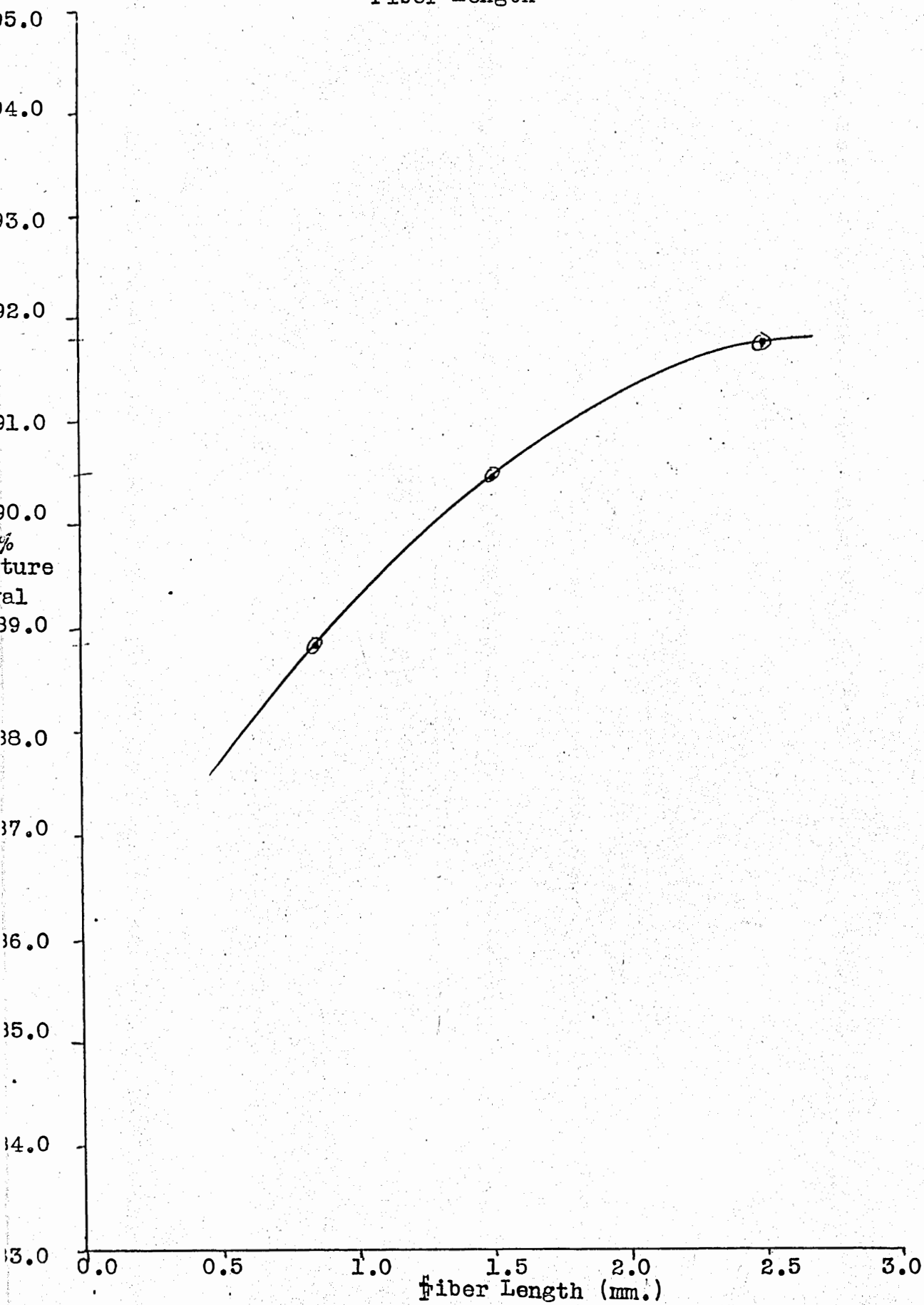
Drainage Moisture Content
vs
Fiber Length



Pressing Moisture Content
vs
Fiber Length

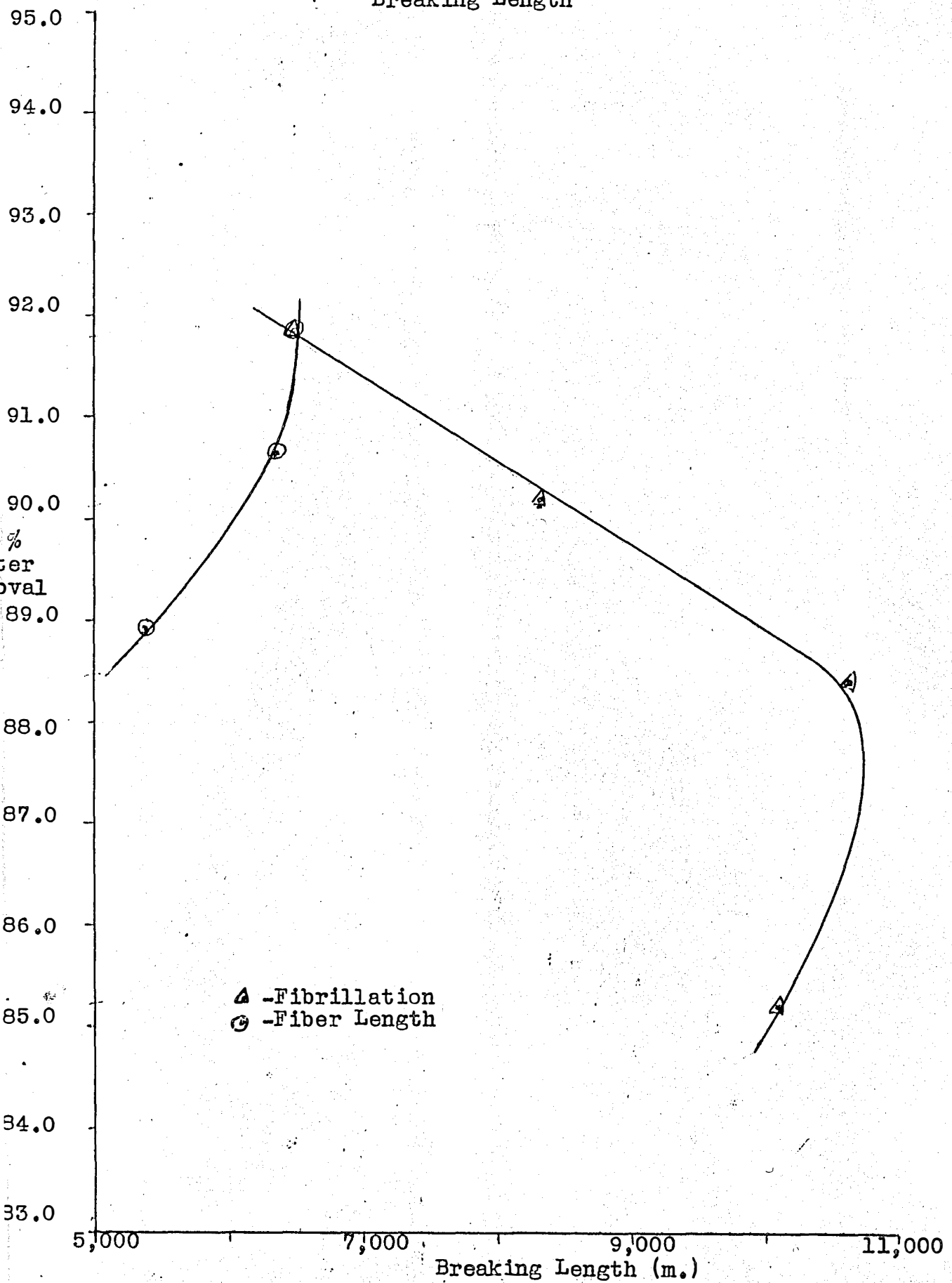


% Water Removal
vs
Fiber Length



VII.
% Water Removal
vs
Breaking Length

-23-



Discussion and Conclusions

The hypothesis proposed that fibrillation and fiber length are factors in determining the specific resistance to water removal by wet pressing has been shown to be correct. As fibrillation increases the amount of water that can be pressed from paper decreases and as fiber length decreases the amount of water that can be removed decreases also. These effects can be seen graphically on graphs 3 and 6.

It appears that the amount of water pressed from fibrillated pulps is inversely proportional to the degree of fibrillation as seen in graph 3. However, a few other factors should be considered. Fiber length determinations of the fibrillated pulps indicate that the fibers are shortened somewhat by ball milling. This would mean that this curve includes the factor of fiber length which as was mentioned before decreases the amount of water removed by pressing. Since the actual amount of shortening was minimal, its effect would only decrease the slope of the line on graph 3 a negligible amount.

Another factor which is effective here is the increased flexibility of the fibers due to the bruising action of the ball mill. This factor was hypothesized as being a possible one in determining the specific resistance so it should be considered as a source of error in graph 3. This would again decrease the actual effect of fibrillation so the most probable slope for fibrillation considering both factors would be slightly less.

Considering these two obvious sources of error, it would decrease the probability of graph 3 being the exact result

of fibrillation on water removal by wet pressing. However, these two factors are not the major factors in this study contributing to resistance. Assuming these results to be representative of the effect of only fibrillation, it is evident that another term corresponding to the degree of fibrillation should be used along with R in the equation of water removal. A good measure of the degree of fibrillation is freeness, and since it has been shown it is a linear function of water removal, the following equation would be a truer relationship.

$$M = K \frac{P t A f}{R^2 W^2 \eta} \quad (4)$$

where F = freeness

As freeness decreases, the amount of fibrillation increases so the amount of water that can be removed by pressing would decrease. It would be necessary to include R because of the specific resistance of the other factors. It should be remembered that this is only an empirical equation so it is not necessary to determine the exact relationship of freeness.

It has been shown on graph 6 that as fiber length decreases the amount of water that could be pressed out decreases also. The procedure of cutting has eliminated any other factors which might be a source of error so it can be assumed that this is the actual relationship due to fiber length.

From the graphic representation of results, it is evident the amount of water pressed from a sheet is not a direct function of fiber length since a curve is obtained. This would make it more difficult to correlate with the amount of water removed, but it could be included as a function of length to give

$$M = K \frac{P t A F f(L)}{R^2 W^2 \eta} \quad (5)$$

This equation would be a more exact relationship to determine the amount of water removed by wet pressing.

The plot of per cent water removal versus breaking length indicates an optimum amount of water that could be removed by pressing a fibrillated pulp to obtain maximum strength. However, the equilibrium moisture content after pressing was much lower than that of paper leaving a press section so it may not be a factor in determining paper strength in ordinary papermaking. The increase in strength would be due to increased bonding while the decrease would probably be due to the actual weakening of internal fiber bonding from extensive mechanical action.

A plot of freeness versus fiber length indicates that it does not affect freeness very much. A plot of freeness against degree of fibrillation indicates an inverse proportion between the two. These results can be seen on graphs 1 and 4.

It would be necessary to do much more work in these areas to obtain any useful equations. In the future work the exact function of length could be determined and the effects of the other factors hypothesized could be studied to give an exact equation for water removal by wet pressing.

In conclusion this study has determined the effect of two factors that determine the amount of water removed by wet pressing. Extensive work would have to be carried out along the above suggested lines before an exact equation of practical significance could be developed.

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