Preferred citation: H.W. Emerton. The outer secondary wall: Pt. 2 – Its possible papermaking significance. In **Fundamentals of Papermaking Fibres**, *Trans. of the 1st Fund. Res. Symp. Cambridge*, *1957*, (F. Bolam, ed.), pp 431–434, FRC, Manchester, 2018. DOI: 10.15376/frc.1957.1.431.

THE OUTER SECONDARY WALL II. ITS POSSIBLE PAPERMAKING SIGNIFICANCE

H. W. EMERTON

BRITISH PAPER AND BOARD INDUSTRY RESEARCH ASSOCIATION, KENLEY

Summary

It is believed that the object of beating is to enhance the plastic deformability of the pulp fibres, at the same time increasing their surface activity. This is achieved by internal fibrillation, which potentially increases the amount of water imbibed. The actual amount imbibed will depend, however, on the ability of the fibre wall to swell freely. Thus, the rupture and partial removal of the swelling-constraining outer secondary wall may be a desirable object of beating.

In this section, we consider S1 (the outer secondary wall) in the light of the beating process. The theory of this operation is considered by other contributors to this symposium and has been treated at some length by the author elsewhere:⁽¹⁾ it will therefore not be discussed in detail here. Suffice it to state that the object of beating for many, if not for most, types of paper is to increase the bonded area between fibres by making them more flexible so that they deform, preferably plastically, under surface tension forces acting during drying of the web. Deformation alone, however, merely provides the opportunity for bonding to occur; the extent of the bonding will depend upon the state of the surfaces brought together. Thus, a concomitant aim

The word *fibre* in this section includes the elongated cells of both gymnosperms and angiosperms.

of beating is partially to disperse the cellulose and other polysaccharides of the surface layers. These two aims are achieved by passing the fibres through regions of high shear, the effect of which is to rupture a proportion of the internal lateral bonds, notably those between the coaxial layers of cellulose in S2 (the middle secondary wall).

An immediate consequence of internal fibrillation, as this process of internal bond breaking is called, is an increase in the amount of water that is sorbed by the polysaccharides exposed on the surfaces opened up within the fibre wall. This results in an expansion of the wall and is consequently generally called *swelling*; however, the phenomenon is better termed *imbibition*, as this name focuses attention on the uptake of water rather than on the

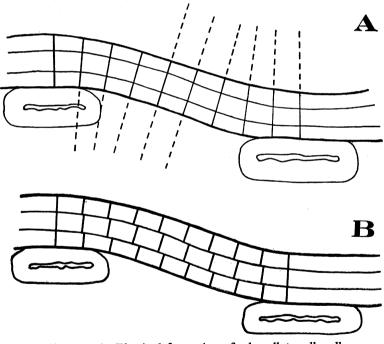


Fig. 1 — A. Elastic deformation of a lamellate cell wall B. Plastic deformation of a lamellate cell wall

dimensional changes of the fibre. Water is imbibed; the fibre wall swells. It cannot be too strongly emphasised that, when the word *swelling* is used in connection with the effect of beating of papermaking fibres, the actual volume change is of no great consequence; the essential feature is the uptake

of water. The imbibed water exerts a plasticising influence upon the (70 per cent. crystalline) cellulose structure so that, during removal of water from the sheet, it deforms more readily, the coaxial layers of S2 sliding over one another and taking up relatively stress-free positions (Fig. 1). Furthermore, the high polarity of water makes it a perfect medium from which to dry cellulosic fibres in order that extensive hydrogen bonding may occur between them.

Thus, imbibition of water is essential for the development of those paper properties that depend upon a high degree of bonding: however, this necessarily results in the simultaneous swelling of the fibre wall. The converse statement is equally true that, if swelling is inhibited, water cannot be imbibed. In mature fibres, the bulk of the cellulose is situated in S2, the fibrils of which are aligned, very roughly speaking, in an axial direction. Consequently, imbibition of water between these fibrils results in a swelling that is more or less radial. (It becomes even more nearly so, because, as the wall swells, the fibre twists in such a way that the fibrils of S2 are aligned more nearly longitudinal.⁽²⁾) We have seen that the fibrils of S1 surround those of S2 and form two counter-rotating helices, the directions of which, particularly in softwood tracheids, are more nearly transverse. This wall therefore imposes a constraint on the swelling of S2 and hence on the imbibition of water by it. Indeed, it may well be that this is a biological function of S1. A thin outer layer, the fibrils of which are aligned more or less transversely, appears, so far as the author has been able to determine from the published literature, to be characteristic of elongated plant cells (for example, those of wood, cotton, bamboo and flax). It is therefore possible that such a layer is necessary to prevent the excessive dimensional changes of the cell in a radial direction that would otherwise accompany the uptake or loss of aqueous liquids by the bulk of the cell wall and that would be transmitted to the growing stem as a whole.

It has often been stated or implied that the primary wall (P) is chiefly responsible for constraining swelling. Because of its thinness and the relatively wide separation of its fibrils, however, this wall contains little cellulose and it is probable that P plays a comparatively small part in inhibiting dimensional changes of the fibre.

The imbibition of water by cellulose is limited — in the study of gels generally, this is termed *limited swelling* — because the water molecules are unable to overcome the cohesive forces between the cellulose chains in those regions with a high density of lateral bonding. Flexing the structure breaks some of these bonds (internal fibrillation) and hence potentially increases the

amount of liquid imbibed, though the amount actually taken up may be less than this owing to the inability of the structure to swell freely. It would therefore seem that a desirable (and perhaps to some extent a necessary) result of beating is to rupture and partly to remove S1 in order that imbibition may proceed freely. If S1 could be largely removed without damage to S2, then the process of enhancing the plastic flexibility of the fibre and the surface activity of the exposed polysaccharides would be more readily promoted. In normal beating practice, this is not carried very far and S1 continues to exert some degree of constraint on the free imbibition of water.

REFERENCES

1. Emerton, H. W., Fundamentals of the Beating Process (B.P. & B.I.R.A., Kenley, 1957)

2. Emerton, H. W., Proc. Tech. Sect. B.P. & B.M.A., 1955, 36 (3), 595

Transcription of Discussion

DISCUSSION

DR. D. ATACK: Some time ago, Dr. W. B. Campbell (*Pulp and Paper Mag. Can.*, 1934, 35 (4), 218) made an estimate of the efficiency of the groundwood process similar in many respects to that given for the beating process by Dr. Van den Akker; both estimates are based on the increase in surface free energy to produce a given kind of pulp as a result of a purely mechanical treatment. Although the surface free energy assumed by Campbell is approximately ten times larger than that calculated by Van den Akker, it is found that, based on the criterion of efficiency —

$Efficiency = \frac{Increase of surface free energy to produce an acceptable pulp}{Total energy input},$

both processes are very inefficient. Campbell measured the surface area of a typical acceptable groundwood pulp and Van den Akker has calculated the increase in surface free energy produced by an idealised beating action.

Both authors suggest that not only may improved efficiency result in economy of energy, but also in more suitable pulps. It is implicit in this suggestion that we have a basic understanding of the energy conversion processes associated with the production of a desirable pulp.

Dr. Van den Akker has listed some of the processes of energy dissipation (fluid friction, surface friction and internal friction) and suggests that they may lead to bond breaking and molecular chain slippage in the fibres. He then implies, presumably with good reason, that these processes contribute very little, if at all, to the desired beating action. There are reasons to challenge this viewpoint and I think he would agree that only when we know the nature of these energy conversion processes is it possible to discuss their merits in the beating action. Moreover, if such studies, which are not easy ones to undertake, show that certain processes are undesirable, it is more than likely that methods for their elimination may be suggested from the results of such studies.

Unfortunately, as Dr. Van den Akker points out, the energy transfer spectrum of processes in such a complex machine as an industrial beater is a wide one and severe difficulties may be encountered in the elimination or drastic reduction of certain energy levels from a practical process. Alteration of the time scale of the beating action is a potential field of investigation; drastic changes of this parameter have indicated that for certain grades of pulp greatly improved efficiency may be obtained.

Session 4

To summarise — all our efforts to estimate efficiency on a satisfactory basis should be made in such a manner that the reasons for any lack of efficiency become abundantly clear. Moreover, the results of such efforts should be suggestive of ways of eliminating inefficient processes.

DR. H. F. RANCE: I do not want to comment on the physics of Dr. Van den Akker's paper: I am not competent to do so and I trust him completely and accept his conclusions. I want to make one or two general comments. A lot of us have probably investigated different mechanical beaters and beating machines in our time and have found comparatively little difference in their mechanical efficiencies. This might lead some people to be rather sceptical of Dr. Van den Akker's conclusions.

To offset such scepticism, however, there is a very interesting analogy that one can point to — the operation of an electric lamp. The efficiency of transformation of electricity into light in that lamp is very low, indeed. Apparently, judging by Dr. Van den Akker's paper, it is not as low as that in the beating process, but it is extremely low. Now, there is a lot of money behind the technology of the electric lamp, yet it took many years to find a commercial improvement based on an entirely different kind of method for transforming electricity into light.

There is a warning here, I think, for any representatives of the press or others who may think that Dr. Van den Akker's work is going to lead immediately and quickly to some new beating process that may use up a lot less energy.

It is also worth remembering that the new methods that have been found for transforming electricity into light require considerably higher initial expenditure on the equipment that carries out the transformation.

MR. L. G. COTTRALL: Dr. Van den Akker's conclusions rather confirm the conclusion I put before you yesterday when showing you the sorption curves of Campbell. The almost identical curves for beaten and unbeaten stocks demonstrate, in my view, that proportionally very few bonds are broken in the beating process in spite of the vast differences in the paper produced from the unbeaten compared with that from the beaten stock. This small reduction of bonds by beating confirms the small amount of power required to do the actual beating compared with the total power used in the beating apparatus. This also makes me rather sceptical about the high degrees of increased swelling and water boiling that very many say take place in the beating process.

Second discussion

This difference in power is mainly used up in frictional losses of one form and another. Some time ago, we built up the floors of our beaters so that they came almost level with the first bar of the bedplate and thereby we saved some 20 per cent. of the power consumed by the beater, even allowing for the smaller amount of pulp the beater held because of building up the floor.

During lunch, a friend suggested that a beater was a very good apparatus for determining the mechanical equivalent of heat. If Joule had been employed in a papermill, I do not think he would have had recourse to any laboratory apparatus, but could just have insulated a beater from radiation to obtain a very good approximation to the true figure and the small amount of power used in beating would have merely come in as a small experimental error.

MR. N. C. UNDERWOOD: I should like to ask Dr. Van den Akker whether the fibrils are, to a certain extent, already present when the pulp is first put into the beater and if the very low force he shows in Fig. 3 is quite sufficient to pull them back at a high angle θ , but after a little while these have all gone and the probability of the breaking away of the new fibrils is then quite low. After that, quite large forces, three decades up, are necessary to start fibrils. I wonder, therefore, whether it is possible that the initial rapid change in properties is due to a process such as Dr. Van den Akker describes, acting on fibrils already existing and then the slow process after that is due to new fibrils being torn away more slowly.

DR. J. A. VAN DEN AKKER: I certainly agree with Dr. Atack that a good study should be made of the way energy is dissipated in existing processes for beating. I deliberately avoided existing processes with the idea that, if we did so, we might arrive at what I have called idealised figures that have no connection with existing equipments and mechanisms. I am afraid that, if we try to reach for the stars from the existing processes, we are going to be held back and, if we can somehow make idealised calculations, we can see how far we may go. This is why that was done rather than to try to analyse actual beating processes.

On Dr. Rance's interesting comment that the efficiencies of beaters are quite similar, I would say that commercial and laboratory beaters, excepting such special types as the Lampén mill and the ball mill, are basically of similar forms. Really great improvements in the efficiency of the electric lamp were not made until a completely new type came along the fluorescent lamp — and, speaking in terms of this analogy, we are looking

Session 4

forward to the day when we can get away from the Hollander type of beating machine to something now unknown, but much more efficient.

To Mr. Cottrall's interesting observation that a beating machine would be a good device for measuring Joule's equivalent, my question would be to how many decimal places could we determine it? One could raise the question about the efficiency of modern beating devices — is the inefficiency in the second figure or the third figure? — 99.99 per cent. or 99.9 per cent. or what?

Mr. Underwood has introduced a very interesting idea in relating the early, easy beating of a pulp with the theoretically low force required to remove fibrils when partial fibrillation of the pulp has already occurred. He then raised a question about the more difficult breaking away of fresh fibrils. Although the force required to start the peeling of a fibril may be substantial, the energy may be small and, of course, the energy expenditure is substantial only when the peeling has progressed a certain distance; but the point is that the *force* may have a greater influence on the probability of peeling than the energy — hence Mr. Underwood's theory of the slowing of beating with time.

THE CHAIRMAN: Now we will proceed to Dr. Mason's paper.

DR. W. GALLAY: Dr. Mason is to be congratulated on a very fine piece of work in the development of a technique to measure strengths of webs having consistencies in such very low regions. I was very much interested in his correlation of these data with others that Mr. Lyne and I published several years ago on wet-web strengths for consistencies ranging from about 8 per cent. upwards. There appears no real conflict in our views concerning the basic mechanism, but the following point deserves mention.

He has noted that the interfibre forces are mechanical in nature and has compared them with those pertaining to dry textile fibres. As I noted in my presentation earlier, my concept involves the inclusion of physicochemical forces, in addition to the ordinary mechanical forces that represent simple entanglement. This is in my view of considerable importance in a unified concept of strength development throughout the course of paper manufacture. I should like to ask Dr. Mason's opinion on this matter.

MR. A. P. TAYLOR: Would Dr. Mason paint his very beautiful experimental lily to the extent of telling us whether the movement of his fibres in the film were the actual movement as the film was taken or whether there was an alteration in time scale?

Second discussion

MR. P. G. SUSSMAN: I have two questions. The first concerns the cohesion of networks under surface tension or other forces. Anyone can make the following experiment. Take two glass plates and press them together under water: they will stick together quite hard. There does not seem to be any 'free' surface involved as there is no change in surface area, only the distance between the plates matters. Sheets of paper, however, do not stick together in this way.

The second point is that Dr. Mason has considered the tensile strengths of networks that were formed, I take it, by random aggregation of fibres. We have carried out some experiments on evening out fibre aggregations. One can even out the fibres in a beaker. I have watched these suspensions or aggregates settle down and become denser: we found that, when they were really even, they settled down much more quickly and formed a much denser final aggregate than did a flocculated fibre suspension. I suggest that the compressive strengths and this speed of settling are at least as important as tensile forces on these fibre aggregates, since papermaking processes on the wire are concerned with the settling down of fibres.

DR. S. G. MASON: In reply, first of all, to Dr. Gallay, I wish to make it clear that in the network and wet-web strength measurements we meant that the interfibre forces are largely frictional. According to modern concepts of friction between solid surfaces, there is adhesion because of intermolecular forces.

All of the ciné film shots were taken at the actual speed at which they occurred.

I am not quite clear about one of the last speaker's questions. I agree that, in sedimenting, a pulp suspension packs under the compression from its own weight and is therefore the reverse of the tension in our network experiments, except that in the latter we took the stress to the point of failure: this does not occur in a sedimentation experiment.

I should like to say a word about the effect of aggregates on network strength. We find it very important to ensure uniform dispersal and we do this by pumping the suspension under conditions of very high microturbulence around and around through the tube carrying the suspension, so that we have what we may consider to be one large floc in the system — that is, one continuous interconnected structure. Without uniform dispersion, we tend to get weak spots, with a resulting high scatter in our measured tensile strengths.