SOLUCELL®: A SPECIAL DISSOLVING PULP FROM EUCALYPTUS

Giácoma Frasson Manhães and Alberto Ferreira Lima

Klabin Bacell
Rua Alfa, 1033 AIN-COPEC
42810-000 Camaçari (BA) Brasil

gfmanhaes@klabinbacell.com.br

Abstract

The dissolving pulp market faces new challenges with the growing diversification of applications. The already long list of cellulose-based materials increases as the end users demand new and improved products. On the textile scene, wrinkle-free lyocell, or the luxurious feel of microfibre are examples of this consumer oriented trend.

The specific needs of high-tech applications and consumer demand for specialty products are forcing the whole supply chain to use more specialized raw materials. Attentive to the very specific needs of different niches, Klabin Bacell, a dissolving pulp producer in Brazil, refocused its production from single viscose grade pulp to tailor made grades of dissolving pulp, based on a wide range of viscosity and purity.

The designed products present superior reactivity, due to their morphological and chemical attributes. The short and thick fibers of eucalyptus provide high specific surface of the fiber material, leading to high affinity to polar solvents. Another feature of Solucell®, the dissolving pulp of Klabin Bacell, is its resistance to chemical degradation, compared to other high purity grade pulps.

The achievement of a variety of grades of Solucell® was possible through intensive R&D work to identify key parameters and efficient technology transfer to leverage the flexibility of Klabin Bacell mill. From the initial concept, based on state-of-the-art technology for environmentally sound production of one single dissolving pulp grade, it succeeded as a specialty supplier to attend chemical, pharmaceutical and textile industry.

Introduction

The modification of the properties of cellulose by derivatisation has been widely used in industrial applications since the first findings on cellulose nitrate back in 1846. The 1900's brought rayon filaments, cellophane, cellulose acetate and ethers, as well as specialized cellulose graft copolymers. [1,2]

Unlike the paper production, where physical interactions play the most significant role in the process, the production of cellulose derivatives requires cellulose in a purified condition. The reaction of process chemicals with any remaining hemicellulose or lignin fragments in the pulp generates undesirable by-products. Therefore the raw materials for cellulose derivatisation are either naturally pure cellulose like cotton; or bleached wood pulp with low hemicellulose content, referred to as *dissolving pulp*.

The last decades were especially intense in regard to the development of cellulose-based materials. Along with new high-tech applications, such as engineered fibers to reinforce aerospace material, also end users demand new and improved products. Thus new textiles are developed to guarantee best performance of sportswear; wrinkle-free fabrics to save busy travelers' lives; luxurious and smooth fabrics for underwear...

The dissolving pulp market faces new challenges with the growing number of cellulose applications. And the specific needs of high-tech applications plus consumers demand for special products forces the whole supply chain towards to more specialized raw materials.[3]

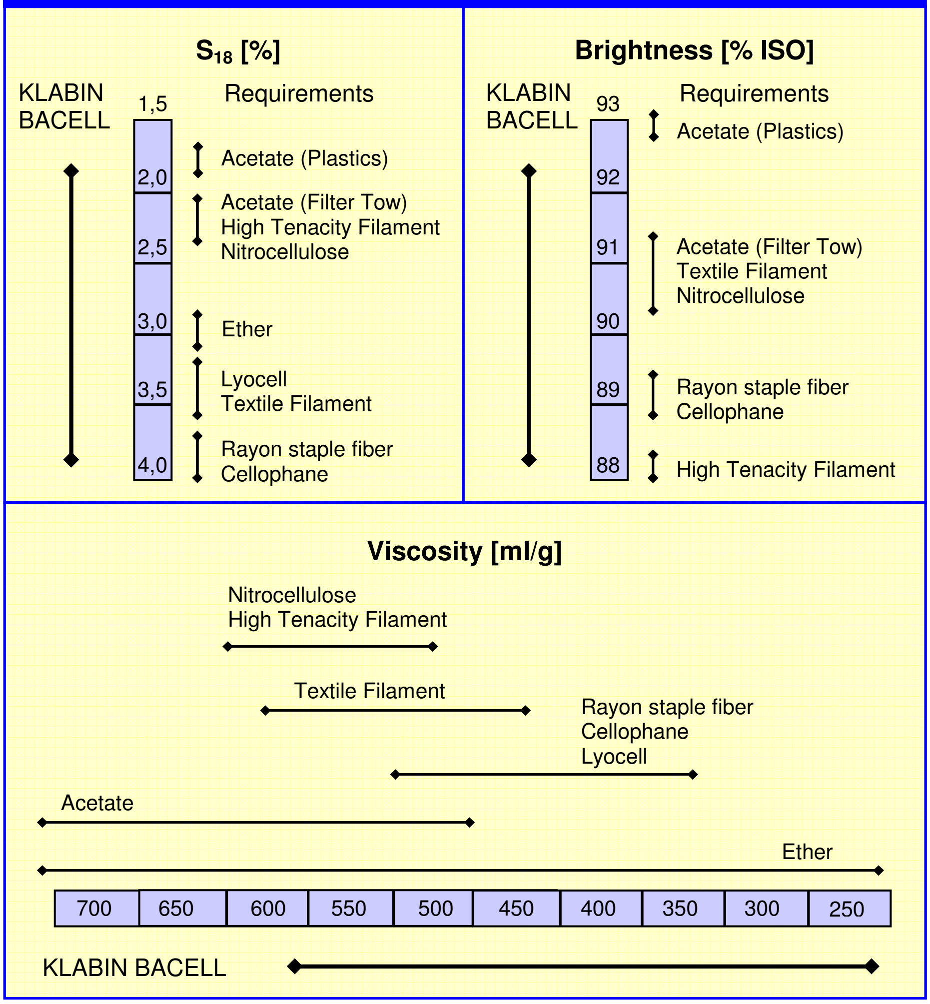
On top of that, the awareness of the natural resources limitations and the need for sustainable operations are leading some industries to evaluate alternatives to their traditional raw materials. Looking at the textile scene, it jeopardizes the future of synthetic fibers made from fossil material, like polyesters, for instance. With continuous technology improvement to achieve high quality products from different sources of cellulose, like lyocell fibers, one can expect even a trend to a reduced use of cotton, which cultivation requires intensive work and large territories. And new technologies support the use of hardwood dissolving pulps in areas where the need for long fibers used to be a paradigm.

That was the atmosphere that stimulated Klabin Bacell, a dissolving pulp producer in Brazil, to refocus its strategic position: competitive fiber source, state-of-the-art technology, and strong R&D support to change from the position of rayon pulp supplier to producer of tailor made grades of high quality dissolving pulp.

Defining the target: different cellulose derivatives require different pulp features

Through literature and market evaluation, general requirements for different applications of dissolving pulp were drawn, which are summarized in Figure 1, in comparison to the range covered by Solucell®, the dissolving pulp from Klabin Bacell.

Figure 1 - Typical ranges of key parameters required by special applications and ranges achievable by Klabin Bacell dissolving pulp.



Note: Lyocell fiber is not a cellulose derivative. It results from the dissolution of cellulose in a suitable solvent, and then reprecipitated to form a cellulose filament. High tenacity filament, textile filament, standard rayon and cellophane are not cellulose derivatives themselves, but result from the regeneration of cellulose xanthate back to cellulose.

"*Purity*" is expressed by means of S_{18}, the pulp solubility in a solution of NaOH 18%. The soluble fraction comprises the majority of the hemicelluloses left in the pulp, and also degraded cellulose chains. The lower the S_{18}, the higher the purity. High S_{18} values strongly impair the derivatisation yield and derivative quality.

Viscosity is an easy to measure indicator of the degree of polymerization of the cellulose, widely used. The uniformity of the length of the cellulose chains is critical to assure homogeneity throughout the derivatisation steps. For the cellulose-based filaments, viscose heterogeneity implies in weaker regions and higher number of breaks.

Besides these general quality parameters, there are several pulp properties as cristallinity degree, molecular weight distribution, fiber specific surface area and pore volume, that influence the pulp accessibility to chemicals and thus its reactivity and further processing.

Making it come true: the right technology

Through good R&D support and close cooperation with clients, a broad range of special grades for high quality applications were developed at Klabin Bacell, based on a superior wood supply and process flexibility.

Uniform wood supply

All the wood is supplied by eucalyptus plantations, mainly composed by *Eucalyptus grandis*, *E. urophylla* and their hybrids *urograndis*. Classical genetic improvement combined with advanced forest management techniques and good climate allows fast maturation of the trees (5 to 7 years).

The uniformity of the raw material used is a major point to guarantee the high quality of Klabin Bacell pulp. Furthermore, the species used have low hemicellulose and resins content, which contributes from the very beginning of the process to the obtainment of higher purity levels of cellulose in the final products.

Designed technology

The mill was based on state-of-the-art technology for environmentally sound production of dissolving pulp. Some processes were specially designed for Klabin Bacell, as the Visbatch cooking, which combines vapor phase pre-hydrolysis and which combines a vapor phase prehydrolysis with kraft batch cooking; the first TCF sequence for prehydrolysis kraft pulp; and also the Tetraformer, a double-wire drying system for low energy water removal.[4]

Each production step can be optimized in regard to the desired parameters in the final product, according to the requirements of the different applications: Acetate, Nitrocellulose, Lyocell, Textile and Technical Filament, Casings, Ethers and Esters.

Pre-hydrolysis: allows the control of hemicelluloses in the pulp that can be adjusted to reach final levels as low as 1.5%.

Cooking: its modern design allows the control of brown stock viscosity in a narrow range, based on the measurement of residual alkali in the liquors.

Oxygen delignification: with efficiency above 70%, it evens out variations in pulp kappa number and keeps effluent COD (chemical oxygen demand) very low.

Bleaching: the short sequence A-Z-P promotes product differentiation while enhancing pulp purity:

A – the acid washing stage guarantees very low metals content in the pulp;

Z – ozone allows adjustment of viscosity down to the desired level in the final product;

P – after activation in Z-stage, peroxide provides the final adjustment to the brightness target, with virtually no viscosity impairment.

Achievements: tracking the quality

Advanced characterization confirmed the successful transition of Klabin Bacell products from viscose to prime quality grades. Studies carried out at Lenzing R&D compared a high purity grade of Solucell® to other commercial dissolving pulps. Results showed that Solucell® is very reactive, and has a high degree of purification.[5]

The degree of purification achieved is comparable to dissolving pulps being treated by cold caustic extraction, as shown by their Molecular Weight Distribution (MWD, Fig. 2).[5] The narrower the MWD, the more homogeneous the reactions and products obtained from the pulp will be.

The narrow MWD of Solucell® derives from:

- eucalyptus morphology itself and the high uniformity of the trees in terms of both species and location, to ensure a narrow fiber length distribution (Fig. 3) [5];
- very sharp control of viscosity, with fine tuning of operational conditions. Mild cooking can be compensated by the high efficiency of oxygen delignification to prevent fiber damage, and then the bleaching strategy is defined to control the length of cellulose chains to the desired level.

Solucell® grades are classified within 50-cm^3/g windows of intrinsic viscosity, between the limits of 250 e 600 cm^3/g. That allows the use of Solucell® for most applications of dissolving pulp, even those that require a very narrow range of degree of polymerization (DP). It enables the pulp to develop very good tenacity values, as observed in pilot plant tests (Fig. 4), an essential parameter for the production of high tenacity filaments, casings and other strength-related applications of dissolving pulp.[3]

Different bleaching strategies can be applied to allow viscosity control at the ozone stage rather independently from brightness control. By means of the peroxide stage, brightness with values as high as 92% ISO can be achieved over a wide range of DP, and the pulp can be used for applications that demand good color properties.

A remarkable feature of Solucell® is its resistance to chemical degradation, compared to other high purity grade pulps. It can be illustrated by the evaluation of acid hydrolysis kinetics (Fig. 5).[5] Considering the low hemicellulose content of these pulps, this effect should be attributed to differences in their supramolecular structure. As a consequence, the initial degree of polymerization (or viscosity) of Solucell® for the production of acetate should be lower than that of other acetate grade pulps.

Regarding reactivity, a very good performance can be expected from the high purity grades of Solucell. Although its crystallinity is comparable to other market dissolving pulps, the accessibility is considerably higher in a very wide range of pore diameter, up to 100 Å, as determined by size-exclusion chromatography (Fig. 6).[5] These findings are also supported by the results of SAXS (small angle X-ray scattering), which indicate a large portion of voids for the high purity grades. Morphological and chemical features also contributes for this superior reactivity. Eucalyptus has short and thick fibers, thus, the high specific surface of the fiber material leads to high affinity to polar solvents. Also the content of carboxyl groups in Solucell® is higher than in other pulps, probably as a consequence of the very oxidative bleaching sequence. It translates into more derivatisation sites of the cellulose chain.

Figure 2 – Molecular Weight Distribution of commercial pulps.

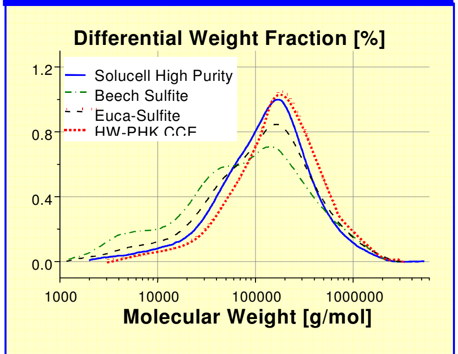


Figure 3 – Fiber Length Distribution of commercial pulps.

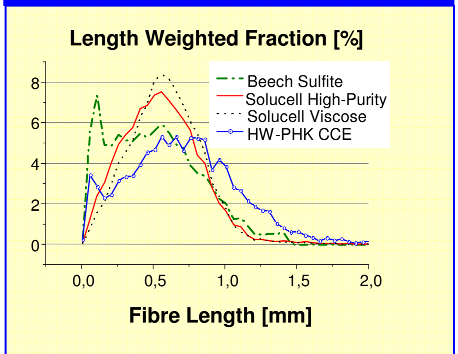


Figure 4 – Strength results from pilot plant tests.

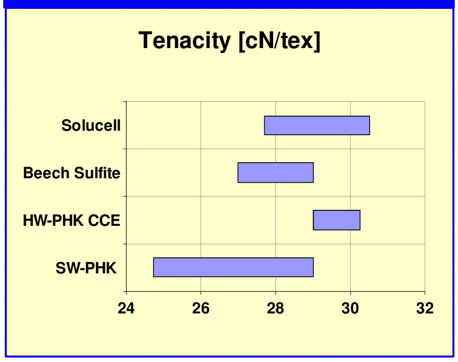


Figure 5 – Chain scissions in acidic degradation of pulp.

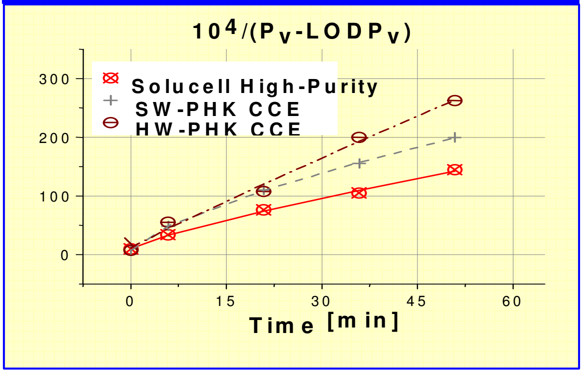
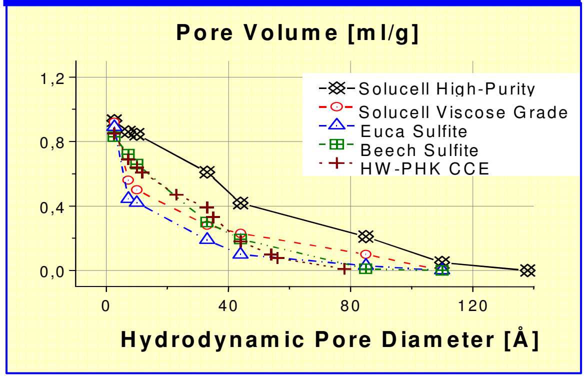


Figure 6 – Acessibility of commercial pulps.



Final remarks

Due to the great flexibility of Klabin Bacell's process, and superior quality of the wood supply, an extensive list of dissolving pulp grades is already in the market.

As a result of in-depth study of the pulp behavior for high quality applications, Klabin Bacell succeeded in translating market claim for tailor-made products from superior quality dissolving pulp into reality.

1. A. Reveley, in *Cellulose and Its Derivatives*, (ed. J. F. Kennedy, G. O. Phillips, D. J. Wedlock and P. A. Williams) Ellis Horwood Ltd., chapter 17 (1985).

2. V. T. Stannet, in *Cellulose and Its Derivatives*, (ed. J. F. Kennedy, G. O. Phillips, D. J. Wedlock and P. A. Williams) Ellis Horwood Ltd., chapter 34 (1985).

3. G. F. Manhães, "Brazilian Mill swallows Dissolving Pill", Pulp & Paper International **2000**, *42 (10)*, 25-27.

4. K. L. Patrick, "Ozone-Bleached Kraft Dissolving Pulp Mill Cracks Tough Nuts in First Year", Pulp & Paper **1997**, *39 (10)*, 61-70.

5. H. Sixta and A. Borgards, "New Technology for the Production of High-Purity Dissolving Pulps". Das Papier **1999**, *53 (4)*, 21-34.