2.3 Wood Pulp Manufacturing and Quality Characteristics

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Summary: Cellulose acetate being important in the fiber and textile industries is usually prepared from high quality cellulose such as cotton linters and wood pulps with an alpha cellulose content of more than 95%. In this section, therefore, wood pulps and cotton linters appropriate for cellulose acetate production were discussed in their chemical and physical properties so as to use them judiciously as natural raw materials for cellulose acetate production.

Keywords: wood pulp manufacturing; quality characteristics of pulp; dissolving wood pulp; linter pulp; acid sulfite pulping; prehydrolyzed kraft pulping; alpha cellulose; cellulose acetate; xylan; glucomannan; hemicellulose acetate; false viscosity; turbidity; filterability; mannose; xylose; DCM extractives; intrinsic viscosity; mullen; burst index; hardness

2.3.1 Introduction

Cellulose acetate being important in the fiber and textile industries is usually prepared from high quality cellulose such as cotton linters and wood pulps with an alpha cellulose content of more than 95%.[1] However, cotton fibers are essentially different from wood fibers in their chemical compositions, the main cell wall component of the former being cellulose, while the latter being a natural composite composing of cellulose, hemicelluloses and lignin, as described in previous sections. Thus, wood has to be extensively pulped and bleached to remove not only lignin but also hemicelluloses. In fact, the lower grade dissolving pulps contain more hemicelluloses, and the formation of hemicellulose acetates such as xylan acetate and glucomannan acetate results in industrial problems on filterability, turbidity (haze), and false viscosity. Therefore, a considerable effort has been made since the mid-1950s to elucidate the relationships between the solution properties of the cellulose acetate and contaminated hemicellulose acetate.[2-17] Still yet, the wood dissolving pulps with an alpha cellulose content of less than 90%, called as "viscose grade pulp",

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cannot be used for manufacturing cellulose acetate. In this section, therefore, wood pulps and cotton linters appropriate for cellulose acetate production were discussed in their chemical and physical properties as raw materials.

2.3.2 Wood Pulp Manufacturing for Cellulose Acetate Production

Chemical pulps for cellulose acetate production are generally produced by acid sulfite or prehydrolyzed kraft pulping process. The raw materials suitable for acid sulfite process are, for example, hemlock, spruce, fir, pine in softwoods, and *Eucalyptus* and *Acasia* in hardwoods. However, kraft pulping process is able to utilize various woods not suitable for sulfite process so that the prehydrolyzed kraft process has a potential to use more kinds of woods and presently, oak, beech and gum wood etc. are used as raw materials for this process (Table 1).

2.3.2.1 Acid Sulfite Pulping Process

In acid sulfite process,[18, 19] the cooking liquor is prepared by burning sulfur to produce SO_2 gas and then absorbing the SO_2 in a cationic base solution. Wood chips are then cooked with the prepared cooking liquor which is composed of sulfurous acid (H_2SO_3) and alkaline base sulfite. The former is referred to as "free SO_2", while the latter is referred to as "combined SO_2". As cationic base chemicals to prevent discoloration of the pulp, calcium, magnesium, sodium and ammonium are available, and a species of the base is determined by appropriate choice of cooking conditions, resultant pulp yield and quality. The traditional calcium acid sulfite cook must be carried out at a low pH of about 1.5 because of the relative insolubility of calcium. However, the use of soluble bases such as magnesium, sodium and ammonium permits to cook in any pH within the range 1.5 to 4.0.

The raw cooking acid after SO_2 absorption is a mixture of free SO_2 and combined SO_2 in the desired proportion where the composition in the cooking liquor is in a range of 5 to 10% in the total SO_2, 3 to 6% in the combined SO_2, and 0.5 to 1.5% in the free SO_2.19) The liquor to wood ratio often used is in a range between 3.5 and 6.1. The wood chips are cooked at the temperature between 130 and 150℃, under the pressure between 75 and 125 psi for 4 to 8 hours so as to avoid undesirable polycondensation reaction of lignin and retain the appropriate yield of pulp, viscosity and 10% NaOH solubility of the resultant pulp (see section 2.3.3 in more detail).

During acid sulfite process, free sulfurous acid combines with lignin to produce relatively insoluble lignosulfonic acid, while in the presence of the base, lignosulfonic salts are formed to be more soluble. The sulfonated lignin then undergoes cleavage into the smaller and more soluble fragments due to hydrolysis reactions. Hemicellulose is also hydrolyzed into soluble sugars but cellulose is relatively stable. By using somewhat higher temperature and acidity with prolonged cooking, hemicellulose is more removed so that high purity cellulose can be produced.

The obtained pulp is then chlorinated in the conventional process followed by the alkaline treatment. The chlorinated lignin which is alkali-soluble is then dissolved by the alkaline treatment, while impurities in pulp such as hemicelluloses are also removed during this treatment. In the alkaline treatment, there exist two methods, hot alkaline treatment and cold alkaline treatment, the latter resulting in the higher purity of pulp. This treatment is followed further by bleaching with hypochlorite or chlorine dioxide, at the temperature of 40 to 60℃ under the conditions of 5 to 6% in pulp concentration, 1 to 2% effective chlorine in the bleaching agent. By this bleaching, the residual lignin is oxidized and delignified. In addition, the cellulose in the pulps is controlled to be appropriate in the degree of polymerization by oxidizing cellulose molecules. Due to the environmental consideration, chlorine-free bleaching or less chlorine bleching has also been studied. Hydrogen peroxide is also used to increase brightness and improve brightness stability of dissolving pulp.

After bleaching, the pulps are treated further with sulfurous acid or hydrochloric acid aqueous solution to remove mineral components present in pulps.

After these lines of treatments, the pulp fibers are screened and dried to be pulp sheets. The drying conditions are important to control the reactivity of the cellulose. For cellulose acetate production, drying temperature should be low at 65-70℃. Also important parameters are the thickness of the pulp sheet, physical properties of pulp sheet such as mullen, density, hardness index and basis weight to control the easiness disintegrating pulp sheet under the dried condition.

2.3.2.2 Prehydrolyzed Kraft Pulping Process

The regular kraft pulps contain carbohydrates, principally pentosans, that interfere with the chemical conversion of cellulose to cellulose acetate. As a consequence, the practice of exposing the wood chips to acid hydrolysis prior to the alkaline pulping was developed as a prehydrolyzed kraft pulping process to reduce the pentosan content with the higher content of alpha cellulose.

In this prehydrolyzed kraft pulping process, the wood chips are pretreated at the temperature between 160 and 170℃ for 1 to 3 hours with direct steaming. The action of the steam liberates organic acids such as formic and acetic acids from the wood which hydrolyze hemicelluloses selectively to the soluble sugars. After this pretreatment, wood chips are cooked with sodium hydroxide and sodium sulfide ($NaOH + Na_2S$) to produce pulps suitable for raw materials of cellulose acetate production. The pulp yield from a prehydrolyzed kraft pulping is in general 5 to 7% lower on dried wood basis than that from ordinary kraft pulping. Total cooking cycle time is 8 hours, including 120 minutes at maximum hydrolysis temperature (170℃) and 70 minutes at maximum kraft cooking temperature (160-170℃).[18, 20]

The following treatment for bleaching and refinery process is basically the same as that in the sulfite process to be chlorination, alkaline treatment, bleaching with hypochlorite, chlorine dioxide, hydrogen peroxide and acid treatment. With these lines of treatments, the alpha cellulose content of the pulps can readily be over 95%.

2.3.3 Quality Characteristics of Wood Pulp for Cellulose Acetate

Table 1 shows the typical properties of representative pulps for cellulose acetate currently available in the market. The important properties and the quality characteristics of wood pulp for cellulose acetate production are described below. By controlling these properties, high quality cellulose can be achieved for cellulose acetate production.

2.3.3.1 Wood Species and Pulping Process

As shown in Table 1, wood pulps for cellulose acetate are produced from various woods, softwoods or hardwoods, by various pulping processes in either acid sulfite or prehydrolyzed kraft pulping process by several pulp manufacturers. It can be categorized as in Table 2. Other than these wood pulps, cotton linters are also utilized as high purity and high molecular weight cellulose for cellulose acetate production. The achieved properties of pulps may be different, depending significantly upon these categories.

Table 1. Typical properties of representative pulps currently available in the market for cellulose acetate production.

Manufacturer	Weyerhaeuser	Weyerhaeuser2	Rayonier	Sappi Saiccor	Rayonier2	Buckeye	Buckeye2
Raw Material	Western Hemlock	Western Hemlock and Douglas Fir	Southern Yellow Pines, Slash Pine and Loblolly Pine	Eucalyptus and Acacia	Southern Hardwood Mixture Gums and Oaks	Slash Pine	Cotton Linters
Process	Acid sulfite	Acid sulfite	Acid sulfite	Acid sulfite	Prehydrolyzed kraft	Prehydrolyzed Kraft	Continuous Digesting and Bleaching
CHEMICAL PROPERTIES							
R_{10} (%)	95.0	94.3	94.4 - 97.1	93.3	97.3 - 98.0	96.4	98.9
R_{18} (%)	96.6	96.1	96.3 - 98.5	97.1	98.5 - 99.0	98.2	99.8
S_{10}(%)	5.0	5.7	2.9 - 5.6	6.7	2.0 - 2.7	3.6	1.1
S_{18} (%)	3.4	3.9	1.5 - 3.7	2.9	1.0 - 1.5	1.8	0.2
Alpha Cellulose (Wt%)	95.5	95.0	95.3 - 97.8	94 - 96	97.9 - 98.4	97.0	99.5
Mannose (%)	1.3	1.5	0.8 - 1.2		0.3 - 0.5		
Xylose (%)	1.5	1.7	0.9 - 2.6	1.1	1.3 - 1.4		
Intrinsic Viscosity (dL/g) [Cuen] (or CPS [Cuam: Tappi T206])	7.8	8.0	7.5 - 9.5	(29 - 35) [Cuam]	6.5 - 7.5	6.8	12.2
DCM Extractives %	<0.01	0.02	0.01 - 0.08	0.02	0.01 - 0.08	0.01	0.02
Ash (%)	0.07	0.12	0.10 - 0.20	0.03	0.05 - 0.15	0.05	0.02
Calcium (mg/kg)	15	20	10-30	30	0.001 - 0.010	25	17
Iron (mg/kg)	2	2	1 - 10	1	1 - 10	1	3
Manganese (mg/kg)	0.1	0.1	0.1 - 1.0	0.4	0.1 - 1.0	<0.08	<0.1
SiO_2 (mg/kg)	40	40	10-50	40	0.001 - 0.008	30	12
PHYSICAL PROPERTIES							
Basis Weight (g/m^2)	680	680	830 - 875	740	740 - 760	709	553
Moisture (%)	7.5	6.5	6.0 - 8.0	6 - 9	6.0 - 8.0	7.0	6.8
Caliper (mm)	1.5	1.2	1.4 - 1.8	1.6	1.4 - 1.8	1.3	1.0
Sheet Density (kg/m^3)	450	570	450 - 650	460	420 - 480	558	573
Mullen (kPa)	320	400	300-500	300	220-400	1000	400
Burst Index (kN/g)	0.47	0.59	0.36-0.57	0.41	0.30-0.53	1.41	0.72
Hardness Index	212	339	180-360	188	150-250	787	412
Tappi Brightness (ISO Equiv)	96.0	95.3	91.0 - 94.0	94.4	92.0-94.0	90.0	90.5
FIBER QUALITY ANALYZER							
FQA WAFL (mm)	1.5	1.7		0.8		2.3	1.8
FQA Coarseness (mg/100m)	14.8	17.6		0.1		25.3	27.7
Fibers/g (X 10^6)	12.4	9.3		-		1.74	2.00

Table 2. Dissolving pulp manufacturers and their pulping process for wood species adopted.

Pulping / Wood	Acid Sulfite	Prehydrolyzed Kraft
Softwood	Weyerhaeuser Rayonier	Buckeye
Hardwood	Sappi Saiccor	Rayonier

2.3.3.2 R_{10}, R_{18}, S_{10}, S_{18}

These values of R_{10}, R_{18}, S_{10} and S_{18} designate the degree in the solubility of pulp in 10% or 18% sodium hydroxide under a specified condition (described in Tappi T 235), indicating the level of cellulose purity. The soluble portion (%) of pulp in 10% and 18% NaOH is referred to as S_{10} and S_{18}, respectively, while the residual portion (%) is referred to as R_{10} and R_{18}. It is generally known that 10% NaOH can dissolve degraded short chain cellulose as well as the most of hemicelluloses in pulp, whereas 18% NaOH dissolves the most of hemicelluloses with a minimum of the degraded cellulose. Therefore, S_{10} minus S_{18} nearly equals the amount of the degraded cellulose, and R_{10} can be a measure of the long chain cellulose.

2.3.3.3 Alpha Cellulose

Alpha cellulose is determined as insoluble portion (%) in 17.5% NaOH under a specified condition (described in Tappi T 203). This is a representative method for the evaluation of cellulose purity, but widely replaced by R_{10} and R_{18}. The alpha cellulose content (%) of pulp usually shows the value between those in R_{10} (%) and R_{18} (%). In general, alpha cellulose content higher than 95% is appropriate for cellulose acetate production. The values in Table 1 are above 94%, all being those between R_{10} and R_{18}.

Impurities of hemicelluloses and degraded cellulose have considerably different properties from those in normal long chain cellulose and give rise to some problems for cellulose acetate production. It has been reported since 1950s that the formation of hemicellulose acetates causes haze, false viscosity, coloring and poor filterability of cellulose acetate solution.[2-17] Degraded short chain cellulose is readily lost during washing or during other process of cellulose acetate production, compared to the long chain cellulose, so that the pulp with the degraded short chain cellulose is more likely to decrease the yield of cellulose acetate from pulp. Therefore, only pulp with alpha cellulose content of more than around 95% has been utilized for cellulose acetate production.

However, there exists a limit to prepare wood pulp with high purity of cellulose from several points of views. The yield of pulp from wood chip decreases with an increase of cellulose purity and the severer pulping condition causes degradation of cellulose in a greater extent. The alpha cellulose content of wood pulps in Table 1 is ranged from 94.0% (Sappi Saiccor) to 98.4% (Hardwood pulp: Rayonier). In more detail, prehydrolyzed kraft pulp is above 97.0%, whereas acid sulfite pulp is between 94.0% and 97.8%. Therefore, prehydrolyzed kraft process is more suitable for producing high purity pulp than acid sulfite process. However, the alpha cellulose content of wood pulp is still considerably lower than that of cotton linter pulp (99.5%: Buckeye).

2.3.3.4 Mannose, Xylose Content

Mannose and xylose are representative neutral monosaccharides contained as hemicellulose in dissolving wood pulp. Mannose is derived from glucomannan, while xylose is derived from xylan. Several methods have been proposed to determine the content of these hemicelluloses. For example, pulp is first acid-hydrolyzed to be monosaccharides. Liquid chromatography can be directly applied to the hydrolysate.[21] Otherwise, gas chromatography can be applied to the sample obtained by full-acetylation following reduction of the monosaccharides (that is an alditol-acetate procedure).[22]

There have been many studies reporting the effect of glucomannan and xylan on cellulose acetate property. It was often reported for acetone solution of cellulose diacetate that glucomannan acetate was a main cause of false viscosity and poor filterability,[2, 4-7, 9, 10, 13] while xylan acetate was a main cause of haze, poor filterability and coloring.[6, 8, 10, 13] Moreover, some papers reported that the effect of hemicellulose acetate on the properties of cellulose acetate depended on their structure such as the degree of branching, species and amounts of functional groups, the crystallinity of cellulose or the combination of wood species and pulping process.[6, 8, 12-14] Therefore, it is essential to remove hemicelluloses as much as possible. Dissolving wood pulps that are available in the market for cellulose acetate production contain mannose in a range between 0.3 and 1.5%, while 0.9 and 2.6% in xylose content as shown in Table 1. Therefore, these levels of mannose and xylose contents are the range of acceptance as raw materials for cellulose acetate production.

2.3.3.5 DCM Extractives

This can measure the amount of the soluble portion (%) of pulp in dichloromethane (DCM) extracted with a Soxhlet extractor, consisting of non-cellulosic organic impurities such as fatty acids, fats, resins, waxes, tannins and sterols. These are minor impurities, but are more likely to affect the color or other acetate properties.

2.3.3.6 Intrinsic Viscosity

The degree of polymerization (DP) of pulp is often estimated by intrinsic viscosity (I.V.) of the solution of pulp in some solvent. In Table 1, intrinsic viscosity measured with cupriethylenediamine hydroxide solution (usually referred to as cuene I.V.) is shown. Weight average DP (DP_w) can be calculated from cuene I.V. by the following formula.[23]

$$\text{Cuene I.V.} = 0.0226 \times DP_w^{0.76}$$

For example, 8.0 in I.V. corresponds to 2,260 in DP_w. As cellulose acetate is produced under a constant condition, DP of pulp should have some influence on DP of resulting cellulose acetate but is not a dominant factor. Other factors such as the fiber structure of pulp and intrinsic properties of pulp due to the differences in pulping process significantly affect the DP of cellulose acetate. It should be noted in Table 1 that I.V. is more or less the same among the wood pulps. However, that of the cotton linter is considerably larger than that of wood pulp which can result in the larger molecular weight of cellulose acetate from cotton linter.

2.3.3.7 Mullen, Burst Index and Hardness Index (refer to Tappi T 403)

Mullen means the bursting strength defined as the pressure required to cause rupture of the pulp sheet under a specified condition. The ratios of mullen (kPa) to basis weight (g/m^2) and caliper (mm) are referred to as burst index and hardness index, respectively.

Physical properties such as mullen, density, hardness index and basis weight are closely related to the easiness in disintegrating pulp sheet, especially under the dried condition. The insufficient disintegration of pulp sheet occasionally increases the amount of unreacted 'insoluble' fiber residues in cellulose acetate and results in haze and poor filterability of cellulose acetate solution. More easily and more uniformly disintegrative sheet with, for example, lower mullen or lower density is required for cellulose acetate production than cellulose ether production in which the stronger swelling agent (NaOH) can be used. These physical properties are also important for cellulose acetate production, although chemical properties, especially the highness of cellulose purity, are the more fundamental characteristics of acetate grade pulp.

2.3.4 Potentials of Low-Grade Dissolving Pulp for Cellulose Acetate Production

It is generally known that only highly purified wood dissolving pulp with an alpha cellulose content of more than 95% or linter pulp can be used as a starting material for cellulose acetate production. The yield for such a highly purified pulp from wood is less than 50% on a wood basis as a result of removal of obstructive impurities such as lignin, hemicelluloses and degraded cellulose. The effective usages of these removed components, which are precious biomass resources, have not been necessarily established in spite of extensive studies. They are so far mainly used for heat fuel for the pulping process. Moreover, pulping is generally known as an energy-consuming process. It is, therefore, significant and efficient to simplify the pulping process if the low-grade wood dissolving pulp with a high yield can be available for cellulose acetate production.

The lower-grade dissolving pulp from wood contains more obstructive impurities. There have been considerable studies since the mid-1950s to elucidate the effects of the impurities on the resulting properties of cellulose acetate. For example, it is known that the main impurity in wood dissolving pulp is hemicelluloses, and the formation of hemicellulose acetates are supposed to result in haze, false viscosity and poor filterability of cellulose acetate in its acetone solution as described in the previous section.[2-17] Some remedies were proposed to solve these problems. However, most of these studies were focused on wood dissolving pulp with an alpha cellulose content of more than 95%, and only a few studies [21, 24-28, 29] were on low-grade dissolving pulp with an alpha cellulose content of less than 90% which has not been used for cellulose acetate production yet.

Saka and coworkers have studied about cellulose triacetates prepared from low-grade softwood sulfite pulp (alpha cellulose: 87.5%) [24-28] and low-grade hardwood prehydrolyzed kraft pulp (alpha cellulose: 86.2%) [21, 29] by a general acetylation system with a reaction medium comprising acetic anhydride, acetic acid and sulfuric acid. In this system, a considerable amount of insoluble residues in the swollen state with fiber structure was present in the acetylation solution for both the low-grade pulps (Tables 3 and 4), while high-grade dissolving pulp was dissolved almost completely.[21, 24] The formation of these insoluble residues was supposed to be the most serious problem to utilize the low-grade pulps. They, therefore, made a characterization of the insoluble residues to elucidate their formation mechanisms and studied remedies for reducing the insoluble residues.

Table 3. Weight fraction and chemical composition of soluble and insoluble portions in cellulose triacetate prepared from low-grade softwood sulfite pulp (alpha cellulose:87.5%).

Sample	Weight fraction (%)	DS	Neutral sugar composition (mol%)		
			Glucose	Mannose	Xylose
Low-grade pulp (Softwood sulfite)	-	-	90.4	7.0	2.6
Soluble	87.0	2.98	92.0	5.7	2.3
Insoluble	13.0	3.01	71.1	28.2	0.7

Table 4. Weight fraction and chemical composition of soluble and insoluble portions in cellulose triacetate prepared from low-grade hardwood prehydrolyzed kraft pulp (alpha cellulose:86.2%).

Samples	Weight fraction (%)	DS	Neutral sugar composition (mol%)		
			Glucose	Mannose	Xylose
Low-grade pulp (Hardwood kraft)	-	-	78.8	0.2	21.0
Soluble	76.2	2.94	94.5	0.2	5.3
Insoluble	23.8	2.22	34.8	0.4	64.8

On chemical composition, the mannose content of insoluble residue for the low-grade softwood sulfite pulp was much greater than those of soluble portion and original pulp (Table 3),[24] while the insoluble residue of the low-grade hardwood prehydrolyzed kraft pulp was rich in xylose (Table 4),[21] indicating that the glucomannan in softwood sulfite pulp and the xylan in hardwood prehydrolyzed kraft pulp play an important role in the formation of insoluble residues.

In conclusion, the insoluble residue from the low-grade softwood sulfite pulp was found to be formed by the physicochemical effects of the molecular interactions of cellulose triacetate (CTA) and glucomannan triacetate (GTA) as well as by the ultrastructural effects of the pulp fibers.[24] The former effects are due to molecular aggregation of CTA and GTA by their compatible nature, whereas the latter effects originate from the ultrastructural distribution of the residual glucomannan in the dissolving pulp. On the other hand, the formation of the insoluble residues from the low-grade hardwood kraft pulp is due only to the ultrastructural effects of the pulp fibers in which intrinsic properties of xylan diacetate (XDA) on solubility in the acetylation solution are involved.[21] In other words, the solubility of XDA to the acetylation solution is poor so as to tend to precipitate and CTA was involved in the precipitate due to the ultrastructural effects of the pulp fibers.

These results show that if physicochemical effects and/or ultrastructural effects can be decreased, it is effective to reduce the amount of insoluble residues.

A model experiment showed that the physicochemical effects are dependent on the molecular weight of GTA for the softwood sulfite pulp, meaning that the degraded glucomannan forms less insoluble residue. For example, insoluble residue was reduced by pretreating the low-grade softwood sulfite pulp with a mixture of sulfuric acid and acetic acid before acetylation or by increasing the amount of sulfuric acid catalyst during acetylation.[25, 26] In these cases, the ultrastructural effects might be also reduced to some degree because pulp fibers were more destroyed than usual during the pretreatment or the acetylation. Moreover, the insoluble residue for the softwood sulfite pulp was found to be significantly reduced by adding methylene chloride or some other good solvents for GTA to acetylation medium.[25, 27, 28] Similarly, the addition of good solvent for XDA such as dichloroacetic acid to the acetylation medium was found to be very effective for the low-grade hardwood kraft pulp.[21, 29] On the whole, treatments increasing the solubility of the problematic component, which is GTA for softwood sulfite pulp and XDA for hardwood kraft pulp, are effective for reducing the amount of insoluble residues without removing the impurities. This finding shows the potential usage of low-grade pulps as raw materials for cellulose acetate production.

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