Molecular weight characterization of wood pulp cellulose: Dissolution and size exclusion chromatographic analysis

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ABSTRACT

Wood pulp celluloses dissolved in N,N,-dimethylacetamide-lithium chloride solubilized cellulose components without prior extraction or derivatization and resulted in stable solutions. Optimum dissolution conditions depended highly on the molecular weight, crystallinity, and lignin content of the sample. Size exclusion chromatography with polystyrene standards provided molecular weight distributions. The data showed different molecular weight distributions, peak locations, and molecular weights for each sample and revealed whether random or uniform depolymerization had occurred during processing.

Application:

An understanding of the physio-chemical processes that affect cellulose during pulping and bleaching provides information in dissolving pulp production where depolymerization control is critical.

IN THE PRODUCTION OF CHEMICAL pulp, wood carbohydrates undergo vigorous depolymerization that can proceed either uniformly or nonuniformly. It therefore is not possible to control the amount of low molecular weight (MW) compounds in the product and of carbohydrates dissolved in the effluent. Monitoring pulp cellulose viscosity cannot minimize these undesirable effects. Accurate information about changes in the MW and molecular weight distribution (MWD) of the wood pulp is necessary.

Previous studies have characterized values of MW of pulp celluloses by methods such as fractionation or gel permeation chromatography—size exclusion chromatography (SEC)—of cellulose derivatives. Fractionation methods are tedious and impractical for routine analysis. Gel permeation chromatography is more practical, but it requires converting cellulose into a derivative that dissolves in organic solvents. This derivatization exposes the cellulose chains to degradation *(1)*. In addition, incomplete or nonuniform substitution may influence the solubility of the product *(2)*. In either case, the MWD of the derivative will differ from that of the underivatized cellulose. There is therefore a need for specific solvents, dissolution methods, and chromatographic techniques suitable for the characterization of pulp cellulose MW.

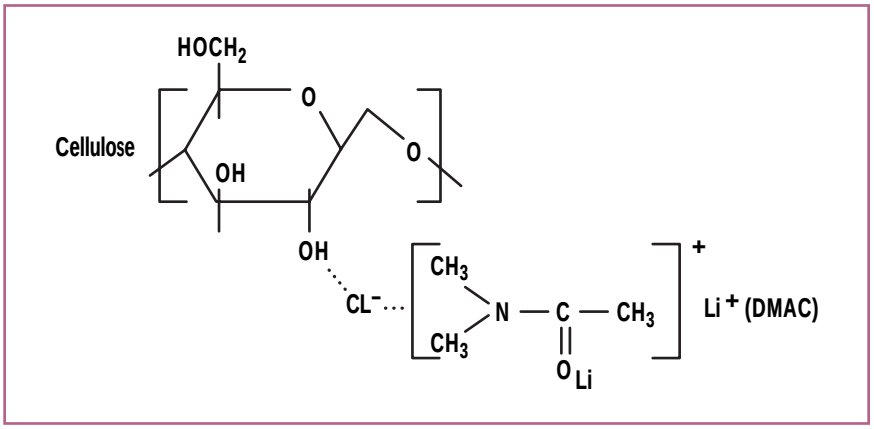
The purpose of this study was to investigate methods of obtaining meaningful values for MW and MWD for pulp celluloses through use of SEC and appropriate dissolution techniques in the nondegradative cellulose solvent system, N-N-dimethylacetamide-lithium chloride (DMAC/LiCl). We assessed total changes in the pulp cellulose MW as a function of various chemical processes including pulping and bleaching.

DMAC/LiCl SOLVENT SYSTEM

A recently discovered solvent system for cellulose is a mixture of N-N,-dimethylacetamide (DMAC) and lithium chloride (LiCl) *(3, 4)*. Evidence suggests that this solvent system effects dissolution by complex formation *(3)*. In McCormick's *(5)* proposed dissolution mechanism in **Fig. 1,** the hydroxyl protons of the anhydroglucose units and the chloride anions from the dissociated salt form hydrogen bonding. The chloride anion also associates with a Li^+(DMAC) macrocation. Each hydroxyl group in a cellulose molecule complexes with only one LiCl molecule *(6)*. Dawsey *(7)* postulated that the interaction of the chloride anion with the hydroxyl protons would result in competitive hydrogen bond formation and disruption of the intermolecular hydrogen bond structure. He thought that the accumulated associations of Cl^- along the cellulose chain would produce an anionically charged polymer with the macrocation $(Li\text{-}DMAC)^+$ as the counterion. The net effect on the molecule would be a charge-to-charge repulsion. Continuous influx of the solvent would further disrupt the cellulose binding forces until there was complete solvation of the polymer *(7)*.

SEC

SEC is the preferred method of determining MW and MWD. Differences in effective molecular size in solution separate sample molecules. A column packed with material having a broad distribution of pore sizes separates solvated molecules. The column packing does not retain molecules too large to penetrate any of the pores so they elute first. The column retains smaller molecules that penetrate some pores causing them to elute later. The smallest molecules that penetrate all the pores retain on the column longest and elute last *(8)*. The consistency of this technique allows for the determination



1. Mechanism of cellulose dissolution in the LiCl/DMAC solvent system

Cellulose samples	Characteristics and treatments
PCELL 1	Softwood, semi-bleached (C-E-H)* kraft pulp
PCELL 2	Hardwood, semi-bleached kraft pulp
PCELL 3	Prehydrolyzed softwood kraft pulp
PCELL 4	Softwood, bleached (D-O-E-D-P)* sulfite/magnesium-based pulp
PCELL 5	Hardwood, unbleached kraft pulp
PCELL 6	Hardwood, bleached (C_D-E_P-D)* kraft pulp
PCELL 7	Softwood, bleached (D_C-E_O-P-D)* kraft pulp
PCELL 8	Softwood kraft pulp (91%-cellulose)
PCELL 9	Softwood sulfite pulp (91%-cellulose)
PCELL 10	Softwood, bleached (O-C_D-E_O-p-D-E-D)* kraft pulp
PCELL 11	Hardwood-blend kraft pulp (89%-cellulose)
ACELL 1	Commercial cellulose (acid-washed)
CCELL 1	Cotton linters
SCELL 1	Nonwood fiber (straw)
RCELL1	Rayon fiber

*Multistage bleaching sequences:
C = chlorination
E = alkaline extraction
H = hypochlorite bleaching
D = chlorine dioxide bleaching
P = peroxide bleaching
C_D = chlorination with addition of chlorine dioxide
E_P = extraction with addition of peroxide
E_O = extraction with addition of oxygen
D_C = chlorine dioxide, with addition of chlorine
O = oxygen bleaching

1. Codes and characteristics of pulp cellulose

of weight-averaged MW, $\overline{M}w$; number-averaged MW, $\overline{M}n$; z-averaged MW, $\overline{M}z$; MWD; and polydispersity (PD) for polymeric materials.

MATERIALS AND METHODS

Pulp cellulose dissolution

The pulp cellulose materials came from pulp and paper mills around the Pacific Northwest. **Table I** gives an identifying code and description for each pulp. The pulp samples underwent equilibration at constant temperature of 23 ± 1°C and relative humidity of 50.0 ± 2.0% for 24–48 h to stabilize their moisture contents followed by grinding in a Wiley mill to pass through a 20-mesh screen.

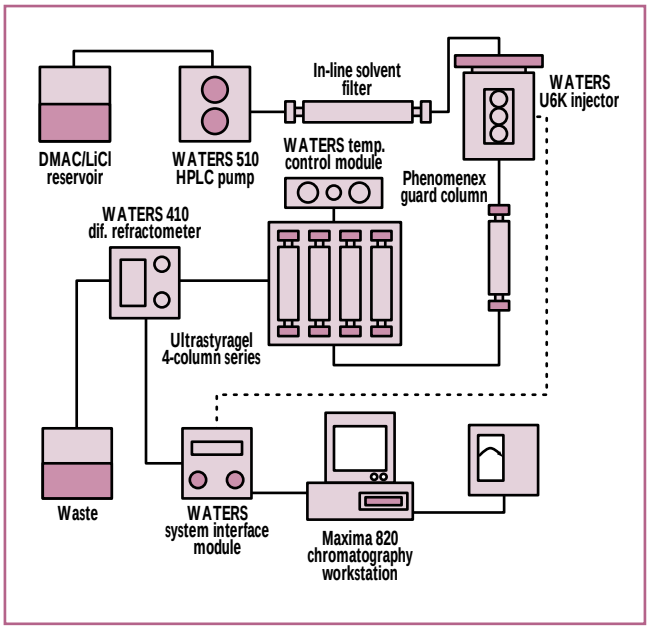
DMAC high-purity, high-pressure liquid chromatography (HPLC)–grade solvent from Burdick and Jackson, Muskegon, MI was dried for 5 days over molecular sieves from Baker. The solvent was degassed and filtered with an FH-type membrane filter having 0.45-µm pore size in a Phenomenex all glass vacuum filtration apparatus.

Pulp cellulose solutions in DMAC/LiCl were prepared by a modified method described by Timpa *(1)* for cotton fibers. Ground pulp samples were suspended in DMAC and heated to 150°C for 0.5–2.0 h. After the solutions had cooled to 100°C, dried LiCl from Baker was added. The mixture was then constantly stirred and cooled to 50°C for 12–48 h. The mixtures were stirred for another 6–24 h at 23°C until all solids were completely dissolved. The clear solutions were transferred to a 50-mL volumetric flask and diluted with DMAC. The solutions were filtered through a Millipore 0.45-µm Millex-HV filter unit before SEC injection.

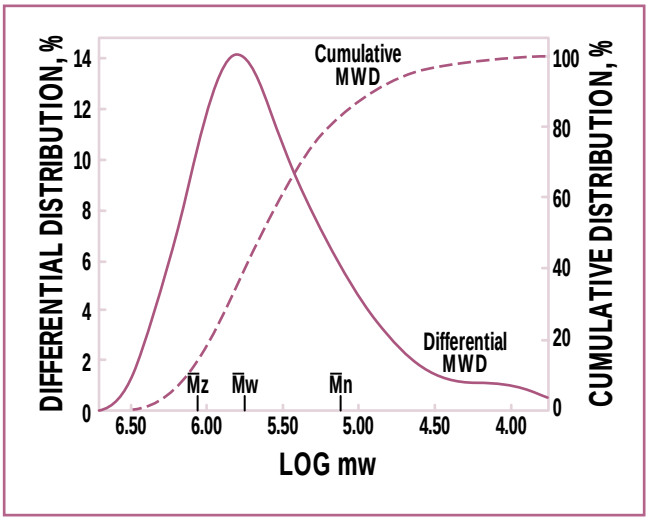
We analyzed a variety of softwood kraft, softwood sulfite, and hardwood kraft pulps bleached using the specified sequences and rayon, straw fiber, and unbleached hardwood kraft pulps. Cotton linters and commercial acid washed cellulose were the reference samples. **Table II** lists every possible combination of the operating variables used to dissolve each pulp sample.

Chromatographic analysis

The SEC system consisted of a WATERS U6K sample injector connected to a WATERS 510 HPLC pump by an in-line solvent filter, a temperature control module, and a WATERS 410 refractive index (RI) detector. Four Ultrastyragel columns from Millipore with pore diameters of 10^3, 10^4, 10^5, and 10^6 Å were mounted in series in the column heater and maintained at 80°C. The columns were preceded by a 10-µm Phenomenex guard column. The injection volume was 400 µL—100 µL per column. The mobile phase, DMAC/



2. Schematic of the size exclusion chromatographic configuration



3. Size exclusion chromatographic differential and cumulative MWD plots for PCELL1

0.5% LiCl, was pumped in at a rate of 1.0 mL/min. Each sample ran for 62 min.

The software package Maxima 820 Chromatography Option *(9)* from Millipore was run on an NEC APC IV PowerMate 2 connected to an NEC multi-mode dot-matrix printer for data acquisition, processing, and multitasking as **Fig. 2** shows. The system was calibrated with narrow distribution polystyrene standards. Three standards for each of four concentrations—0.3, 0.5, 1.0, and 1.5 mg/mL polystyrene in DMAC/0.5% LiCl—were prepared. These were used to construct the calibration curve—cubic and third order—required to determine apparent values for MW and MWD of the cellulose samples.

After chromatographic separation, the RI detector monitored the concentration by weight of the pulp cellulose in the eluting solvent. Differential and cumulative MWD curves were calculated for the SEC chromatograms. The differential MW fraction distribution curve plotted on a log MW scale was identical to the raw data SEC elution curve. The cumulative MW fraction distribution was obtained by dividing the partially integrated area for each log MW value by the total area under the curve *(10)*. Each MW curve therefore provides a graphical representation of the MW fraction vs. the logarithm of MW. The high MW region is to the left center in the distribution and the low MW region is to the right.

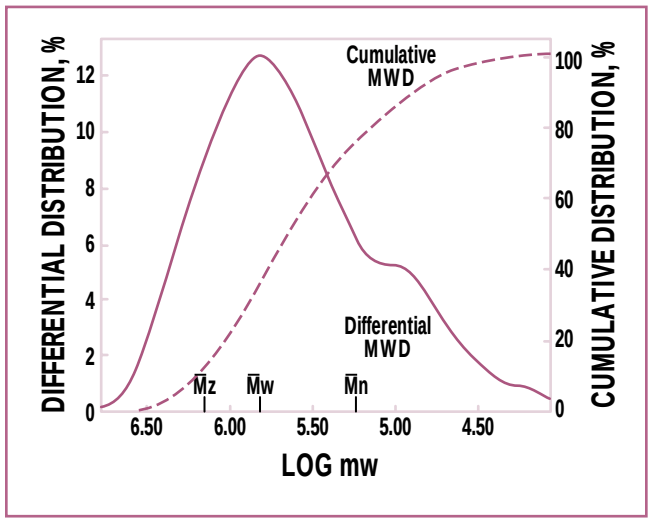
The MWD plots depict $\overline{M}w$, $\overline{M}n$, and $\overline{M}z$. A change in the high MW region affects the $\overline{M}w$ and $\overline{M}z$ values but has little effect on $\overline{M}n$. Variations in the low MW portions of the distributions—especially the presence of long, low MW tail—greatly affect the $\overline{M}n$ but have very little effect on $\overline{M}w$ and $\overline{M}z$. The breadth of the MWD is the PD defined as $\overline{M}w/\overline{M}n$. A monodisperse sample—one in which all molecules are identical—has a PD value of 1.0. Some polymers have PD values over 20 *(8)*.

RESULTS AND DISCUSSION

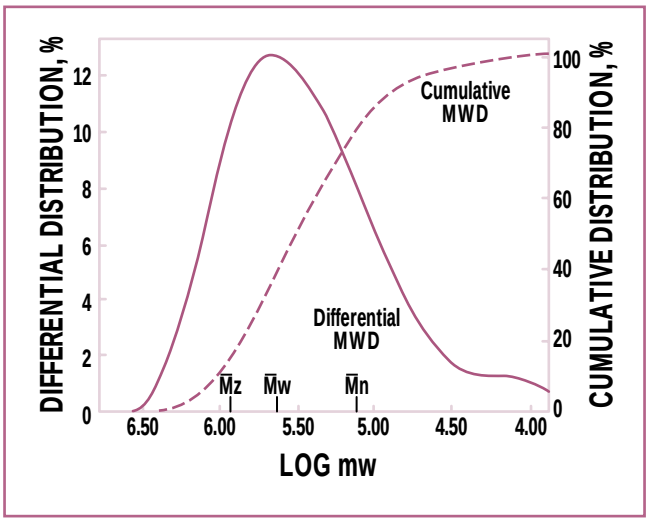
Pulp cellulose dissolution

Only a few combinations of the variables and treatments in Table II produced soluble products. A sample concentration from 0.8–1.6% weight/volume (40–80 mg/5 mL) dissolved in the solvent system. We compared these sample concentrations with those for dissolution of LiCl in the solvent system. At LiCl concentrations of 6% weight/volume (0.3 g/5 mL), suspended insoluble particles appear in the solvent even at the lowest cellulose concentration of 0.8% weight/volume. With LiCl concentrations of 8% weight/volume (0.4 g/5 mL), complete dissolution of cellulose occurred. At higher concentrations of 12% weight/volume (0.6 g/5 mL) and 16% weight/volume (0.8 g/5 mL), the solution became saturated with LiCl preventing dissolution. The mechanism of dissolution proposed by McCormick *(5)* in Fig. 1 described earlier can explain this interaction. For dissolution to occur, some complexed Li^+ (DMAC)-cellulose-Cl^- sites must form. Once the sites are fully complexed, however, addition of more salt will lead to saturation of the solution and precipitation of salt. If we ignore activation, dissolution, and stirring, these observations led to the hypothesis that only a narrow range of cellulose/LiCl values will result in acceptable dissolution. To ensure that the analysis focused on the more important elements of the dissolution process, the concentrations of pulp cellulose and the amount of LiCl added were fixed at 60 mg/5 mL (1.2% weight/volume) and 0.4 g/5 mL (8% weight/volume), respectively, throughout the subsequent dissolution analysis.

The optimal dissolution condi-



4. Size exclusion chromatographic differential and cumulative MWD plots for PCELL2



5. Size exclusion chromatographic differential and cumulative MWD plots for PCELL3

Variable	Treatments
Sample concentration, mg/5 mL	40, 50, 60, and 80
LiCl concentration, g/5 mL	0.3, 0.4, 0.6, and 0.8
Activation time, h	0.5, 1.0, 1.5, and 2.0
Dissolution time, h	12, 24, 36, and 48
Stirring time, h	6, 12, 18, and 24

II. Operation variables and treatments for dissolution of pulp samples

Cellulose samples	Activation time, h	Dissolution time, h	Stirring time, h
PCELL 1	2	48	18–20
PCELL 2	2	48	18–20
PCELL 3	2	36	18–20
PCELL 4	2	36	18–20
PCELL 5	2	48	18–20
PCELL 6	2	36	18–20
PCELL 7	2	48	18–20
PCELL 8	2	48	18–20
PCELL 9	2	48	18–20
PCELL 10	1.5	36	18–20
PCELL 11	2	48	18–20
ACELL 1	1	36	10–12
CCELL 1	1.5	48	18–20
RCELL 1	1	36	10–12
SCELL 1	2	48	18–20

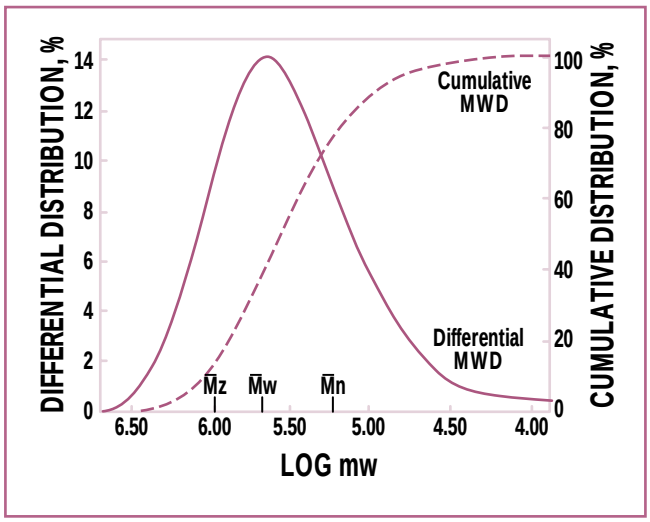
III. Optimum conditions for pulp cellulose dissolution

tions for each pulp cellulose sample were established through the dissolution analysis of **Table III**. The sample weight for the data in this table was 60 mg with 0.40 g of dried LiCl added. After dissolution, all solutions were clear. The results indicated that activation, dissolution, and stirring mainly governed the complexing of cellulose with the DMAC/LiCl solvent. The importance of each element to the process appeared to change depending on the cellulose source due to differences in MW, crystallinity, and lignin content *(1)*. Longer activation, dissolution, and stirring times were necessary in cellulose that was more crystalline (cotton linters), higher in MW (semi-bleached pulps), higher in α-cellulose content, and higher in lignin content (unbleached pulp). The shortest activation, dissolution, and stirring times were in the two samples with the lowest MW as **Table IV** shows. Results in Table IV are the average of four replicates—two dissolutions per sample with two SEC runs per dissolution.

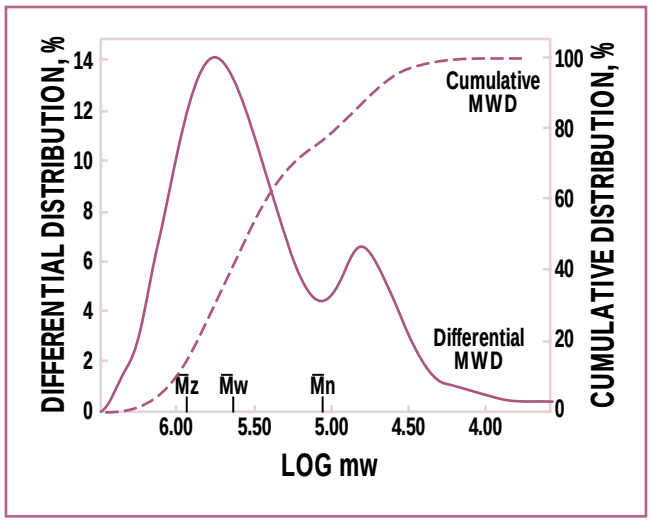
Despite its lignin content, the unbleached pulp dissolved completely after the dissolution reaction. The fact that this sample had a slow rate of dissolution was problematic given its less crystalline nature compared to cotton linters. Perhaps the chemical reactions that occur in pulping provide an explanation for the phenomenon. Because lignin and carbohydrate components are closely associated in wood *(11)*, it is not surprising that bonds exist between them. Although lignin components degrade in kraft pulping of wood, condensation reactions could occur almost simultaneously. Some condensed lignin material might have redeposited on the separated fibers resulting in the longer dissolution time.

SEC analysis of the pulp cellulose solutions

Table IV summarizes the average values for MW and PD obtained from SEC analysis of the cellulose solutions. The highest MW values occurred in pulp samples of different wood origin—PCELL1 and PCELL2. This was not surprising since both pulp samples were semi-bleached. In semi-bleached pulps, the application of chemicals was lim-



6. Size exclusion chromatographic differential and MWD plots for PCELL4



7. Size exclusion chromatographic differential and cumulative MWD plots for PCELL5

ited to minimize cellulose degradation and still attain a target brightness. The substantial amount of materials intentionally retained in the samples likely resulted in the high MW values. A comparison of the SEC MWD plots for PCELL1 and PCELL2 in **Figs. 3 and 4** suggests a broader and semi-bimodal curve for PCELL2. Its higher PD value reflects this.

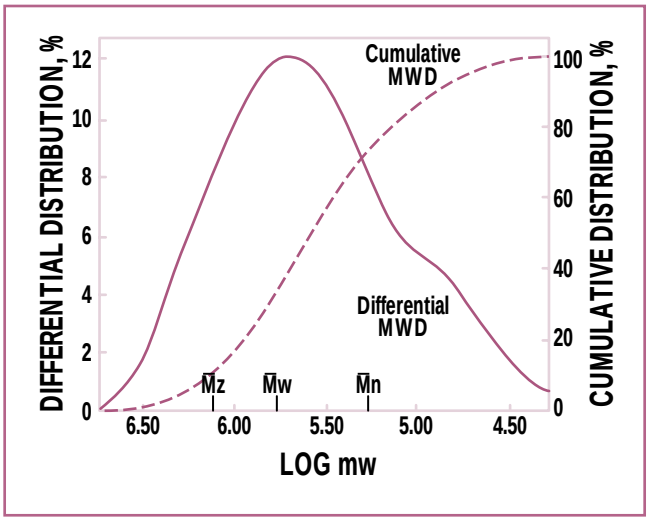
The MW averages for PCELL3, a prehydrolyzed, softwood kraft pulp, were low. As the SEC MWD plot in **Fig. 5** shows, a wide but symmetrical distribution occurred despite the high PD value obtained. The low MW averages probably resulted from the hydrolytic degradation of cellulosic components in the sample during prehydrolysis—a pulping step used to partially depolymerize hemicelluloses with little effect on cellulose *(12)*. Considerable amounts of low MW components occurred in the low MW region of the distribution plot resulting in the high PD value.

PCELL4 was a softwood sulfite, magnesium-based pulp bleached according to the D-O-E-D-P sequence. As Table IV shows, the MW averages for the sample were low. The low PD value of 2.777 is apparent in the narrow symmetrical distribution observed in the MWD plots of **Fig. 6**. A plausible explanation for the low MW value is that the combined effect of chlorine dioxide (D) and oxygen (O) in the bleaching process resulted in drastic cellulose depolymerization. Because of the symmetrical MWD, one may further theorize that the depolymerization took place randomly leading to substantial losses in both high and low MW molecules during the bleaching process.

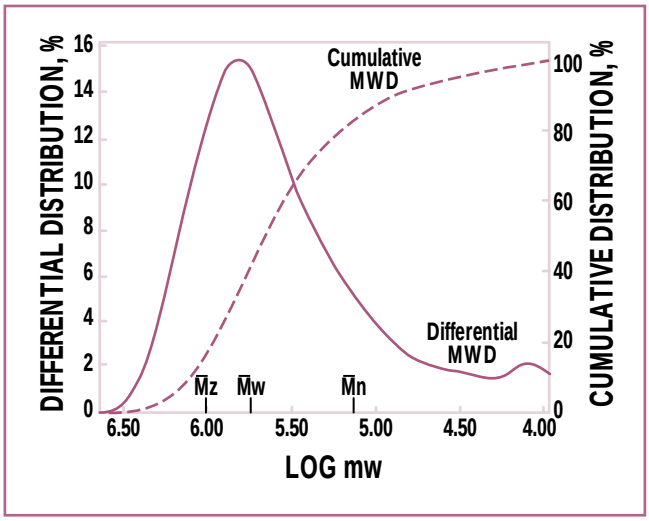
Cellulose samples	M̄w	M̄n	M̄z	PD
PCELL 1	645,745	167,782	1,495,538	3.773
PCELL 2	640,995	161,767	1,424,815	4.912
PCELL 3	419,923	125,163	853,816	3.031
PCELL 4	465,946	166,202	922,958	2.777
PCELL 5	546,423	137,926	1,099,437	6.266
PCELL 6	433,517	119,078	839,743	3.391
PCELL 7	524,920	145,227	1,091,947	3.308
PCELL 8	551,109	132,240	990,805	4.140
PCELL 9	559,243	106,995	1,424,933	5.378
PCELL 10	379,532	113,776	755,208	3.340
PCELL 11	529,449	101,232	1,580,853	4.232
ACELL 1	211,987	58,152	524,264	3.635
CCELL 1	360,535	196,879	642,547	1.678
RCELL 1	219,128	115,799	382,604	1.784
SCELL 1	424,443	118,368	852,929	8.853

IV. Apparent average MW and PD values of the pulp celluloses from SEC analysis using 60 mg sample weight and 0.40 g dried LiCl added

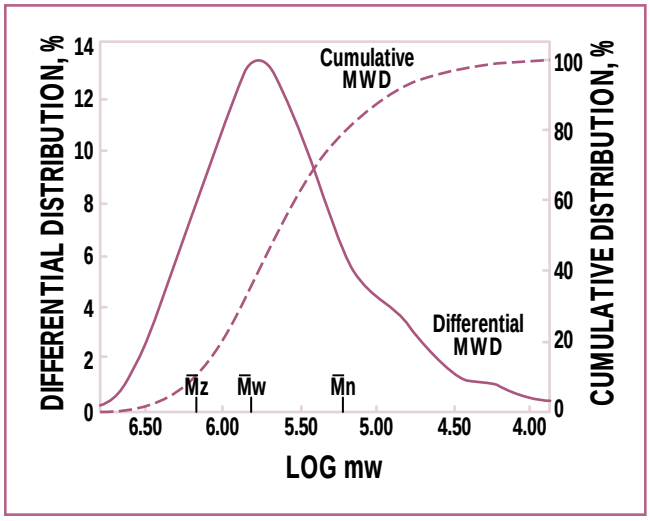
An unbleached, hardwood kraft pulp, PCELL5, analyzed for comparison gave intermediate MW averages and PD values as Table IV shows. As noted earlier, this pulp dissolved in DMAC/LiCl although it contained lignin. The bimodal distribution of **Fig. 7** led to the appearance of a double peak in the MWD. The major elution peak corresponded to higher MW components, and the smaller elution peak corresponded to lower MW components—possibly hemicellulose and lignin fragments. Identification of the high MW components posed some problems. The distribution of the molecules in the higher MW region and the high PD value seemed to confirm hypothetical explanations of how the kraft



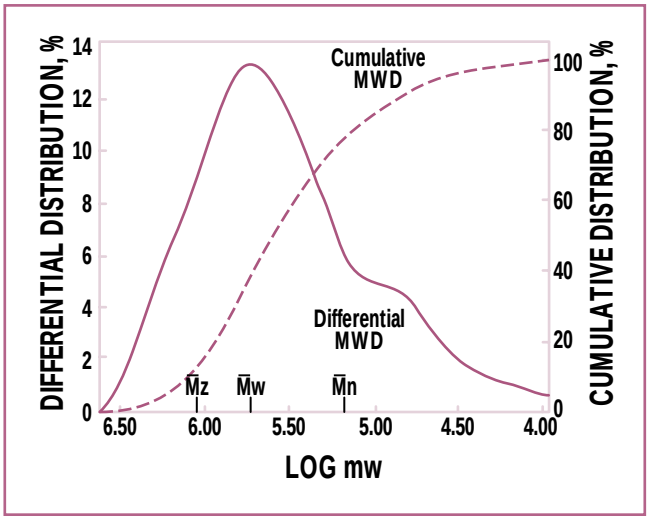
8. Size exclusion chromatographic differential and cumulative MWD plots for PCELL6



9. Size exclusion chromatographic differential and cumulative MWD plots for PCELL7



10. Size exclusion chromatographic differential and cumulative MWD plots for PCELL8



11. Size exclusion chromatographic differential and cumulative MWD plots for PCELL9

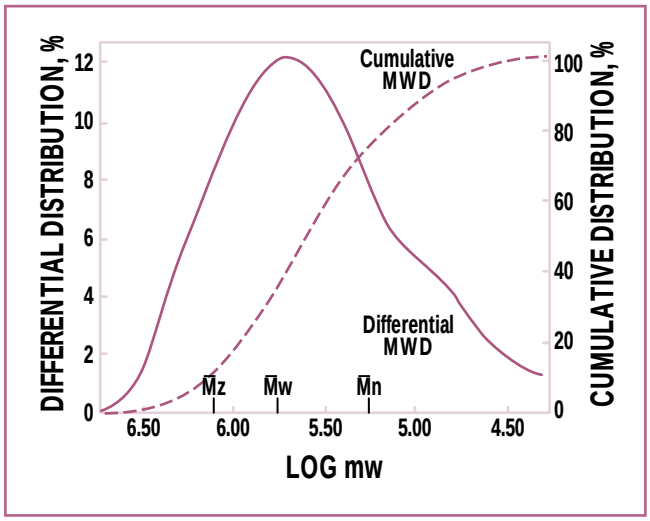
process proceeds in pulping. Smook *(13)* explained that during a typical kraft cook approximately 80% of lignin, 50% of hemicellulose, and 10% of cellulose dissolve. With the proper conditions, the lignin fragments can take part in condensation reactions with other lignin fragments, undissolved lignin, and possibly with carbohydrates. It therefore would be difficult to determine the composition of the high MW components since these components may be partially condensed lignin.

PCELL6 and PCELL7 are samples of bleached kraft pulp from hardwood and softwood, respectively. The sequence C_D-E_P-D bleached PCELL6, and the sequence D_C-E_D-P-D bleached PCELL7. The MWD values of **Figs. 8 and 9** appear skewed and asymmetrical in the low MW region. The high PD value in both pulp types is the result of the small peaks for each distribution. The MW averages were higher in the softwood kraft pulp.

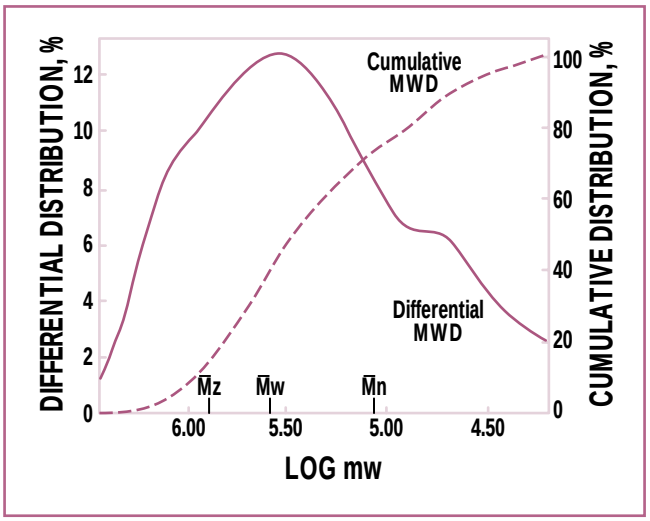
Figures 10 and 11 show the MWD for two softwood kraft pulps—one kraft, PCELL8, and one sulfite, PCELL9—having roughly the same α-cellulose content of 91%. Distinct distortions in the low MW region of the MWD for both samples indicated the presence of hemicellulose. The high PD values reinforced this. There were higher MW values for the sulfite pulp.

Figure 12 shows the MWD plot of a softwood kraft pulp, PCELL10, bleached using the O-C_D-E_O-P-D-E-D sequence. Because of the wide variation in the MWD, the PD value is high. MW averages were low. The most likely explanation is that extensive cleavage caused by the bleaching chemicals occurred within the cellulose molecule in the successive bleaching sequences.

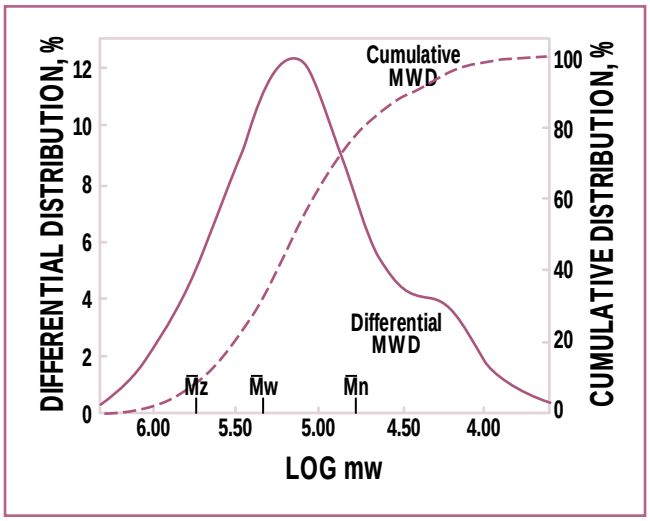
A hardwood blend kraft pulp, PCELL11, having high strength,



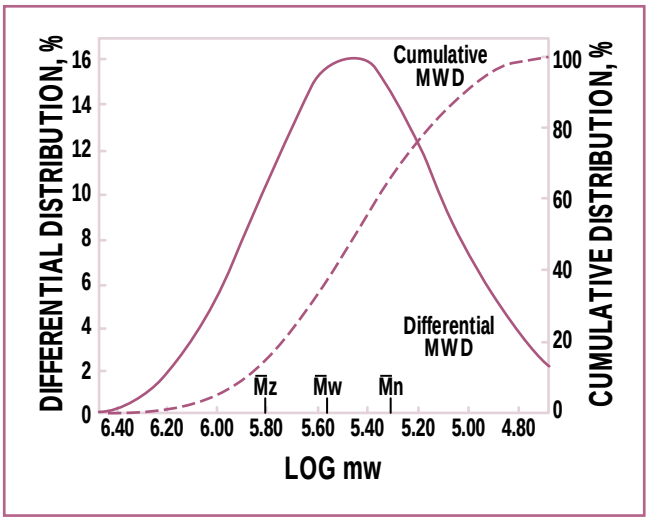
12. Size exclusion chromatographic differential and cumulative MWD plots for PCELL10



13. Size exclusion chromatographic differential and cumulative MWD plots for PCELL11



14. Size exclusion chromatographic differential and cumulative MWD plots for ACELL1



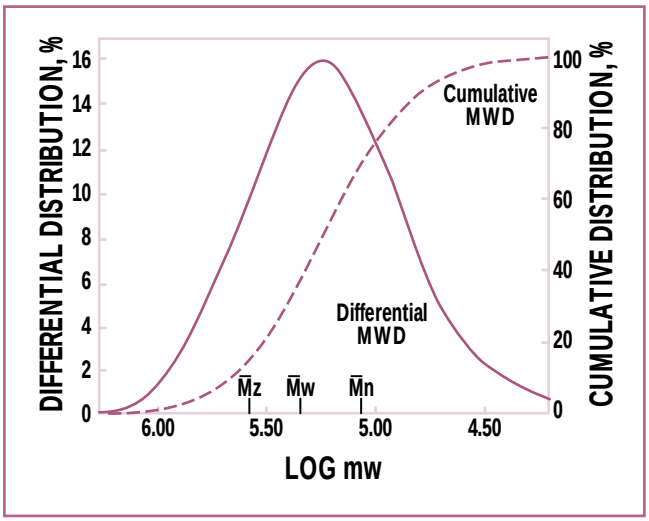
15. Size exclusion chromatographic differential and cumulative MWD plots for CCELL1

excellent opacity, and 89% α-cellulose content had high MW averages and PD values. The MWD in **Fig. 13** reveals that the high PD value was probably due to the presence of high MW components in the distribution as evidenced by a conspicuous shoulder in the higher MW region.

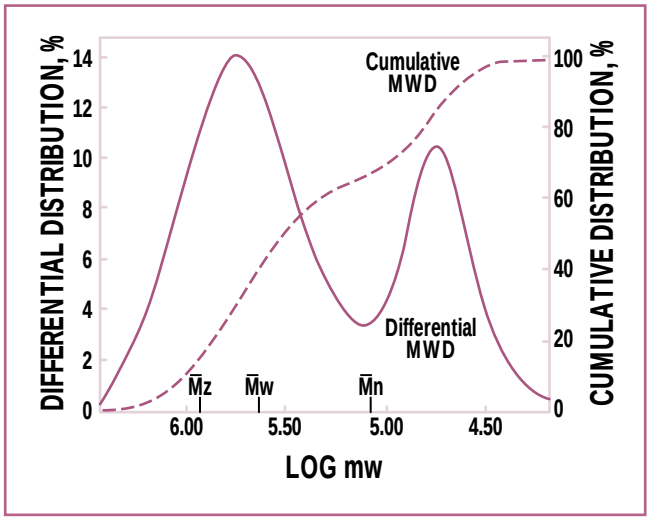
Figure 14 reveals the MWD plots of a commercial acid-washed cellulose sample, ACELL1. A shoulder in the low MW region caused the PD value to increase. The MW averages were the lowest among the analyzed samples. This is probably due to the dramatic effect of acid on the sample. To confirm the results obtained by our method and to demonstrate the validity of this conventional calibration, it was necessary to compare our findings to Timpa's *(1)* universal calibration method. The MW averages for this sample agreed with those of Timpa for the same type of sample. The similarities between the results obtained with the divergent calibration methods supports the use of conventional calibration techniques in SEC analysis provided the polymer samples are completely dissolved and not derivatized.

Cotton linters are the short fibers remaining on the seeds after removal of long fibers. The MWD for cotton linters, CCELL1, was narrow and symmetrical as **Fig. 15** shows. The low PD value of 1.678 reflects this. MW averages were low because the sample consisted of short fibers. A sample of rayon fiber, RCELL1, exhibited the uniform, symmetrical MWD shown in **Fig. 16**. The MW averages in this sample were also low.

We included a sample of nonwood fiber, straw, SCELL1, in the analysis to test further the applicability of this method. Straw has less cellulose but more pentosan than wood *(14)*. The MW averages in Table IV are intermediate, although the PD value of 8.853 was the highest



16. Size exclusion chromatographic differential and cumulative MWD plots for RCELL1



17. Size exclusion chromatographic differential and cumulative MWD plots for SCELL1

obtained among the samples. The appearance of two major peaks in the MWD plots in **Fig. 17**—one in the higher MW region and the other in the lower MW region—was reflected in the two-fold increase in the PD of the sample. They suggested the wide range of molecular sizes present in the sample. The major peak in the lower MW region was most likely due to the pentosans.

CONCLUSIONS

The DMAC/LiCl solvent system dissolves pulp celluloses without prior extraction or derivatization. Under optimal conditions, it yields controlled soluble products. The dissolution conditions highly depended on factors like MW, crystallinity, and lignin content of the cellulose sample. SEC can analyze the resulting cellulose solutions.

KEYWORDS

Acetic acid, amides, cellulose, chlorides, chromatography, depolymerization, dissolving, lithium chloride, lithium compounds, methyl groups, molecular weight, molecular weight distribution, number average molecular weight, pulps, weight average molecular weight.

The SEC experiments revealed a variety of information regarding the characteristics of the cellulose samples. Identification of small fractions of both high and low MW material present in the pulp samples provides considerable information on the degree of depolymerization in pulp processing operations. In addition, the symmetry of the MWD curves clearly supported the MW averages and PD values.

The findings of this study provide a basis for understanding the many physio-chemical processes that affect cellulose during pulping and bleaching. Such information is vital in dissolving-pulp production where the control of depolymerization at certain processing stages is a critical consideration. **TJ**

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