

QUANTIFICATION OF UF AND PF RESINS IN MDF FIBER WITH AN X-RAY FLUORESCENCE SPECTROMETER

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ABSTRACT

This article describes methods to quantify urea-formaldehyde (UF) resin and phenol-formaldehyde (PF) resin contents in medium density fiberboard (MDF) using a wavelength dispersive X-ray fluorescence spectrometer (WDXRF). The methods are based on the principle that a specific metallic element shows its characteristic X-ray fluorescence spectrum, the intensity of which is correlated quantitatively to its concentration. In the case of UF-blended MDF fiber, 2.4% copper sulfate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (based on resin solids) was premixed with the resin as a labeling agent. Quantification of copper ion was performed using XRF. Based on calibrations with laboratory-prepared standard fiber samples of known UF resin and copper quantities, the results of XRF measurements were converted to resin loading rates. In the case of PF-blended fiber, the PF resin contents in the MDF fiber samples were successfully quantified by measuring the existing sodium ion Na^+ in the resin with XRF. Linear calibration curves between fluorescence intensity of copper or sodium and resin content were established respectively for UF and PF resins. Test results show that the methods were precise and reliable.

Keywords: X-ray fluorescence spectrometer, urea-formaldehyde resin, phenol-formaldehyde resin, copper sulfate, sodium, medium density fiberboard, distribution, uniformity, resin content, resin distribution and fiber.

INTRODUCTION

X-ray was discovered by the German scientist Röntgen in 1895 (Bertin 1971). It is an electromagnetic wave. For over 100 years, it has been widely used in many areas and different scientific disciplines, including medical science and

service, biology, genetics, nuclear physics, structure of materials, photochemistry, and many other scientific fields. It also has a long history of application in the field of wood science and forest engineering (Clark 1955). In 1939, Preston used X-ray to study the cell-wall structure of softwood species (Preston 1939; Preston and Allsopp 1939). Wangaard (1942) studied the structure of wood using X-ray diffraction. Preston

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(1947) carried out further research on the differentiation of fiber between normal wood and tension wood in beech. Bersadskii (1956) analyzed stress distribution of lumber during the sawing process using X-ray photography. A U.S. government report was presented (1946) on using X-ray diffraction as a measure of degree of cure of phenolic resin in laminated wood products. Chow (1974) developed a method to test resin cure using X-ray spectrophotometry and KBr mixed within resin matrix. Ryan (1986) presented a technique for X-ray analysis in the transmission electron microscope of wood treated with chromated copper arsenate. With this technique, a reliable and reproducible X-ray photography was obtained from tracheid S2 layer. In recent years, use of X-ray technology is more common in the industry and research of forest and wood composite products. X-ray technology, coupled with modern computer technology, has been applied to the research of wood density, moisture content, detection of internal defects, wood structure, etc. This paper describes the quantification of resin content and distribution uniformity in MDF with a wavelength dispersive X-ray fluorescence spectrometer.

BACKGROUND

Metallic ion emits fluorescence during X-ray illumination. Different elements show different wavelengths of fluorescence and different intensities. For a uniform multicomponent mixture, the element content and the fluorescence intensity have the following general relationship (Walter 1960):

$$I_1 = \frac{K_1 x_1}{\rho_1 [x_1 (\mu_1^* - \mu_M^*) + \mu_M^*]} \quad (1)$$

where, I_1 is the intensity for a chosen line from component 1; X_1 , ρ_1 , and μ_1^* represent the weight fraction, density, and mass absorption coefficient of the measured component; μ_M^* is the effective mass absorption coefficient of the matrix; and K_1 is a constant, being a function of the apparatus geometry and component 1.

To make practical use of the Eq. (1), the following three special situations can be considered:

(1) $\mu_1^* = \mu_M^*$, Eq. (1) reduces to

$$I_1 = \frac{K_1}{\rho_1 \mu_M^*} x_1 = K x_1 = (I_1)_0 x_1 \quad (2)$$

which states that the intensity from component 1 is proportional to its concentration in the sample. Thus, all the prior calibration information needed is a line intensity measurement from a pure sample of 1 to fix $(I_1)_0$.

(2) Mixture of two components, known identification but $\mu_1^* \neq \mu_2^*$. In this instance, the intensity-concentration curve will not be linear as the absorbing powers of the unknown and diluent are unequal. A calibration curve can be prepared experimentally from synthetic mixtures of the two materials, and an equivalent calibration curve can be calculated from Eq. (3)

$$\frac{I_1}{(I_1)_0} = \frac{\mu_1^* x_1}{x_1 (\mu_1^* - \mu_2^*) + \mu_2^*} \quad (3)$$

Here $(I_1)_0$ is the line intensity from a pure sample of material 1.

(3) A mixture of n components ($n > 2$) and $\mu_1^* \neq \mu_M^*$. In this case, the absorbing power of the desired component differs from that of the matrix, which is usually unknown. Here one must resort to use of an internal standard. It can be shown that when a weight fraction, X_s of internal standard is added to the sample under analysis, the concentration of the desired component is given by

$$x_1 = \frac{K'}{1 - x_s} \left(\frac{I_1}{I_s} \right) \quad (4)$$

with I_1 and I_s being the intensities for a chosen line from component 1 and the internal standard, respectively, and

$$K' = \frac{K_s \rho_1 x_s}{K_1 \rho_s} \quad (5)$$

Values of K_1 and K_s can be established from line intensity measurements $(I_1)_0$ and $(I_s)_0$ on the pure

materials. Provided that a constant weight fraction of internal standard is always added, Eq. (4) is simplified to

$$x_1 = K'' \left(\frac{I_1}{I_s} \right) \quad (6)$$

and a linear calibration curve of $\left(\frac{I_1}{I_s} \right)$ versus x_1 results. A sample consisting of component 1 with the constant proportion of internal standard added suffices to establish K'' .

There are two essential components in medium density fiberboard: refined fibers from wood or other cellulosic materials and adhesive binder. UF, melamine-urea-formaldehyde (MUF), and PF resins are the most commonly used adhesive binders. The efficiency of resin consumption in MDF production, which accounts for a very significant part of the overall production cost, has been the major concern in the industry. Annual resin cost for a typical MDF plant in North America is estimated in the range of U.S. \$5,000,000–\$7,000,000 and accounts for 47–62% of the material cost (RISI 2003). If the resin loading rate can be reduced from 12% to 10% with the help of this method, it will represent an annual saving of U.S. \$830,000–\$1,170,000 for one MDF plant (Feng 2001). The resin loading rate (or resin content) is normally defined as the ratio of dry resin weight to the oven-dry wood weight (as percentage). Actual resin content in the MDF fiber can vary substantially from the target resin content due to quality of blending, process variation, and limitation of equipment and instrumentation. If resin distribution uniformity is poor or resin content in the fiber varies greatly, variation in MDF panel quality can be expected. As a result, higher resin usage is usually needed to compensate for the decreased product consistency, which leads to higher production cost. Therefore, a simple, reliable, and accurate method for quantitative determination of resin content in MDF furnish or panels is highly desirable for MDF research and production improvement.

To trace a UF resin effectively, labeling of the resin is needed for detection. The label should be

chemically stable and stay with the resin at all times. The label should not adversely affect the resin performance. Feng (2001) discovered that cupric ion can be used to effectively label a UF resin in MDF fiber or panels. The copper concentrations can be quantitatively measured by XRF and then converted to resin contents via calibrations with standard samples. This XRF method is based on the rationale that UF resin molecules contain highly electronegative atoms such as oxygen and nitrogen, which can form stable coordination bonds with X-ray active metallic ions of a water-soluble salt. The experimental results suggested that copper ions can chemically bond with UF resin molecules and do not separate from the resin even under severe process conditions, such as high temperature fiber drying and hot pressing. With this approach, many laboratory experiments and mill trials have been carried out.

During the manufacturing process of a resol type of phenol-formaldehyde resin, a large amount of sodium hydroxide (NaOH) is usually used as a catalyst. Like many other metallic ions, sodium ion is X-ray active and hence a natural label for a PF resin. The resin content and its distribution uniformity in MDF furnish or panels can be measured via the sodium ion Na^+ within the PF resin using XRF. This provides a reliable method to examine the relationships of resin distribution uniformity and panel properties. It can also be used to monitor the panel manufacture process and lower production cost.

MATERIALS AND EQUIPMENT

Unresinated fiber was made from spruce-pine-fir (SPF) mixed green chips at the Forintek MDF Pilot Plant in Quebec, Canada. The chips were refined at a refiner speed of 3000 rpm with specific energy of 250 kWh/t. A UF resin manufactured by Borden Chemical Canada Inc. was used for the experiments. It had a solids content of 64.9%, a viscosity of 423 cps (25°C), and a specific gravity of 1.31 kg/m³ (25°C). A PF resin produced at the Forintek laboratory was used for the experiments. It had a solids content of 54.89%, a viscosity of 673 cps, and a specific

gravity of 1.41 kg/m^3 (25°C). Cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was obtained from Mat Laboratoire Inc. (Quebec). It has a molecular weight of 249.68, of which 25.45% is cupric ion. A wavelength dispersive X-ray spectrometer shown in Fig. 1 was used for the experiments. Other equipment used for the experiments included a resin blender, a 100-ton press, a 25-mm-diameter sample press mold, a 24-liter oven, and a top loading balance ($\pm 0.001 \text{ g}$).

SAMPLE PREPARATIONS

The copper-traced UF resin was obtained by premixing a water solution of copper sulfate pentahydrate with a commercial liquid UF resin (64.9% solids content) so that the diluted resin had a solids content of 50% and contained 0.61% of copper ion based on dry resin weight. Before resin blending, the wood fiber was oven-dried at 105°C for 12 h to a constant weight. The dry fiber was then blended with the copper-traced UF resin at a 14% resin solids add-on rate using a laboratory blender. The resin was injected into the blender via a small sprayer over a 5-min period, after which the mixing continued in the blender for 30 min. The resinated fiber was dried at 105°C for 12 h. The resulting dry resinated fiber (14% resin) was subsequently

mixed with some dry unresinated fiber at specific ratios respectively to obtain fiber samples at 2%, 4%, 6%, 8%, 10%, and 12% resin solids add-on rate. Each sample was mixed carefully and thoroughly with the laboratory blender. Five XRF sample tablets (25 mm in diameter) were prepared from each type of resinated fiber sample. Each XRF tablet was made by pressing 3 grams of fiber into the tablet mold under a pressure of 20 tons for 60 s. The tablets were air-tight sealed immediately after pressing. The same sample preparation procedure was applied to the fiber blended with a PF resin. The PF resin was diluted with water to reduce its viscosity so that the small laboratory sprayer could be operated more effectively. The solids content of the PF resin was reduced from 54.9% to 28.0%.

XRF MEASUREMENTS

The X-ray measurements were performed on a wavelength dispersive X-ray spectrometer (Panalytical PW2400) in the laboratory of Ministry of Transportation of Québec. A 3000 watt X-ray tube with rhodium target produces high energy X-ray primary photons. A lower power (2500 watts) was used to avoid overheating of the fiber samples.

Each sample tablet was directly introduced to the sample holder of the XRF spectrometer and then irradiated by the X-ray tube. Prior to X-ray radiation, vacuum was applied to the measurement chamber of the X-ray spectrometer, followed by helium. The helium atmosphere was used to avoid loss of natural humidity or dehydration of the fiber samples. Net measurement time was 60 s. The net intensity of X-ray fluorescence from copper or sodium was obtained via the SuperQ software. Based on the calibration data from the net intensities of the fiber samples with known resin contents (0%, 2%, 4% . . . 12%, and 14%), the resin contents of resinated fiber samples were quantitatively determined.

RESULTS AND DISCUSSION

Typical XRF spectra for copper and sodium in wood fiber are illustrated in Fig. 2 and Fig. 3, re-

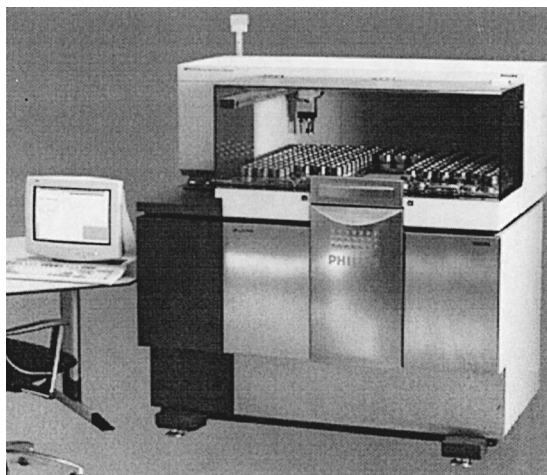


FIG. 1. PW2400 X-ray spectrometer.

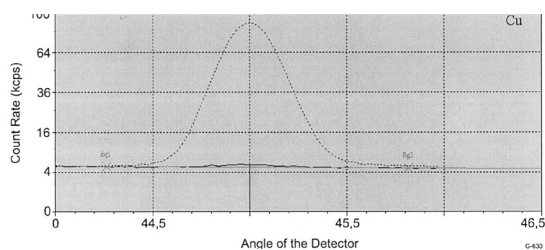


FIG. 2. XRF spectra of Cu of fiber samples. Dotted line: Cu spectrum of resinated fiber (nominal UF resin content 14%, see note 2 in Table 1). Solid line: Cu spectrum of control fiber (0% UF).

spectively. The intensity of a peak is proportional to the concentration of the corresponding metallic element. Figure 2 shows the copper XRF spectra of fiber samples with and without UF resin. Compared with the resinated fiber (14% copper-traced UF resin), copper content in the control fiber was very small and negligible. Figure 3 shows the sodium XRF spectra of fiber samples with and without PF resin. Similarly, sodium content in the control fiber was very small and negligible. Figures 2 and 3 also demonstrate the importance of defining and setting right angle for the detector. The detector angles for getting peak reading are 44.9984° and 28.5876° for Cu and Na, respectively. The information obtained from these spectra are used for setting up the detector angle and getting the background data from unresinated fiber for calibration.

As can be seen from Fig. 2, the X-ray intensity of copper ion as a UF resin label within fiber was very high and hence overwhelmingly covered small signals from all other trace elements in the

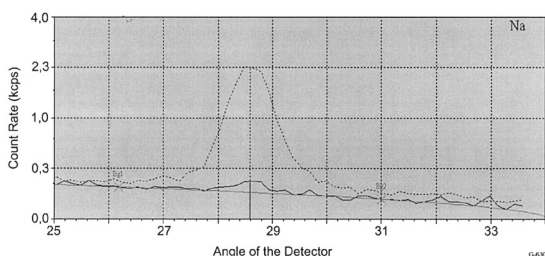


FIG. 3. XRF spectra of Na of fiber samples. Dotted line: Na spectrum of resinated fiber (nominal PF resin content 14%, see note 2 in Table 2). Solid line: Na spectrum of control fiber (0% PF).

nearby spectrum regions. Sodium ion (Na⁺), which is actually an integral part of the PF resin, also appeared to be a very effective chemical marker, and its XRF intensity linearly correlates to PF resin content in the fiber. In comparison with heavier elements such as copper, its XRF intensity is weaker. Therefore, vacuum and then helium were applied to the sample chamber prior to the XRF measurements of sodium.

Contents of Na⁺ ion in PF resins can be very different depending on the formulations of the resins. Therefore, calibration should be carried out on the same PF resin as that used for the test samples. A calibration curve can be established with standard fiber samples with known copper or sodium content and known resin loading levels. As can be seen in Fig. 4, the calibration curve for a UF resin is clearly a straight line. This conforms to the theory presented in Eq. (2) and establishes the linear correlation between fluorescence intensity and the ion content and hence the resin content. The result of regression analysis of UF resin contents and the X-ray intensities in the fiber samples is:

$$X = 0.1706Y + 0.10018 \quad (7)$$

with RMS of 0.97406.

Similarly, the calibration curve for a PF resin (resol) is also a straight line (Fig. 5). The result of regression analysis of PF resin content and the X-ray intensities in the fiber samples is:

$$X = 6.74054Y - 0.30724 \quad (8)$$

with RMS of 0.55856

where RMS is root mean square and is calculated using the following formula:

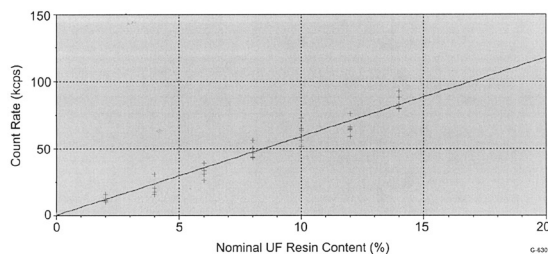


FIG. 4. X-ray fluorescence intensity for Cu vs. UF resin solids add-on rate.

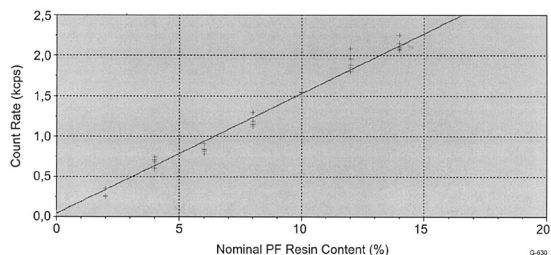


FIG. 5. X-ray fluorescence intensity for Na vs. PF resin solids add-on rate.

$$RMS = \sqrt{\frac{1}{n-k} \sum (C_{chem} - C_{calc})^2} \quad (9)$$

where n is the number of included standards and k is the number of coefficients calculated from the regression. C_{chem} is the theoretical chemical concentration, and C_{calc} is the chemical concentration calculated from the regression.

Equations (7) and (8) do not give an intercept value of zero, as shown in Figs. 4 and 5. This was due to the fact that fiber before resination did contain trace amounts of copper and sodium. The interference from these background levels of copper and sodium would be very small. For example, in the case of fiber with 10% UF resin, the background reading represented only about 1% of total UF resin content. In the case of fiber with 10% PF resin, the background reading represented only about 3% of total PF resin content.

From each group of UF-resinated fiber, one sample was randomly taken and then measured against the calibration curve. Test results are shown in Table 1. Similarly, from each group of PF-resinated fiber, one sample was randomly

taken and then measured against the calibration curve. Test results are shown in Table 2. As shown in Table 1 and Table 2, the test results fit the regression equations well. Differences in nominal resin content and measured resin content reflect the variation of resin distribution in the fiber. The systematic error derived from the high power XRF instrument is usually very small. Study conducted in the Forintek Vancouver laboratory using an XRF instrument with an X-ray tube showed that the coefficient of variation for measuring the same UF-resinated fiber sample repeatedly for 20 times was only about 3%, indicating very good reproducibility. The inherent variation of the XRF instrument was obviously much smaller than those shown in Table 1 and Table 2. Therefore, this XRF method is precise enough to show the variation of resin content and the uniformity of resin distribution in fiber.

Comparing the test results between the UF and PF resinated fiber, it appeared that the difference between nominal resin content and measured value was smaller in the PF samples (maximum difference 5.80%, average difference 0.99%) than the UF samples (maximum 15.03%, average difference 1.31%). This may be due to the fact that the diluted PF resin (28% solids content) had a much lower viscosity than the diluted UF resin (50% solids content) in the experiment. It suggested that better resin distribution or uniformity can be achieved with lower resin viscosity.

CONCLUSIONS

Based on the experimental results, the following conclusions are made:

TABLE 1. XRF test of random samples with UF resin.

Sample ID ¹	UF14#4	UF12#5	UF10#2	UF8#1	UF6#5	UF4#2	UF2#3	UF0#3
Nominal resin content % ²	14.0	12.0	10.0	8.0	6.0	4.0	2.0	0.0
Copper intensity (kcps) ³	79.32	65.98	59.09	46.82	39.36	20.51	13.27	0.01
Measured resin content %	13.432	11.157	9.981	7.887	6.614	3.399	2.164	0.01
Difference ⁴	0.57	0.84	0.02	0.11	-0.61	0.60	-0.16	-0.01
Difference in percentage ⁵	4.06	7.03	0.19	1.41	-10.23	15.03	-8.20	-

Notes: 1. First two characters of a sample ID represent the type of resin, followed by resin content. The last number is the sample code within a group of resinated fiber samples. 2. Nominal resin content is theoretical resin solids add-on rate based on oven-dry fiber weight in percentage. 3. Copper intensity is the X-ray fluorescence intensity for Cu. The unit used is kilo count per second (kcps). 4. Difference presents the weight difference between nominal resin content and measured resin content. 5. Difference in percentage = (nominal resin content - measured resin content) / nominal resin content \times 100%.

TABLE 2. XRF test of random samples with PF resin.

Sample Code ¹	PF14#3	PF12#1	PF10#2	PF8#2	PF6#4	PF4#3	PF2#1	PF0#3
Nominal resin content % ²	14.0	12.0	10.0	8.0	6.0	4.0	2.0	0.0
Na intensity (kcps) ³	2.11	1.80	1.55	1.18	0.91	0.61	0.36	0.05
Measured resin content %	13.89	11.85	10.16	7.67	5.83	3.79	2.12	0.01
Difference ⁴	0.11	0.15	-0.16	0.33	0.17	0.21	-0.12	-0.01
Difference in percentage ⁵	0.83	1.21	-1.56	4.13	2.83	5.25	-5.80	-

Notes: 1. First two characters of a sample ID represent the type of resin, followed by resin content. The last number is the sample code within a group of resinated fiber samples. 2. Nominal resin content is theoretical resin solids add-on rate based on oven-dry fiber weight in percentage. 3. Sodium intensity is the X-ray fluorescence intensity for Na. The unit used is kilo count per second (kcps). 4. Difference presents the weight difference between nominal resin content and measured resin content. 5. Difference in percentage = (nominal resin content - measured resin content) / nominal resin content × 100%.

- A liquid urea-formaldehyde resin in wood fiber can be effectively labeled with copper ion in the form of a water-soluble copper salt such as copper sulfate pentahydrate, and measured by X-ray fluorescence under normal atmospheric environment. The relationship between copper X-ray intensity and resin content in fiber is linear.
- This XRF method can be used for precise measurement of UF resin content in MDF furnish or panels if the resin is labeled with copper sulfate.
- The precision of this XRF method allows the determination of variation or uniformity of UF resin distribution in MDF furnish or panels.
- The sodium ion in the resol type of phenol-formaldehyde resin is an effective label for the PF resin in wood fiber, which can be quantified by X-ray fluorescence under a helium atmosphere. The relationship between sodium X-ray intensity and resin content in wood fiber is linear.
- This XRF method can be used for precise measurement of PF resin content in MDF furnish or panels.

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