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Characterization of urea–formaldehyde resin penetration into medium density fiberboard fibers

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Abstract The amount of UF resin penetration into fibers, used for the production of medium density fiberboard (MDF), is unknown. To evaluate the relationship between resin viscosity and resin penetration depth, an experimental procedure involving confocal laser scanning microscopy (CLSM) and a Toluidine Blue O staining system was performed. The results indicate that CLSM in combination with a Toluidine Blue O staining system is a good way to characterize UF resin penetration into wood fibers. The main penetration direction is toward the fiber lumen. For wet fibers, whose moisture content is about 88%, the effect of resin viscosity with a range of 80 cps – 340 cps on penetration is very similar, with all adhesives reaching or almost reaching the fiber lumen after 60 min at room temperature. For MDF industrial samples, the highest depth of penetration of the adhesive was attained in the second dryer stage. After the second dryer stage, the resin penetration into the fiber did not increase.

Introduction

In the manufacture of medium density fiberboard (MDF), urea–formaldehyde (UF) adhesive plays a very important role. The development of mechanical and other MDF properties relies mainly on the added adhesive. It is generally believed that the optimal resin efficiency will produce boards with the required properties and least costs. While this is not the only factor, penetration of adhesive into the porous network of wood cells is believed to have a strong influence on bond strength (Brady and Kamke 1988; Collett 1972; Jakal 1984; Marra 1992). Damaged wood cells may be reinforced by the adhesive, and stresses may be more effectively distributed within a larger interphase region.

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For a good resin bonding, a moderate amount of penetration is desirable. However, excessive penetration may waste adhesive and lead to a starved bondline, with insufficient adhesive remaining at the interface and low resin bonding efficiency (Marra 1992; Sernak et al. 1999; Wang 1995). Some researchers believe that the resin solution may penetrate and diffuse into fibers too easily, since the fiber in the blowline blending process is wet and hot, which explain the greater resin consumption (Frashour 1990). On the other hand, resin penetration into the fibers may be counteracted when moisture inside the fiber diffuses from the interior of the fiber to its surface during drying. However, no evidence or measurements have been made, as far as literature is concerned, to optimize resin penetration into fibers.

Many methods have been used to study resin penetration into solid wood. The most widely used method appears to be scanning electron microscopy (SEM) with energy-dispersive x-ray analysis (EDAX) (Koran and Vasishth 1972; Bolton et al. 1988). Other techniques include light microscopy, fluorescent microscopy and Electron energy loss spectroscopy (EELS). Hameed and Roffael (2001) used an optical microscope to investigate the penetrability of various glues (urea–formaldehyde resin (UF-resin), phenol–formaldehyde resin (PF-resin), melamine–urea–phenol–formaldehyde made of pine sapwood and heartwood. Fluorescent microscopy and dye staining methods were used to evaluate the effects of hot-pressing parameters on liquid phenol–formaldehyde (PF) resin penetration into wood flakes (Brady and Kamke 1988). A similar method was used to characterize liquid urea–formaldehyde adhesive penetration into beech wood (Sernak et al. 1999). Electron energy loss spectroscopy (EELS) in combination with transmission electron microscopy (TEM) was applied to quantify melamine resin penetration into the Norway spruce cell wall (Rapp et al. 1999). Thus, research on UF resin penetration into wood fibers is quite limited. This might be attributed to the following reasons. First, UF resin, which is the dominant adhesive for MDF panels, is colorless even after it is cured. Second, methods of measuring resin penetration into wood fibers are not well established.

Confocal fluorescence microscopy in combination with dye staining techniques may be a good way to evaluate penetration of resin into a wood fiber. In a laser scanning confocal fluorescence microscope, both the area of illumination and the area from which measurements are made is confined to a single spot. The laser (or other point source) and a pinhole in the emission measuring system are focused on the same spot in the object plane, and the spot is scanned systematically over the specimen. The illuminated volume elements are sampled in such a way that fluorescent emission from the volume elements in the focal plane are detected. The signals from outside the plane of focus are removed by a pinhole detector, which further reduces out-of-focus information. Thus the illumination, specimen, and detector, all have the same focus, that is, they are confocal (Rost 1992). CLSM offers several advantages over conventional light and electron microscopy. First, the shallow depth of field (0.5–1.5 μm) of confocal microscopes allows information to be collected from a well-defined optical section rather than from most of the specimen as in the conventional light microscope. Consequently, out-of-focus fluorescence is virtually eliminated, which results in an increase in contrast, clarity, and detection sensitivity (Wilson and Sheppard 1984; Inoué 1989). Second, the confocal microscope optically sections specimens so that physical sectioning artifacts observed with light and electron microscopy

is eliminated. Because optical sectioning is noninvasive, living as well as fixed cells can be observed with greater clarity. Another advantage of confocal microscopy is that specimens can be optically sectioned not only in the *xy* plane (perpendicular to the optical axis of the microscope), but also vertically (parallel to the optical axis of the microscope) in the *xz* or *yz* plane. With vertical (*xz* or *yz*) sectioning, cells are scanned in depth (*z* axis) as well as in lateral (*x* or *y* axis) direction, generating images in parallel to the optical axis of the microscope. This gives the effect of looking at a focal plane from the side of the specimen and can show variations in specimen height. Stacks of optical sections taken at successive focal planes (known as *z* series) can be reconstructed to produce a three-dimensional view of the specimen (Rost 1992). Toluidine blue O ($C_{15}H_{16}ClN_3S$) can be used to distinguish UF resin from fiber in this study. Combined with this dye, UF resin becomes fluorescent and wood fluorescence is quenched (Xing et al. 2004). So, by combining confocal microscopy and staining techniques, the penetration depth in three dimensions can be evaluated. Thus, resin droplet penetration into wood fiber can be characterized.

The objectives of this study are: (1) to characterize the relationship between resin viscosity and penetration; (2) to investigate the depth (or amount) of resin penetration into fibers and determine where in the process the highest depth of penetration occurs during MDF manufacture.

Materials and methods

Preparation of UF resin with various viscosities

UF resins were prepared at a U:F molar ratio of two. The preparation procedure is as follows. Urea and formaldehyde were mixed in the reactor with a mechanical agitator. The pH of this solution was adjusted to 8.5 by adding sodium hydroxide (50%). The temperature was kept constant for 60 min after heating the solution to 70°C, and then cooled down to 60°C. Ammonium chloride (10%) was slowly added to adjust the pH of the solution to 4.8. When the temperature rose to 85°C, the resin was cooked until the viscosity reached 65 cps (measured at 25°C). The resin was then cooled to 50°C. When the viscosity reached 80 cps, 140 cps, 200 cps, 250 cps, 340 cps, about 100 ml resin was taken out from the reactor. All the samples were kept in a refrigerator before being used.

Fiber preparation

Fresh fiber (100% softwood) was obtained from the MDF-La Baie (Ville La Baie, Québec, Canada) plant with a moisture content of 88%. UF resins of various viscosities were applied onto fibers with a small glass pipet (Cat No. 14672–200) in our laboratory. After allowing penetration for 30 and 60 min, final curing of the adhesive was conducted by placing the resinated fibers into a vacuum oven at 140°C and 29.5 Hg for 20 min to cure the UF resin.

Industrial samples preparation

The different fiber samples (100% softwood) selected from the first dryer stage, second dryer stage and prior to the hot-press, were obtained from the MDF-La

Baie plant (Ville La Baie, Québec, Canada) were put into a vacuum oven at 140°C and vacuum of 29.5 Hg for 20 min to cure the UF resin.

Sample staining and microscopy slide preparation

All fiber samples were put into a 0.01% Toluidine Blue O solution for 48 h respectively, and then rinsed in distilled water several times until the water remained clear. Finally, the fiber samples along with some distilled water were placed between a microscope slide and a cover glass before confocal scanning. Thus, fibers were not embedded in resin in any way, nor microtomed.

Image acquisition

All samples were scanned under Leica TCS SP2 confocal microscope and Leica confocal software version 2.00 to acquire series section images in University of Maine (USA) as shown in Fig. 1.

The parameters of confocal scanning were set as follows: xyz mode, Objective HC PL APO 10.0 × 0.40NA, laser wavelength 514 ηm, pinhole 63.73 μm, zoom 8, average scanning times 3, scanning speed 400 Hz, resolution 8, channels 2, excitation beam splitter FW: DD 458/514, PMT1 (HV) 717.00, PMT1 (offset) – 30, SP mirror 538 (left) to 654 (right), size-height 187.50 μm, size-width 187.50 μm, step size-depth 0.2 μm. Amount of 80 to 170 section images were obtained for each sample depending on the size of fluorescent body.

In this procedure, all the resin droplets, which were chosen to section were located on the top of fiber surface. The Leica TCS-SP2 is capable of simultaneous imaging on four detection channels.

For this research, one detection channel captured the fluorescent signal on the range of 538 – 654 ηm (Fig. 2a). The second channel acquired a transmitted light image as shown in Fig. 2b. Spatial registration of the two detectors allows an overlap of the signals as shown in Fig. 2c. This figure indicated the resin droplet location on the fiber surface.

Image processing

Leica confocal software version 2.00 used the stack of optical sections taken at successive focal planes (0.2 μm-apart) to reconstruct *z*-series sectioned fluorescent images to produce a three-dimensional view of fluorescent body as shown in Fig. 3. If assuming an effective Nyquist sampling rate of 2.5, this section results in an effect resolution in the *z*-direction of 0.5 μm. The lateral resolution of the lens and detectors used was 8 μm.

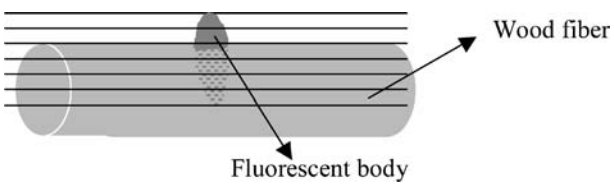

Fig. 1 Diagram of sample section

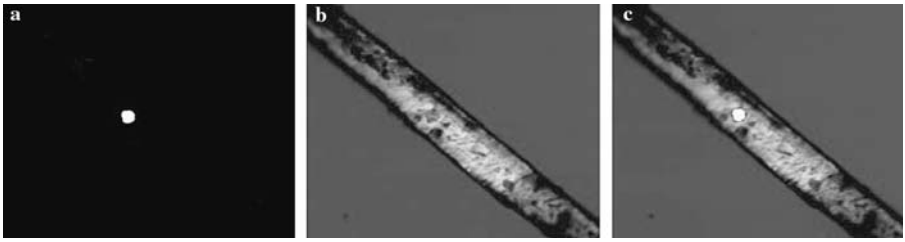

Fig. 2 Fiber and resin droplet image **a** Fluorescent image; **b** Transmitted image; **c** Overlapped image

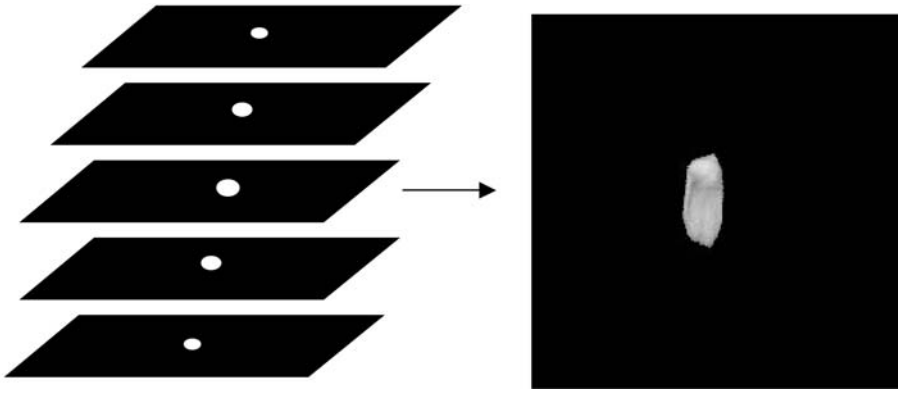

Fig. 3 Reconstruction images to form a three-dimensional view of the fluorescent body

The WinCell v5.6d (Instruments Regent Inc.) software was used to measure the series of sectioned fluorescent areas. The volumes of fluorescent bodies (V_f) were calculated by Eq. 1:

$$V_f \approx \sum_{n=1}^{k-1} (S_n \times 0.2) = 0.2 \sum_{n=1}^{k-1} S_n(\mu m^3) \tag{1}$$

where:

S_n: fluorescent area of n^{th} section (μm^2)

k: the number of total sections

0.2: the depth per section (μm)

The heights of fluorescent bodies (H_f) were calculated by Eq. 3.2:

$$H_f = 0.2 \times (k-1)(\mu m) \tag{2}$$

Results and discussion

Fluorescent body shape

The shapes of the fluorescent bodies can be obtained by stereoscopic imaging with Leica confocal software version 2.00. All of the bodies had an oval- or finger-like shape as shown in Fig. 4.

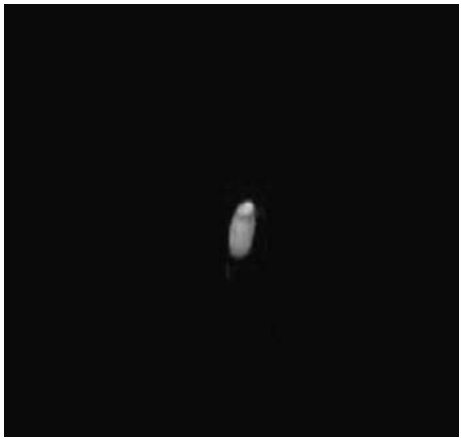

Fig. 4 The shape of fluorescent body

A fluorescent body should contain the UF resin and also wood fiber. The resin that remained on fiber surface and penetrated into fibers should form a closed body after the resin is cured. The part of the wood fiber within this, that is, inside of this body probably cannot be stained by Toluidine Blue O. It will thus fluoresce with the UF resin when scanned. Therefore, it is impossible to quantify the volume of the resin, which penetrates into the fibers in this way, but the distance of resin penetration into fibers can be calculated if the height of resin droplet, which remained on fiber surface is known.

The direction of penetration

Figure 4 indicates that the penetration is directional. Contrary to expectations, the resin preferably diffuses towards the lumen, rather than laterally along the fiber wall surface, and thus goes through the P, S_1, S_2, S_3, T and W sections of the cell wall, seemingly unaffected by the different fiber alignments. Less resin diffuses along the fiber wall. This case may be due to the porous structure of the fiber wall (Duchesne and Daniel 1999).

There are many pits and micropores through the fiber wall. These pits and micropores enable the resin to easily penetrate from the fiber surface into the lumen. The high moisture content also makes the direction of penetration along the passage of water. If we consider all penetration is toward the fiber lumen, the section which contains the largest fluorescent area (largest transverse section) should be the interface between the resin and fiber for one fluorescent body. So, the distance from this section to the bottom of the fluorescent body should be the depth of resin droplet penetration into the fiber as shown in Fig. 5.

The effect of resin viscosity on resin penetration into fiber

The depth of penetration results for different viscosity resins, after 30 and 60 min are summarized in Tables 1 and 2. The results indicate that resins with different viscosities (80, 140, 200 and 250 cps) exhibit a similar average penetration depth. Although the resin with a viscosity of 340 cps has a smaller

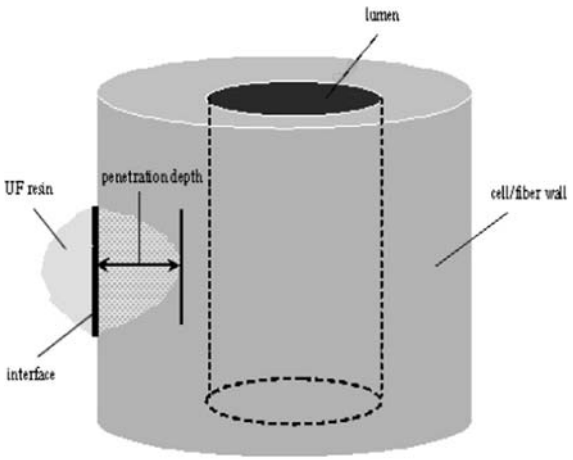

Fig. 5 Schematic representation of the resin droplet on a wood fiber showing penetration depth

average penetration depth than the other four resins after 30 min, there is no obvious difference in the amount of penetration among these five resins after 60 min, all of the resins penetration being rather similar into or almost into the fiber lumen.

The results suggested that an amount of adhesive that has penetrated into the fiber lumen after 60 min under room temperature conditions. This should result in starved bondlines during hot-press. Thus, the elapsed time between adhesive blending and hot-press should be appropriate in order to optimize the amount of adhesive penetration for wood-based composites.

Resin penetration into industrial MDF fibers

The depth of penetration results of fibers at different commercial processing stages is summarized in Table 3. The results indicate that the highest penetration took place between blowline blending and the first dryer stage. The penetration depth is more than 4.7 μm. This suggested that the penetration occurred when the moisture inside the fiber evaporated to the surface. This can be due to the vapor pressure (< 1 MPa) less than the surface tension of wood fiber (> 50 MPa) (Scheikl et al. 2001). From second dryer stage to prior to hot-press, the additional penetration is limited. The depth of penetration is less than 1.8 μm. After the second dryer stage, the penetration was nearly complete. This can be attributed to the following factors. Fibers out of the refiner are very wet and hot, and the moisture content is very high. When UF resin is applied onto these wet and hot fibers, the UF resin penetrates and diffuses easily into fibers. Afterwards, penetration/diffusion will become more difficult with the decrease in moisture content and the solidification/cure of the UF resin. The average final penetration depth is about 6.5 μm. This suggested that the penetration did not reach the fiber lumen. The results of Chapman (2002) support this. He reported that the dominant IB failure point of MDF panels occurred in S_2 layer of the fiber wall. This penetration depth may be beneficial to resin efficiency.

Table 1 Penetrations of resins with different viscosities after 30 min (25°C)

Samples	0.08 pa s			0.14 pa s			0.2 pa s			0.25 pa s			0.34 pa s		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Fiber diameter (μm)	28	36	27	30	26	44	32	46	23	26	27	59	33	29	42
Volume of fluorescent body (μm^3)	160	114	247	158	492	664	428	307	228	617	187	99	132	22	22
Height of fluorescent body (μm)	11.4	14.0	11.0	13.8	14.0	18.0	19.6	16.0	11.6	19.6	13.6	9.4	9.2	7.4	6.6
Largest transverse area of fluorescent body (μm^2)	27	18	44	20	75	60	36	27	33	52	21	16	28	7	9
Distance from the largest fluorescent area to the bottom of fluorescent body (μm)	5.8	6.8	5.0	5.2	6.8	10.8	9.2	7.8	6.0	7.8	6.6	5.8	3.6	3.0	3.2
Average distance of penetration (μm)	5.9			7.6			7.7			6.7			3.3		
Standard Deviation	0.9			2.5			1.6			1.0			0.3		
Variance	$F = 3.84$, $Pr > F$ (0.04)														

Table 2 Penetrations of resins with different viscosities after 60 min (25°C)

Samples	0.08 pa s			0.14 pa s			0.2 pa s			0.25 pa s			0.34 pa s		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Fiber diameter (μm)	68	45	26	49	44	44	38	36	51	38	27	21	27	58	54
Volume of fluorescent body (μm^3)	1406	761	209	1404	963	104	693	179	1867	232	1463	549	119	1972	113
Height of fluorescent body (μm)	30.0	20.2	16.6	23.6	16.2	11.6	22.6	14.0	26.0	11.8	22.8	17.0	13.0	23.8	14.2
Largest fluorescent area of sections(μm^2)	86	72	24	96	95	15	46	21	127	40	124	56	18	127	16
Distance from the largest fluorescent area to the bottom of fluorescent body (μm)	13.2	7.4	7.0	10.0	8.0	6.2	10.6	7.0	10.2	6.4	11.5	8.6	6.0	10.4	6.6
Average distance of penetration (μm)	9.2			8.1			9.3			8.8			7.7		
Standard Deviation	3,5			1,9			2,0			2,5			2,4		
Variance	$F = 0.24$, $Pr > F$ (0.91)														

Table 3 Depth of resin penetration of commercial MDF fibers

Samples	First stage dryer		Second stage dryer		MDF mat	
	1	2	1	2	1	2
Fiber diameter (μm)	32	45	42	24	60	36
Volume of fluorescent body (μm^3)	34	49	249	457	210	435
Height of fluorescent body (μm)	12	11.2	12.8	11.6	14.8	13.6
Largest fluorescent area of sections (μm^2)	5	10	32	63	24	52
Distance from the largest fluorescent area to the bottom of fluorescent body (μm)	4.6	4.8	6.4	5.6	6.6	6.4
Average distance of penetration (μm)	4.7		6.0		6.5	
Standard Deviation	0.1		0.6		0.1	
Variance	$F = 14.4$, $Pr > F$ (0.03)					

FPL (1987) reported that wood-adhesive joint strength decrease with density as wood density above 0.7 – 0.8 g/cm^3, because dense wood tends to have low porosity and it is difficult for adhesive to penetrate it. Thus, for a good bonding strength, a moderate amount of penetration is desirable. Insufficient penetration or overpenetration will reduce the bonding strength.

Conclusions

The results indicate that CLSM in combination with a Toluidine Blue O staining technique is a good way to understand UF resin penetration into wood fibers. The main direction of resin penetration in the fibers is towards the lumen. Resins, with viscosities ranging from 80 cps to 250 cps, exhibit similar penetration depths after 30 min at room temperature. The maximum depth of penetration reached or almost reached to the fiber lumen, after 60 min. For commercial MDF fibers, the penetration was rapidly occurring although fibers residence times in blender and dryers were very short after blending, typically in the order of 6 – 8 s. This suggested that the penetration of UF into wood fibers is very easy and rapid under the high moisture and temperature conditions. Along the different processing stages of the MDF industry, maximum penetration depth was reached in the second dryer stage. After the second dryer stage, the penetration/diffusion was practically almost terminated.

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