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Investigation of Urea-Melamine-Formaldehyde (UMF) resin penetration in Medium-Density Fiberboard (MDF) by High Resolution Confocal Laser Scanning Microscopy

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Abstract A confocal laser scanning microscope (CLSM) was used to investigate the distribution and penetration of urea-melamine-formaldehyde (UMF) resin in the fiber when injected through blowline blending in a medium density fiberboard (MDF) pilot plant. Samples were prepared with respect to industrial parameters and were collected at the dryer's end. The samples were later dyed in a Dye Star-Brilliant Red solution (0.01%) and rinsed with distilled water to remove excess. The samples were scanned with the CLSM to build three-dimensional reconstructions of MDF fiber cross-sections. With proper lenses and optimized CLSM settings, it was possible to obtain fiber reconstructions with a resolution greater than the laser wave length (514 nm). The Zeiss CLSM built-in software image analyzer enabled to rebuild them in rotation on any of the three axes with up to 64 images per rotation. The resin penetration sites were identified using this software option. The penetration sites were numerous and well dispersed. The largest openings (lumen, pits and cracks) were responsible for most of the resin lost by over-penetration. The presence of resin in the cell walls (detected with the CLSM) proves their porosity without giving much information about the resin concentration. Finally, the atomic force microscope (AFM) enabled to recreate the finest surface details for these fibers samples. It was found that the fibrils aggregates orientation and size can influence the resin penetration and distribution.

It was concluded that the porous structure of wood fibers and their affinity to water enable the resin to penetrate through capillary force. This phenomenon is stimulated by the high pressure, saturated steam, turbulent flow and heat. When injected in the pilot plant blowline, UMF resin was uniformly distributed over the fiber surface (22.5% coverage). The resin penetration was however important and also occurred in nanometric defaults of the wood fibers. Thus, industrial panels made out of very porous, damaged or small fibers will need more resin to fill the gaps in order to make a strong board.

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Hoch auflösende konfokale Laserscanning-Mikroskopie zur Bestimmung der Eindringung von Harnstoff-Melamin-Formaldehydharz (UMF) in die Fasern von MDF-Platten

Zusammenfassung Mit Hilfe eines konfokalen Laserscanning-Mikroskops (CLSM) wurde die Verteilung und Eindringung von Harnstoff-Melamin-Formaldehydharz (UMF) in die Holzfasern bei einer Beleimung mit dem Blowline-Verfahren in einer Versuchsanlage untersucht. Die Proben wurden wie in der Praxis üblich hergestellt und nach dem Trocknen entnommen. Danach wurden die Proben in einer Dye Star-Brillant Red Lösung (0,01%) gebleicht und zur Entfernung von Rückständen mit destilliertem Wasser gespült. Zur dreidimensionalen Rekonstruktion von MDF-Faserquerschnitten wurden die Proben mit dem CLSM gescannt. Mittels geeigneter Linsen und optimalen CLSM-Einstellungen war es möglich, die Fasern mit einer höheren Auflösung als der Laserwellenlänge (514 nm) zu rekonstruieren. Mit der eingebauten CLSM Bildanalyse-Software

von Zeiss konnten die Fasern unter einem beliebigen Winkel dargestellt werden. Damit konnten die zahlreichen und gut verteilten Eindringstellen des Harzes bestimmt werden. Die größten Öffnungen (Lumen, Tüpfel und Risse) waren aufgrund der großen Eindringmenge überwiegend für den Harzverlust verantwortlich. Das Auftreten von Harz in den Zellwänden (mit dem CLSM bestimmt) belegt deren Porosität, wobei nur wenig Aussagen zur Harzkonzentration möglich sind. Mit dem Rasterkraftmikroskop (AFM) konnten die kleinsten Oberflächendetails für diese Faserproben nachgebildet werden. Es stellte sich heraus, dass die Richtung und die Größe der Fibrillenaggregate das Eindringen und die Verteilung von Harz beeinflussen können.

Daraus lässt sich schließen, dass das Harz wegen der porösen Struktur der Holzfasern und deren Wasseraffinität aufgrund von Kapillarkräften eindringen kann. Hoher Druck, gesättigter Dampf, turbulente Strömung und Wärme tragen dazu bei. Beim Einsprühen in die Blowline-Versuchsanlage verteilte sich das UMF-Harz gleichmäßig über die Faseroberfläche (22,5% Abdeckung). Einen großen Einfluss hatte die Eindringung auch in kleine Öffnungen im Nanobereich. Folglich benötigen industriell hergestellte Platten aus sehr porösen, beschädigten oder kleinen Fasern mehr Harz, um die Lücken zu füllen und um eine stabile Platte herstellen zu können.

1 Introduction

Medium density fiberboard (MDF) is a composite material mostly used in the furniture industry. The production of this board requires a large volume of adhesive which can account for up to 20% of the production costs. Urea-formaldehyde based resins used for particleboard (PB) and MDF commercial productions are colorless once sprayed on fibers, thus it is very hard to distinguish them from the fibers. Since 1960, industrials have found cost-effective ways to produce MDF even if this process consumes more resin when compared to other wood composites like PB. The high surface to volume ratio of MDF fibers can justify a part of this higher consumption but there are other explanations.

The commercial resins made out of urea and formaldehyde (UF) can be applied to dry wood particles to produce particleboards. But mixing these UF resin with dried MDF fibers is somewhat problematic. It causes clogging in most inline dry gluing systems and fiber aggregation in rotary blenders. This is why industrial MDF mills are equipped with wet gluing systems. In the blowline mixers of industrial MDF mills, the resin is injected into a stream of saturated steam where wet fiber travels near the speed of sound. Many techniques have been developed to distinguish resin on the fibers, including ultraviolet microscopy (Gindl et al. 2002), fluorescence microscopy (Murmanis et al. 1986), resonance Raman microscopy (Saariaho et al. 2004), Jamin-Lebedeff interference microscopy (Donaldson and Lomax 1989), electron energy loss spectroscopy (EELS) (Rapp et al. 1999), X-ray spectroscopy (XPS) (Grigsby and Thumm 2004), cathodiluminescence/scanning electron microscopy (SEM) (Thumm et al. 2001) and confocal laser scanning microscopy (CLSM) (Xing 2003). The study with CLSM and XPS (Pakdel et al. 2007) has shown that the sonic and wet conditions of the resin system favor a good resin distribution over fiber and thus, uniform MDF mechanical properties. But there are drawbacks: the dryer carries a fraction of the resin in the chimney and also reduces resin reactivity (pre-cure). This resin loss is compensated by injecting more resin and also by changing the resin formulation. In North America, a urea-melamine-formaldehyde (UMF) resin is generally used because it gives the MDF boards a better resistance to swelling and lower formaldehyde emissions. But this resin also costs more than the UF resin.

Another consequence of this inline gluing system is a deeper penetration of the resin into the refined wood fibers cell walls. It is well known that UMF resin penetration is necessary to promote a good fiber to fiber adhesion. But when excessive, it results in a resin starve at the fiber to fiber bond line. The scope of this paper is to present the resin penetration sites on MDF fibers with the highest resolution possible. These sites were located using a new confocal microscopy technique, a built-in 3D rendering software and an atomic force microscope (AFM).

2 Material and methods

2.1 Fiber preparation

Pure spruce (*Picea* spp.) chips were refined into fibers at FPInnovations-Forintek Division in their pilot plant (Quebec City). Spruce chips moisture content (MC) was previously controlled in a chamber. Conditions were 20 °C and 65% RH, resulting in a moisture content (MC) of about 12%. The refiner pressure was set to 8 bars. The fibers were inline glued with different MUF grade resins having a F/(U + M) molar ratio of 1.12. We used Arclin resins with 0, 3 and 6% Melamine/(Urea + Melamine) molar ratio and Hexion resins with 0 and 12% M/(U + M). Hexion also supplied us with a commercial resin named MDF UMF-302. All resins had about 65% solids content, a viscosity around 200 cps at 25 °C and were injected undiluted. No wax was added to the resin or the fiber prior and after the treatments. Each batch of fiber was collected at the dryer's end. To be able to identify aminoplastics resins while scanning spe-

cimen under the CLSM, the fiber samples were immersed into a fluorescent marker (Dye Star-Brilliant red) solution (0.01%) and rinsed with distilled water. After air drying of the samples, some fibers were plunged into a large droplet of low fluorescence oil placed on a glass slide. A thin cover glass was put on top before being scanned on the inverted CLSM.

2.2 AFM surface analysis

A Digital Instrument – multifunctional AFM (at centre de recherche en science et ingénierie des macromolécules (CERSIM), Université Laval) was used to scan the fiber surface microstructure. The reader should refer to our latest paper (Cyr et al. to be published) for information about AFM settings and results for MDF wood fibers.

2.3 CLSM image acquisition

All samples were scanned under a Zeiss LSM 510META confocal microscope. The microscope was controlled by a Zeiss LSM v.3.2 SP2 confocal software. Two lenses were used: A 40X Plan Apo/1.3 Oil DIC for bound fibers and a 100X Plan Apo/1.4 Oil DIC for single fibers. Their respective fields of view (XY) were $230.3\,\mu m \times 230.3\,\mu m$ (512×512 pixel) and $92.1\,\mu m \times 92.1\,\mu m$ (1024×1024 pixel). The height of the stack (Z) was limited by the computer capacity to collect data. For bound fibers, the lower resolution (512 pixels^2) enabled to collect up to 273 layers of pixels, giving a total Z value of 89.5 µm. For the highest resolution, we were limited to 100 layers, giving a total Z value of 32.7 µm. The laser excitation wavelength was 514 nm with a 405/514 dichroic used to remove any reflection. Using this wavelength suggests the smallest observable detail must be greater than 500 nm. But with the 100X lens and 327 nm horizontal increments (ΔZ), the software rendering is capable of recreating smaller details. Spectral emissions in the range of 518–529 nm (for the resin) and 530–600 nm (for the fiber) were measured. No signal amplification was done through the Z axis even if the signals slightly fade when scanning through the fiber.

2.4 CLSM 3D reconstructions

The built-in software has a function called "maximum projection" which gives a 3D view of the fiber sample. The 3D reconstructed images can be rotated on 3 different axes (XYZ) in order to show any angle of view needed to evaluate penetration with accuracy. The reconstructions can be composed of up to 64 images for partial or full rotations. The images presented in this paper were converted in black and white with Photoshop.

3 Results and discussion

The degree of UMF resin penetration in MDF fibers is strongly affected by the injection system used to blend the resin with the fibers. Our first work on that subject showed that when UMF resin was injected on dry MDF fibers (drum blender), the penetration was limited to 1 or 2 microns (Cyr et al. 2006). In this current study, the resin was injected in a pilot plant equipped with a tubular blender (blowline) and an inline flash dryer similar to industrial systems. When compared to dry blended fibers, the penetration was found to be 5 to 10 times more important. The resins of both manufacturers were spread evenly on the fibers. The resins containing different level of melamine were able to penetrate the fibers as far as does UF. We thus have chosen to show images from fibers glued with the commercial UMF resin from Hexion (UMF MDF-302).

Figure 1 shows the UFM resin on MDF fibers as if they were sliced by a microtome to show the cross section of four bounded resinated fibers. As mentioned, the resin penetration is very important when the fiber is prepared according to industrial practices. Some of the resin penetrated the fiber toward the lumen without going through pits or large openings. It would be interesting to lower this penetration since

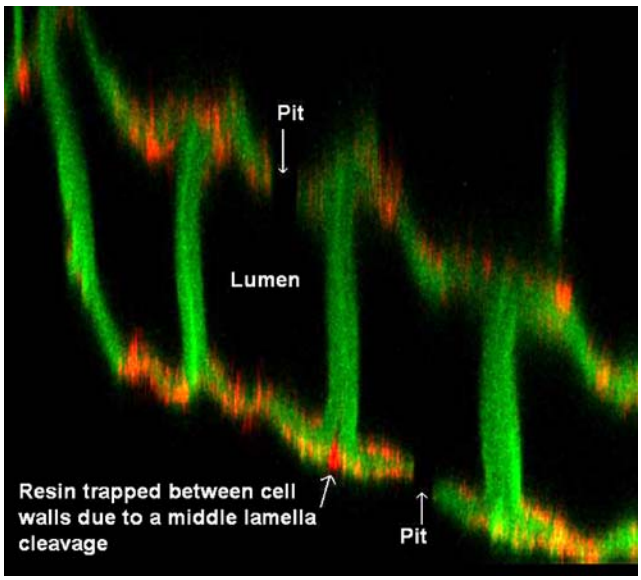

Fig. 1 Resin penetration in bounded fibers (*Picea* spp.) – Orthogonal cut view from ZEISS CLSM 3D projections. The resin is shown in *white* and the fibers in *grey* (as if they were cut with a blade). Some of the resin penetrated the fiber from surface to lumen without going through pits. Result of refining, a cleavage between two fibers was filled by a considerable amount of resin

Abb. 1 Harzeindringung in Faserbündel (*Picea* spp.) – orthogonales Schnittbild (wie mit einer Klinge geschnitten) auf Basis der Zeiss CLSM 3D-Projektionen. Harz ist *weiß* und die Fasern sind *grau* abgebildet. Etwas Harz drang in die Zellwand ein, ohne dabei durch die Tüpfel zu gehen. Der durch das Refining entstehende Riss zwischen zwei Fasern wurde durch eine beachtliche Menge Harz gefüllt

providing resin to the lumen is useless. A cleavage in the middle lamella is completely filled by the UMF resin, showing the consequences of high pressure refining on resin consumption. Figure 2 presents the same angle of view of a single fiber. To show how a CLSM works, the figure is composed of 3 images (height = 92.1 μm). Figures 2a and 2b show two different projections for the resin (518–529 nm) and the fiber (530–600 nm), respectively, built with the fluorescent readings from the two detectors of the CLSM. The two signals combined form a projection where resin and fiber are visible as shown in Fig. 2c. Again, resin was found everywhere in the wood cell walls. The outer and inner layers of the wood cell walls (compound middle lamella (CML), S1 and warty layer (WL)) are more porous and absorb more resin than the S2 layer. With this angle of view, most of the resin seems to be in the fiber but this is not the case. Figure 3 shows the same part of the MDF fiber on a perpendicular angle of view. The resin was concentrated on the surface, well distributed but deeply anchored. Resin distribution measurements were made with Photoshop as shown in Fig. 3c. For a 12% resin load, the averaged distribution was 22.5% measured by the CLSM and 22% by the XPS (Pakdel et al. 2007). Theses measurement techniques are reliable for resin surface distribution measurements. Unfortunately, XPS and CLSM measurements cannot give a clear reading of the UMF resin to fiber polymer ratio deep in the fiber cell walls. This is why it is still hard to tell how much resin is lost by over-penetration.

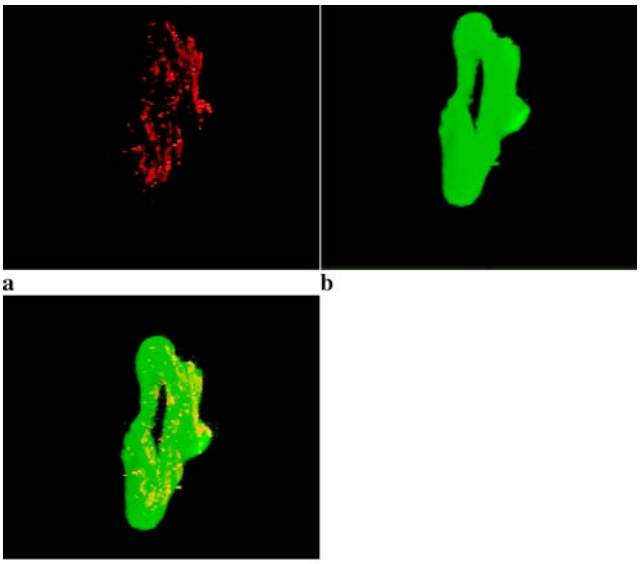

Fig. 2 Resin penetration in a single fiber (*Picea* spp.) – Orthogonal cut view from ZEISS CLSM 3D projections. The resin signal (518–529 nm) is shown on the *top left* and the fiber signal (530–600 nm) on the *top right*. On the *bottom*, the white resin is shown on and also in a grey fiber. A relatively important fraction of the resin is located in the fiber. The three images are all 92.1 μm in height (corresponding to the *X* axis of the scan)

Abb. 2 Harzeindringung in eine einzelne Faser (*Picea* spp.) – Orthogonales Schnittbild auf Basis der Zeiss CLSM 3D-Projektionen. Die Harzkomponente (518 × 529 nm) ist *oben links* und die Faserkomponente (530 × 600 nm) *oben rechts* dargestellt. *Unten* ist das weiße Harz auf und auch in der grauen Zellwand zu sehen. Ein relativ großer Anteil Harz befindet sich in der Zellwand. Alle drei Bilder entsprechen 92,1 μm (*x*-Achse)

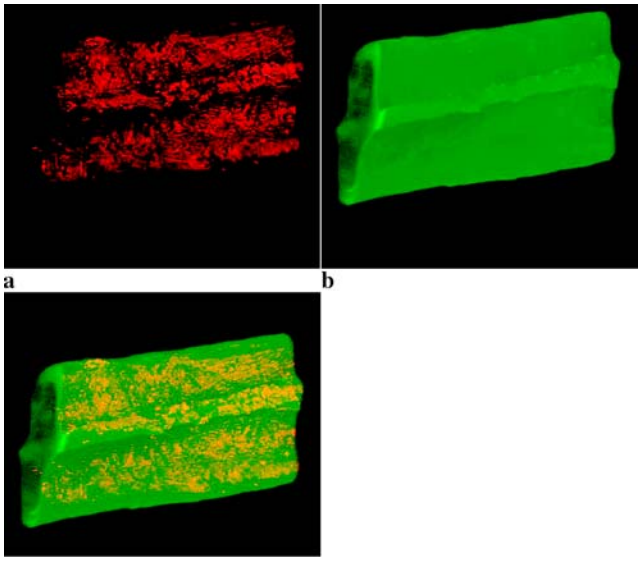

Fig. 3 Resin penetration in a single fiber (*Picea* spp.) – Side view from ZEISS CLSM 3D projections. This view was generated using the same scan as in Fig. 2. Even if the resin had penetrated deeply in the fiber, the surface is still well covered. The three images are also 92.1 μm in height

Abb. 3 Harzeindringung in eine einzelne Faser (*Picea* spp.) – Seitenansicht auf Basis der Zeiss CLSM 3D-Projektionen. Dieses Bild stammt vom gleichen Scan wie die Bilder in Abb. 2. Trotz der hohen Eindringtiefe des Harzes ist die Oberfläche noch gut bedeckt. Die drei Bilder entsprechen ebenfalls 92,1 μm

A typical MDF group of fibers is shown in Fig. 4. The resin was well distributed over the irregular fiber surfaces. Hundreds of micrometric resin droplets were landed on the fibers besides larger resinated areas. To make a comparison, Fig. 5 was made to show the normal distributions curves of UF and UMF (3 and 6% M/(U + M)) resin aggregates diameter of gyration. They were evaluated with a low angle laser light scattering (LALLS) device on fresh but diluted resins. The 12% M/(U + M) resin formed a paste like material when diluted at room temperature so it was discarded from the LALLS test. Measurements showed that the smallest droplets have a diameter similar to the average UMF resin aggregates (600–1000 nm). These microscopic resin droplets on the fiber surface are an indicator of a good resin atomization. The resin aggregates are the most stable thermodynamic state of the UMF polymer when chains are in contact with water. According to our LALLS study, their diameter can vary from 60 to 10 000 nm and resins are made with up to 65% (weigh/weight) of

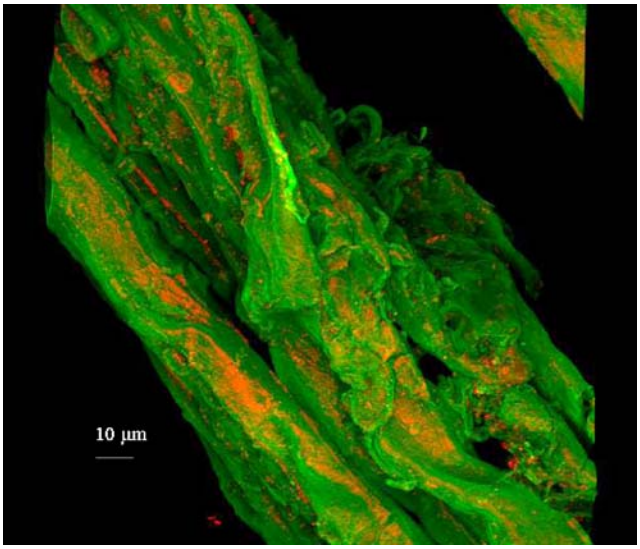

Fig. 4 Resin distribution on bounded fibers (*Picea* spp.) – Side view from ZEISS CLSM 3D projections. This section shows how irregular the surface of refined fibers can be. Good resin coverage was achieved. Resin droplets with a diameter of about a micron are spread all over the fibers. Many large areas are covered with resin revealing patterns similar to the microstructure of these fibers (particularly on the middle part of the left fiber)

Abb. 4 Harzverteilung auf Faserbündel (*Picea* spp.) – Seitenansicht auf Basis der Zeiss CLSM 3D-Projektionen. Dieses Bild zeigt, wie unregelmäßig die Oberfläche gemahlener Fasern sein kann. Es wurde eine gute Harzabdeckung erzielt. Harztropfen mit einem Durchmesser von ca. 1 µm sind über die Fasern verteilt. Viele große Flächen, die mit Harz bedeckt sind, entsprechen der Mikrostruktur dieser Fasern (insbesondere im mittleren Bereich der linken Faser)

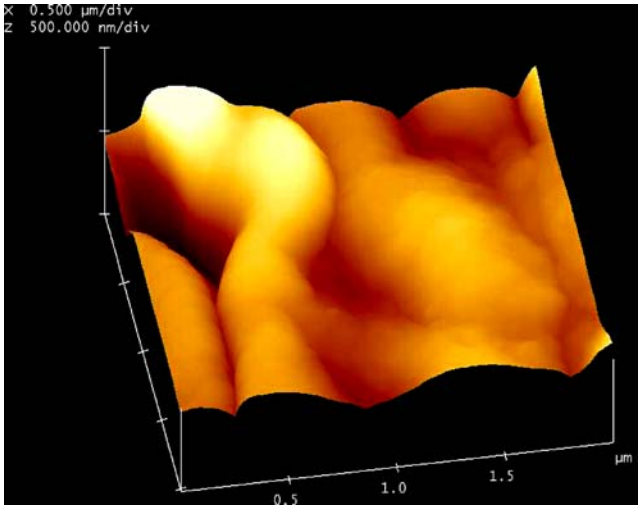

Fig. 6 Surface microstructure of refined spruce fiber (*Picea* spp.) depicted by the atomic force microscope (AFM). These are large fibrils aggregates (±500 nm). They are generally oriented toward the fiber length. The fibrils aggregates are the smallest observable details of the CLSM. This fibrous structure of the fiber can be revealed by the resin as seen in Fig. 4. This AFM representation suggests that the resin can penetrate the fiber through small gaps between fibrils aggregates

Abb. 6 Mittels Rasterkraftmikroskop (AFM) ermittelte Oberflächen-Mikrostruktur gemahlener Fichtenfasern (*Picea* spp.). Es handelt sich dabei um große Fibrillenaggregate (±500 nm), die generell in Faserlängsrichtung ausgerichtet sind. Die Fibrillenaggregate sind die kleinsten mit dem CLSM erkennbaren Details. Diese feinfaserige Struktur der Faser wird durch das Harz erkennbar (siehe Abb. 4). Diese AFM-Darstellung weist daraufhin, dass das Harz durch kleine Spalten zwischen den Fibrillenaggregaten in die Fasern eindringen kann

them. A considerable amount of energy would be needed to split them into smaller parts when spraying them on fibers.

Figure 6 shows a MDF wood fiber microstructure reconstruction made with an AFM. It represents a typical fiber surface of the fiber with very large fibrils aggregates (±500 nm). They leave few spaces for resin penetration but the CLSM proved that resin can go through any layer of fibrils aggregates. The affinity of the UMF molecules is much greater for the fiber polymers than for the water and/or air.

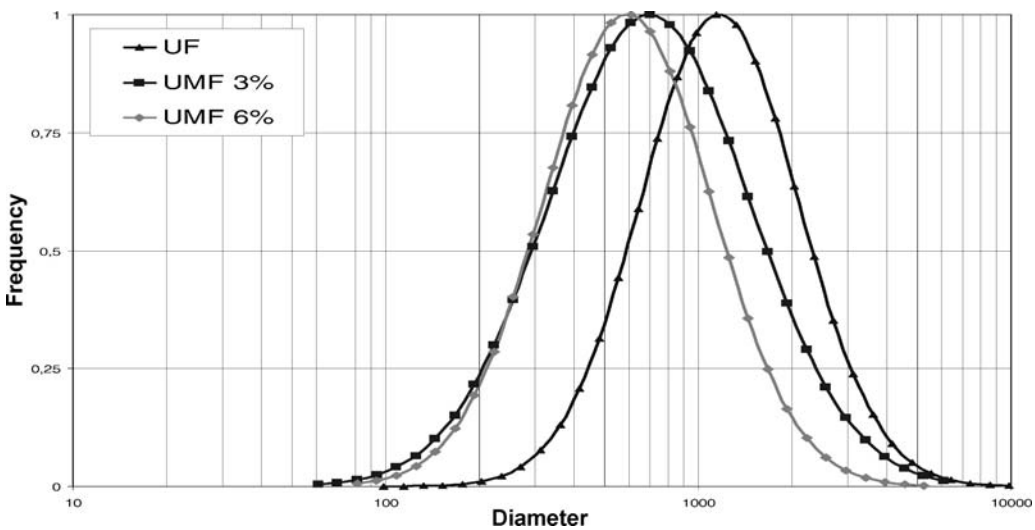

Fig. 5 Low angle laser light scattering (LALLS) measurements on resin with different level of urea to melamine substitution (0, 3 and 6%). The gyration radius of UMF aggregates follows a normal distribution for the three resins

Abb. 5 Kleinwinkel-Laserlichtstreuung (LALLS) Messwerte auf Harz mit verschiedenen Harnstoff-Melamin-Mischungsverhältnissen (0, 3 und 6%). Die Werte der drei Harze sind normal verteilt

This is why the pressure on UMF molecules to aggregate is released when the injected droplets hit the fiber. This allows the molecule to disperse in fiber voids. UMF resins are slightly soluble in water so when fiber voids are filled with water, the smaller molecules are allowed to freely penetrate them. The resin molecules could be sorted by size in that process as does a chromatograph but this is still a hypothesis. Water desorption (in the dryers) may also help the resin to penetrate fibers by slightly enlarging the voids between fibrils aggregates (Abe and Yamamoto 2005).

4 Conclusion

MDF fibers prepared according to the industrial process were glued and dried in line. The CLSM reconstructions proved that in this process, the resin can penetrate into any layers of the wood cells (but meets more resistance in the S2 Layer). The final depth of penetration and the surface coverage was the same for all resins (0, 3, 6 and 12% M/(U + M)). Many pores of spruce wood fibers are resulted from the fibrils aggregates irregular diameter and alignment. The resin uses its affinity to both water (medium) and wood polymers (strong) to penetrate through pores from surface to lumen (2–10 μm). Possible resin interaction with water (dilution effect, hydrolysis) and the extreme heat in the tube blender surely keeps the resin viscosity and molecular weight down thus penetration rates very high. But this extensive penetration is the drawback of a process that is well known for its high resin coverage (22.5% measured with the CLSM) and efficiency. Some sections of the fibers surface can have over 50% of their surface covered with resin. It is interesting to notice that the fiber microstructure is revealed by the resin in these areas. It was concluded that the AFM and CLSM (high resolution) techniques could provide useful information to explain how UMF resin penetrates in MDF fibers. The future work will be focused on finding a way to slow down the resin penetration rate without lowering its reactivity.

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