

CHAPTER 4

Fiber Surface Modification by Steam-Explosion. I. Analysis of co-refined wood and polyolefin by microscopy.

Abstract

Wood chips were processed with polyolefins (polyethylene and polypropylene) by steam-explosion. The resulting material was analyzed by a combination of microscopy methods to understand the dispersion and association of thermoplastic on the wood fiber. Factors such as polyolefin (PO) type, molecular weight, and polyolefin form were examined and related to fiber coating. A method for tagging a maleated polyolefin with a fluorescent label was developed and used in confocal laser scanning microscopy to enhance the understanding of low molecular weight PO interaction with cellulose fiber. Autofluorescence of the steam-exploded fiber was shown to inhibit the determination of the location of the fluorescent PO. Instead, the autofluorescence was used to understand the redistribution of wood bio-polymer components during steam-explosion. The study demonstrated that molecular weight is an important factor for polyolefin dispersion and wood fiber coating.

Introduction

Microscopic examination of wood and wood-composites has elucidated the fine structure of wood down to the nanolevel. Primarily, electron microscopy has been used to probe the morphology and orientation of wood cell wall components [1]. Advances in technology, such as atomic force microscopy and the field-emission gun for scanning electron microscopy, have increased resolution of certain specimens to the sub-nanometer range [2] and have reduced charging of biological samples during scanning [3]. Additionally, 3-D modeling is realized with confocal laser scanning microscopy (CLSM) [4]. Many of these technologies are currently being used in a variety of applications to characterize wood and fiber composites. Alone, each microscope technique can probe specific research questions, however, a combination of microscopy methodologies facilitates a comprehensive understanding of the material. An overlap of data is apparent, but using multiple microscopes to image a material surpasses the limitations of an individual microscopic technique.

Background on Microscopy Techniques

Field emission scanning electron microscopy utilizes a “field emission cathode” that generates the probing electron beam [5]. Typically for scanning electron microscopy, a tungsten wire is used as the source to generate electrons for the beam. In contrast, the field emission cathode has a sharp tip from which electrons can easily tunnel. A result of using the field emission cathode is a probe that has increased brightness and reduced probe size that produces a higher resolution image at lower accelerating voltages. Non-conducting specimens with no coating or thin coating (2nm) can be imaged with reduced charging by low voltage scanning [6]. This allows viewing of greater detail of the specimens because the coating is not blocking surface structures.

One drawback of the technique is the limited representation of the highly magnified surface of a heterogeneous material. In other words, micrographs contain a small section of the fiber surface that is very heterogeneous, which may or may not be representative of the whole fiber. Additionally, it is difficult to differentiate components that appear similar in a micrograph. Energy X-ray analysis may be used to resolve chemical knowledge, but in this study the polyolefins contain hydrogen and carbon, the same elements found in wood. Furthermore, there are a variety of methods to dry wood samples for use in electron microscopy. These methods

include air-drying, critical point drying, and freeze-drying. Artifacts found with each type of drying for microscopy studies related to wood and fiber science were reviewed [1].

Confocal laser scanning microscopy is similar to traditional fluorescent microscopy except for utilizing a pinhole aperture that only allows light in a certain focal plane to exit to a detector [8]. For quantitative data, a three dimensional image of the specimen can be created. By restricting the detection of light to the focal plane of the sample, out-of focus light is filtered. Samples are optically sectioned with the laser light into planes and each plane is raster scanned. The light source for this microscopy is laser light of wavelengths in the mid 300 nm to low 600 nm range that excites chromophores, either stained into the material or inherent of the material, and causes an emission of light at higher wavelengths. Autofluorescence of wood pulps was reviewed in detail by Olmstead and Gray [9].

A drawback of this method compared to other techniques is that maximum resolution of the microscope is about 200-500 nm. This value is significantly greater (lower resolution) than what can be achieved with electron microscopy and atomic force microscopy. Additionally, fluorescence can only reveal general chemical information limiting the identification to certain compounds.

In an introduction to the CLSM for use with wood pulp, Moss et al. reported that the instrument could be used to determine fiber morphology, external/internal fibrillation and wet fiber flexibility, distribution of fines, sheet structure, and surface roughness [10]. Measuring fiber collapse was another application of the CLSM [11]. Singh and Donaldson have investigated variations in lignification within individual cell wall layers and relative lignin concentrations with brightness ratios [12]. Donaldson et al. measured the influence of laser light on the autofluorescence of wood fibers and holocellulose [13]. The authors reported that wood fibers strongly autofluoresce at wavelengths of 530 nm, while holocellulose fibers show only slight autofluorescence at this wavelength and autofluoresce more strongly at 600 nm.

From the above review it can be highlighted that each microscope has its own particular information that it can add to describing the relationships and interactions of components for the emerging class of wood thermoplastic composites. SEM can be considered surface sensitive, while transmitted light microscopy is not. CLSM can be viewed as surface sensitive and possessing the ability to optical section the material. In this research the microscopy techniques are applied to the study of thermoplastic wood material produced from a new processing method

of co-refining wood and polyolefine (PO) by steam-explosion. With this method there is the possibility to produce a fiber bundle that may be suitable for use in wood thermoplastic composites. A processing technique with the potential to produce a PO-coated fiber bundle would be advantageous because the performance of wood plastic composites depends on the dispersion of the fiber and the interaction of the wood and PO domains. Therefore, the aim of the study is to explore the relationship of PO parameters (molecular weight and initial PO form) and the resulting PO domain size within the co-processed steam-exploded material.

Methods and Materials

Steam-explosion

A 1-gallon Parr reactor vessel was converted into a steam-explosion vessel by modifying the lid with a steam inlet port and the base of the reactor with a 3/8" ball valve. Additionally, the reactor had a port to evacuate the atmosphere air prior to the introduction of steam and replace it with compressed gas. *Quercus rubra* (red oak) chips were obtained from a local sawmill and the polyolefin (PO) was obtained from a number of suppliers and one commercial source. The PE had a density of 0.92 and a number average molecular weight (M_n) of 1,400. The molecular weight for a variety of isotactic polypropylenes (iPP) used in this experiment is reported in Table 4.1. Red oak chips and either polyethylene or polypropylene were placed in the reactor and the reactor lid was bolted in-place. The air atmosphere was removed and replaced with one of the following gases from compressed cylinders: argon, air, and a 50:50 mixture of argon:oxygen obtained from Linde Gas. After the materials were combined in the reactor, a ball valve was opened, steam with a temperature of 230°C was introduced in the reaction vessel, and the stirrer was turned to 100 rpm. After a residence time of five minutes, the exit ball valve was opened ejecting the material through a cyclone (steam-solids separator) into a collection container. The resulting material was washed with warm water in an Erlenmeyer flask and recovered by filtering in a Buchner funnel. The material was rinsed with twice the volume of water that was in the Erlenmeyer flask. The material was dried in a desiccator and stored until further analysis. This procedure was repeated for each wood and polyolefin combination. Additionally, the procedure was used with regenerated cellulose (Lyocell staple fiber, a product of Acordis) fiber and maleated polyethylene with the fluorescent label. The lyocell fiber had a diameter of 10 μ m and length of 10mm.

Table 4.1 Polyolefin properties

Description	Form	Source	Mn	Mw	Intrinsic Viscosity	melt flow index	Viscosity* (Pa-s)
1-iPP	Course Powder	SP ²	x	x	2.2-2.5	4g/10min	3777
2-iPP	Pellet	Aldrich	9,502	35,843	x	1000g/10min	23
3-iPP	Pellet	Aldrich	5,000	12,000	x	x	0.4
4-iPP	Pellet	Aldrich	50,000	190,000	x	35g/10min	2016
5-iPP	Fiber	Fiber Visions	x	x	x	40g/10min	x
1-PE	Fine Powder	SP ²	1,400	x	x	x	0.35**

*Polypropylene viscosity values are reported for 1 Hz shear rate at 195°C.

**Polyethylene viscosity is reported at 140°C.

Preparation of the fluorescent labeled maleated polyethylene

Fluorescein and polyethylene-graft maleic anhydride (0.05%) were obtained from Sigma-Aldrich. Both of these materials were dried in a desiccator under vacuum over phosphorus pentoxide. Tagging of the maleated polyolefin was adopted from the techniques described by Tong et al. and Li et al. [14, 15]. The maleated polyethylene (20.07g) was added to a triple neck round bottom flask that contained a magnetic stir bar and was fitted with a condenser and water collector. The polyolefin was heated to 180°C for 2 hours under a nitrogen blanket. Anhydrous o-xylene (325 ml) was transferred to the flask and refluxed until the maleated polyethylene was dissolved. Next, fluorescein powder (0.706g) was added to the flask and the flask continued to reflux for 24 hours (see Figure 4.1 for reaction scheme). After the reported reaction time, octyl amine (0.403g) was added to the solution and reacted with any unmodified anhydride for an additional 8 hours. Subsequently, the solution was cooled and precipitated by pouring it into 650 ml of acetone. The solution was filtered across Whatman filter paper recovering the precipitated polyolefin. The precipitated polymer was then dissolved in hot xylene, cooled, precipitated in acetone, and recovered by filtering. This process was repeated three times to remove excess or unreacted fluorescein.

For the control CLSM experiment, the fluorescein-tagged maleated polyethylene was dissolved in xylene and subsequently the lyocell fiber was dipped into the solution. Next, the fiber with adsorbed polyolefin was stained with either Congo red in a water solution or rhodamine B in an acidic ethanol solution as counter stains. The success of tagging the maleated polyolefin was demonstrated by fluorescence of the polyolefin.

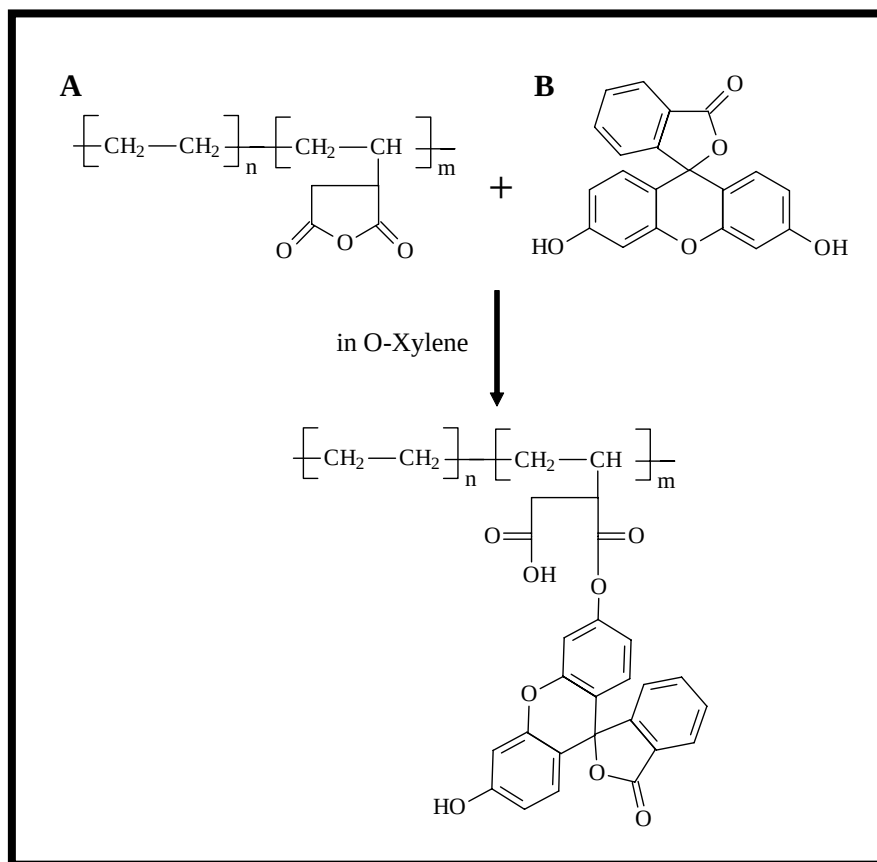


Figure 4.1 Reaction scheme for the fluorescent labeling of maleated polyethylene. A) maleic anhydride-g-polyethylene (0.05%) and B) fluorescein

Digital Photography and light microscopy

A Nikon Coolpix digital camera was used to record images of the steam-exploded material. Digital images did not undergo any editing, filtering, or enhancement. Steam-exploded material was placed in distilled water and the resulting slurry was transferred to glass microscope slides by pipette. A Nikon microscope fitted with a polarizer, analyzer and a CCD camera was used to record images of the material. The analyzer was manually rotated so it was perpendicular to the polarizer for the polarized optical micrograph images.

Field Emission Scanning Electron Microscopy

Material from steam-explosion was prepared for scanning electron microscopy by two procedures. The first technique incorporated freeze-dried fiber that was placed on double sided carbon tape attached to a sample stub. The second method used a pipette to place droplets of a dilute water solution of the material directly on a clean metal sample stub and subsequently allowed to dry. The second method was employed to ensure the adhesive from the tape was not adding artifacts to the wood cell surface. Fiber bundles from co-steam-exploded wood and iPP did not adhere to the clean stub surface without the double-sided tape.

Stubs and fibers were then coated with two nanometers (nm) of gold palladium in a Cressington 208HR sputter coater. The stubs were transferred to a Leo 1550 field emission scanning electron microscope. Accelerating voltage between 2-5 kV was used with a working distance that varied between 3 and 8mm. Digital images were recorded with either the “in lens” or secondary electron detectors.

Confocal Laser Scanning Microscopy

A Zeiss 510 confocal laser scanning microscope was used to record fluorescent images of the material. The same method outlined above in the light microscopy section was used to prepare the specimens for CLSM. Each image was recorded with an average of two to eight scans to eliminate background noise. For the co-steam exploded wood and polyolefin experiments, excitation wavelengths of 364 and 633nm were used with a band pass (385-470nm) and a long pass (650nm) emission filters, respectively. For the steam-exploded lyocell and fluorescent tagged maleated polyethylene, excitation wavelengths of 543 and 488nm were used with two emission filters, long pass (560nm) and band pass (505-550nm), respectively. Note that colors presented in CLSM images are artificial and do not result from the true wavelengths of light.

Rheology

Steady-state viscosity experiments were performed on a TA Instruments AR 1000 Rheometer using parallel plate geometry. Using a temperature control unit, the experiment was conducted at 195°C at shear rates that ranged from 0.025 to 10.0 s⁻¹. It should be noted that repeatable results were derived from using a minimum amount of material that filled the plate opening of

approximately 100 μm . The material was placed on 25mm disposable plates at room temperature and conditioned for approximately 30 minutes at 195°C before experimentation.

RESULTS

Dispersion of Polypropylene

Low magnification images of co-steam-exploded wood and iPP are displayed in Figure 2a-c. Each treatment was performed under the same conditions, differing the polypropylene form, pellet (Figure 4.2a and Figure 4.2c) or fiber (Figure 4.2b), and polypropylene melt flow index, 35g/10min (Figure 4.2a), 40g/10min (Figure 4.2b), and 1000g/10min (Figure 4.2c). Low melt flow index iPP (Figure 4.2a-b) resulted in distinct clusters of wood fiber intermixed with globules of iPP. The iPP cluster diameter size (1.5-2cm) corresponds approximately to the 2cm diameter of the exit pipe of the steam-explosion reactor. The largest iPP clusters contain a network of strings with an average string diameter of one millimeter. The steam temperature is 60°C above the melting temperature of iPP, yet the low melt flow index iPP does not “fluidize” in the melt state on account of the time of exposure. It should be noted that although the samples differ in initial iPP form, both samples result in a distinct separation of wood and polypropylene. These two forms of iPP, fiber and pellets, have different specific surface areas (iPP fibers=400mm²/g and iPP pellets=2mm²/g, calculated) and hence, heat transfer to the interior of the material occurs with different thermal gradients. In other words, there is a larger thermal lag for the iPP pellets than for iPP fiber, but this does not appear as a limiting factor for the dispersion of iPP with wood fiber. By increasing the melt flow index of the iPP to 1,000g/10min, the iPP no longer separates into large strings and clusters with macroscopic dimensions (Figure 4.2C). Instead the co-steam-exploded iPP and wood material appears as a uniform material on the macroscopic level. This is apparent in the loose nature of fiber bundles (Figure 4.2C) in relation to the wood fiber agglomerations (Figure 4.2a-b). From the above observations, melt flow index, which is related to molecular weight of the polymer is an important factor for polymer dispersion among the wood fiber.

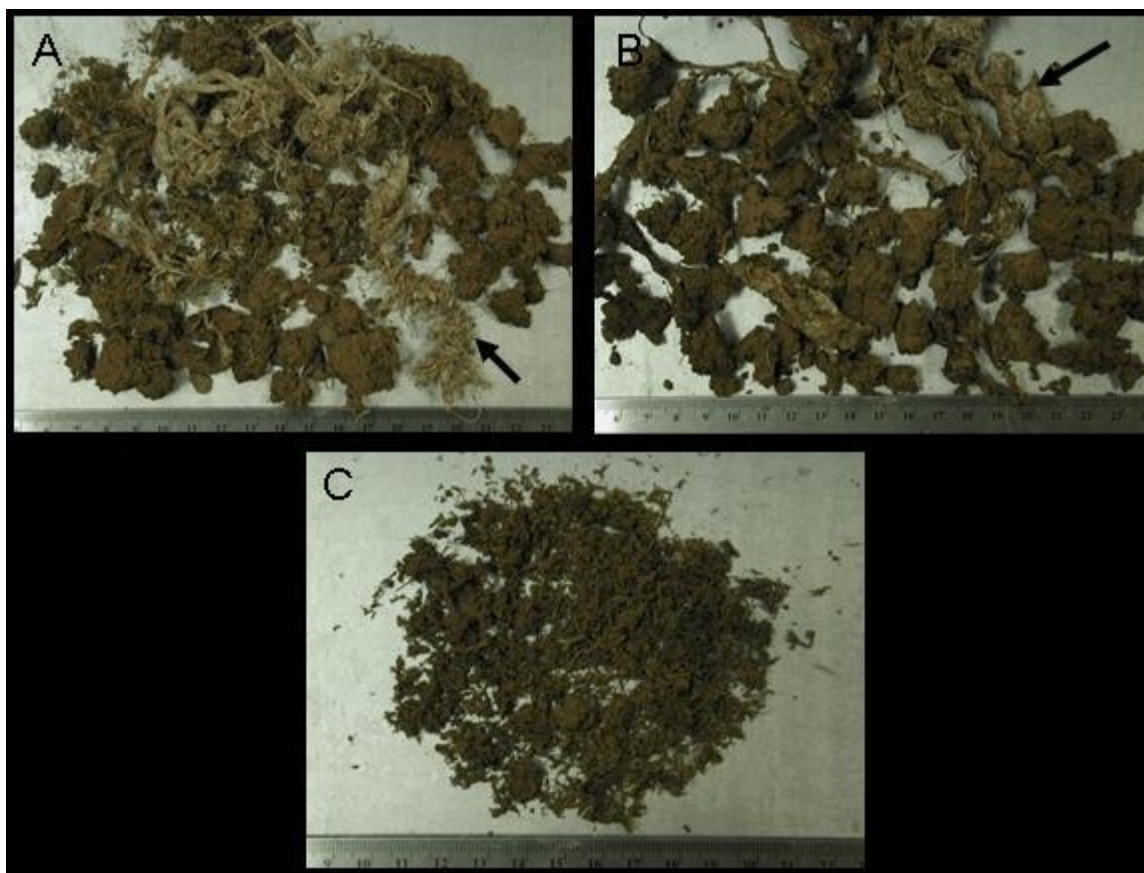


Figure 4.2. Co-steam-exploded wood and iPP as a function of polyolefin form and molecular weight.. A) iPP used in experiment was initially in pellet form (MFI 35g/10min), B) iPP used in experiment was initially in chopped fiber form (MFI 40g/10min), C) iPP used in experiment was initially in pellet form (MFI 1000g/10min). Arrows indicate examples of polypropylene clusters (cm scale shown).

Further examination of the influence of molecular weights on the dispersion of iPP was performed with transmitted light microscopy (Figure 4.3a-d). The material in Figure 4.3a-b is co-refined wood and iPP with a M_n of 5,000, while Figure 4.3c-d contains co-refined wood and iPP with iPP of molecular weight M_n 9,500 (note this is the same iPP as for Figure 4.2c). Dark portions are evident in the polarized images (Figure 4.3b and 4.3d) along with birefringence from the wood cells. Typically, iPP crystallites will show birefringence as a result of the ordered crystal lattice structure. However, there is quenching of the iPP below the crystallization temperature during the decompression step resulting in marginal crystallization. Therefore, dark globules are attributed to iPP. Furthermore, co-steam-exploded material with iPP (M_n 5,000)

contains dark coalesced droplets distributed among wood cells (Figure 4.3b). There is a wide range of cluster size documented in the standard deviation. The average diameter of the clusters along their major axis is $52\mu\text{m}$ with a standard deviation of $28\mu\text{m}$ ($n=48$). Additionally, steam-explosion with low molecular weight polyethylene (M_n 1,400) demonstrates similar behavior to the low molecular weight iPP-- separation of PE into micron sized droplets (later shown in Figure 4.13). The distribution of iPP clusters among wood fibers (Figure 4.3b) is distinctly different from co-steam-exploded material with iPP (M_n 9,500) (Figure 4.3c-d). This material consists of fiber bundles that appear coated. These images demonstrate that there is a lower molecular weight limit of the iPP that will no longer coat fiber bundles.

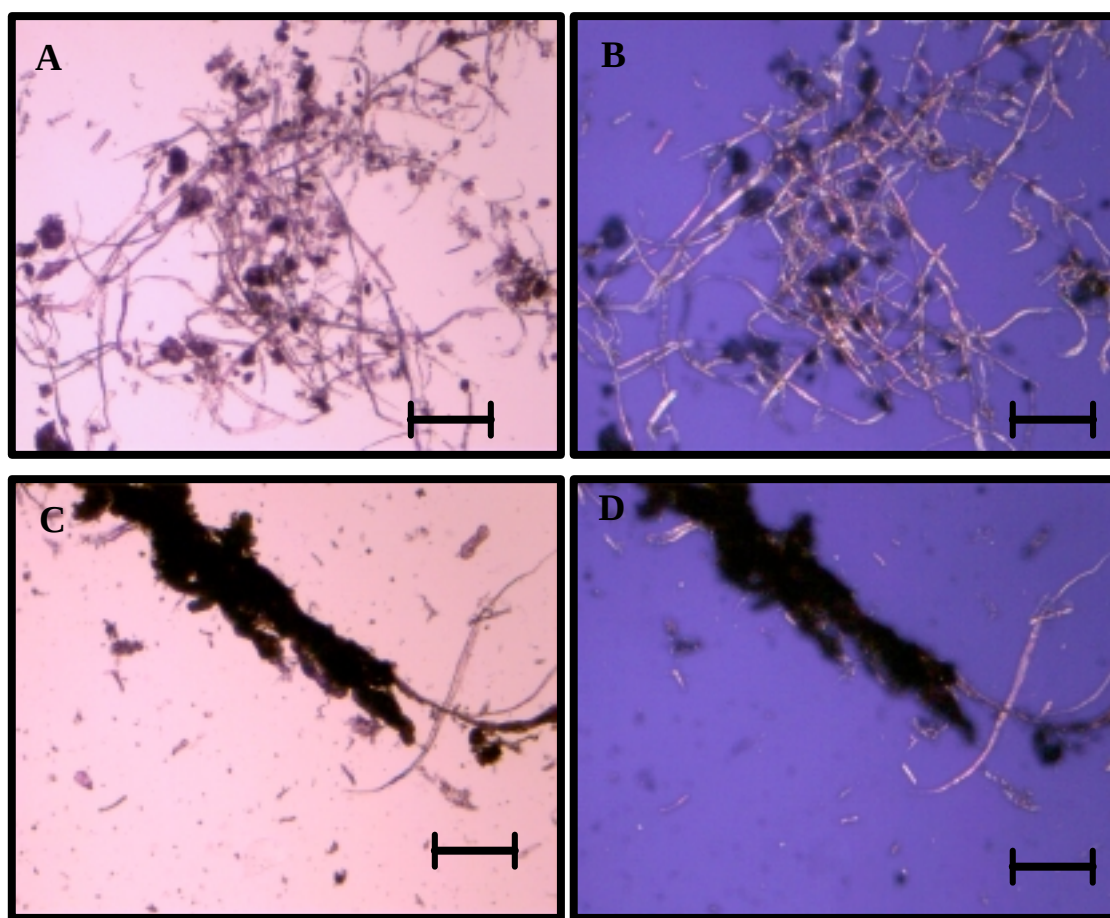


Figure 4.3. Distribution of polypropylene in co-steam-exploded material as a function of molecular weight. A and B are light and polarized light optical micrographs from iPP with a M_n 5,000. C and D are light and polarized light optical micrographs of iPP with M_n of 9,500. The images illustrate the presence of micron sized aggregates for the lower MW iPP and the coating of fiber bundles for the higher MW iPP. Bar is $300\mu\text{m}$.

The melt rheology for three different molecular weight iPPs (M_n 5,000, M_n 9,500, and M_n 50,000) was tested at 195°C to determine their viscosity as a function of shear rate (Figure 4.4). The lowest molecular weight iPP has an average viscosity of 0.34 (+/- 0.08) Pa-s. This value is within the range of the Brookfield Thermosel value supplied by the manufacture of 0.60 Pa-s at 190°C. The lowest molecular weight iPP has a corresponding viscosity that is 2 decades lower than the iPP with M_n 9,500 and 4 decades lower than the iPP with M_n of 50,000 for shear rates under 1s^{-1} . Additionally, the two highest molecular weight iPPs demonstrated shear thinning behavior, while the lowest MW iPP did not have reproducible shear thinning behavior. The data indicate a large difference (decades of magnitude) in melt rheologies of the iPP as a function of molecular weight.

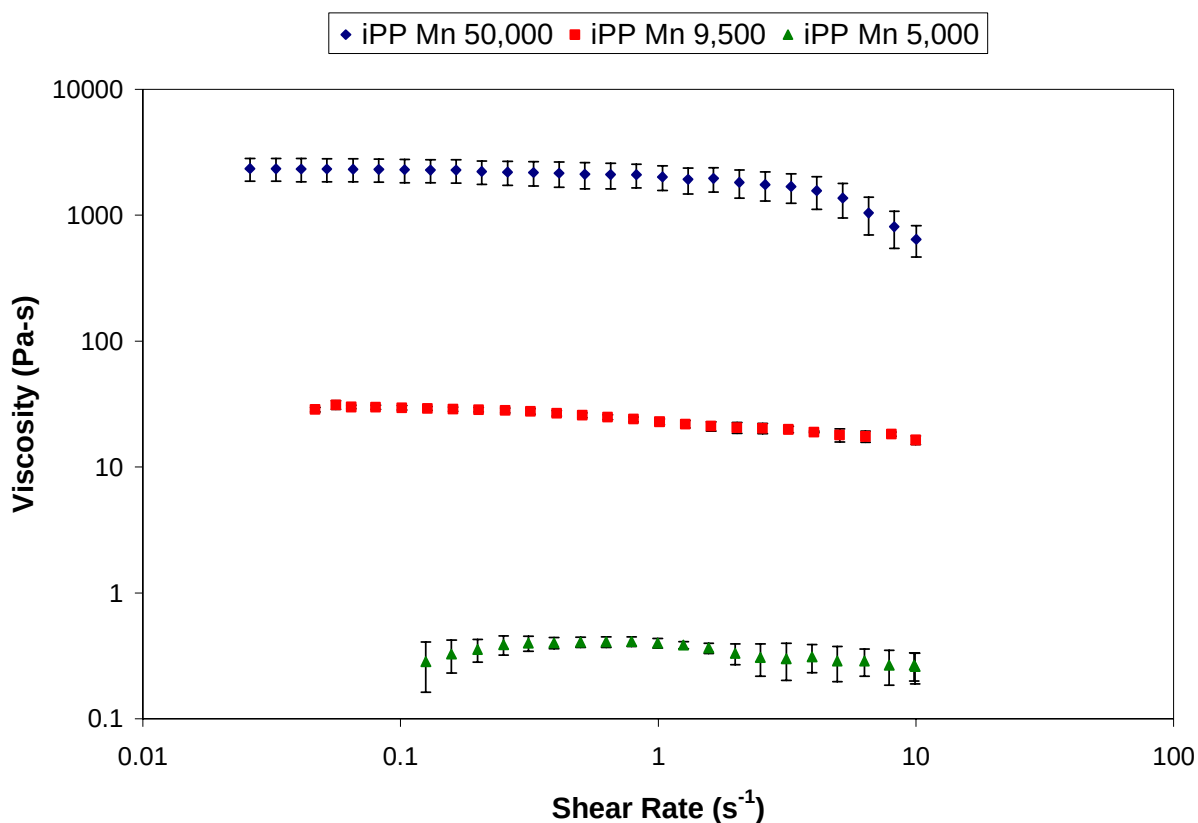


Figure 4.4. Melt viscosity of polypropylene as a function of molecular weight at 195°C.

The apparent differences in iPP melt viscosity are reflected in the distributions of iPP among the wood fiber (Figure 4.2 and 4.3). The low melt viscosity iPP has part of its molecular weight distribution below the critical chain entanglement molecular weight. Evidence of this is found in the lack of reproducible shear thinning behavior of the polymer (Figure 4.4). This means the majority of polymer chains in the melt are not affected by diffusion and entanglements. In other words, there is less cohesiveness of the polymer in the melt. As the molecular weight increases above the critical chain entanglement molecular weight, the melt viscosity scales to a power of 3.4 of the degree of polymerization (DP). The cohesiveness reflected in the melt viscosity quickly increases as the DP rises. The iPP with a Mn of 9,500 that is just above the critical chain entanglement molecular weight (MW 7000) forms a coating on fiber bundles (Figure 4.3). Furthermore, when the molecular weight of the iPP is increased to a Mn of 50,000, the cohesiveness of the melt is too great. The result of the high melt viscosity is that the iPP cannot be dispersed easily with the fiber bundles and is separated into macroscopic domains. From these observations there appears to be a window of molecular weights that occurs right above the critical chain entanglement molecular weight that allows for a high interfacial area between wood fiber and iPP by forming film-like coating on the fiber (Figure 4.5).

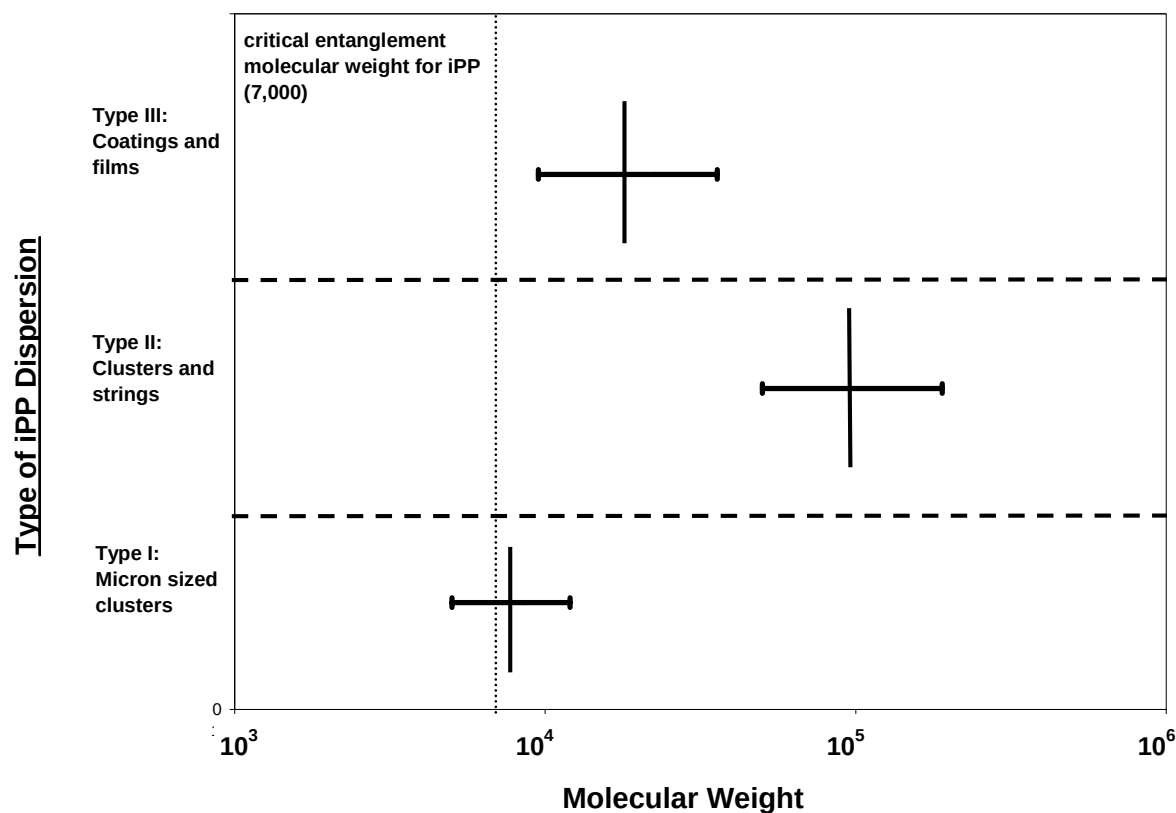


Figure 4.5 The effect of molecular weight on the association of wood fiber and iPP. Horizontal lines are distance between M_w and M_n . Vertical lines are empirically judged position in dispersion behavior.

Surface morphology and polyolefin spatial arrangement

Field-emission scanning electron microscopy determined the fiber surface morphology of the steam-exploded material. The heterogeneous nature of the steam-exploded wood surface is evident from the micrographs (Figure 4.6A-E). Two steam-exploded wood fibers are shown in Figure 4.6A that demonstrate typical characteristics of the fibers as a whole: fibrillation of the fiber surface layers, coalesced material on the fiber surface, and ridges and folds along the fiber surface. Moreover, Figure 4.6B shows both coalesced polymer and disrupted microfibril structures, while Figure 4.6C contains sections of cell wall partially detached (seen as wood cells connected together). Figure 4.6D,E contain evidence of fiber damage by the shearing of fiber perpendicular to the fiber axis and parallel to the fiber axis. Likewise, steam-exploded lyocell

fiber also has damage in the form of shearing perpendicular to the plane of the fiber axis and fibrillation parallel with fiber axis (Figure 4.6F). It is apparent that the steam-exploded wood surface is highly textured because of the mechanical disruption of the wood, rearrangement of lignin [18,19], and the adsorption of wood cell parts/polymers on the wood surface [20].

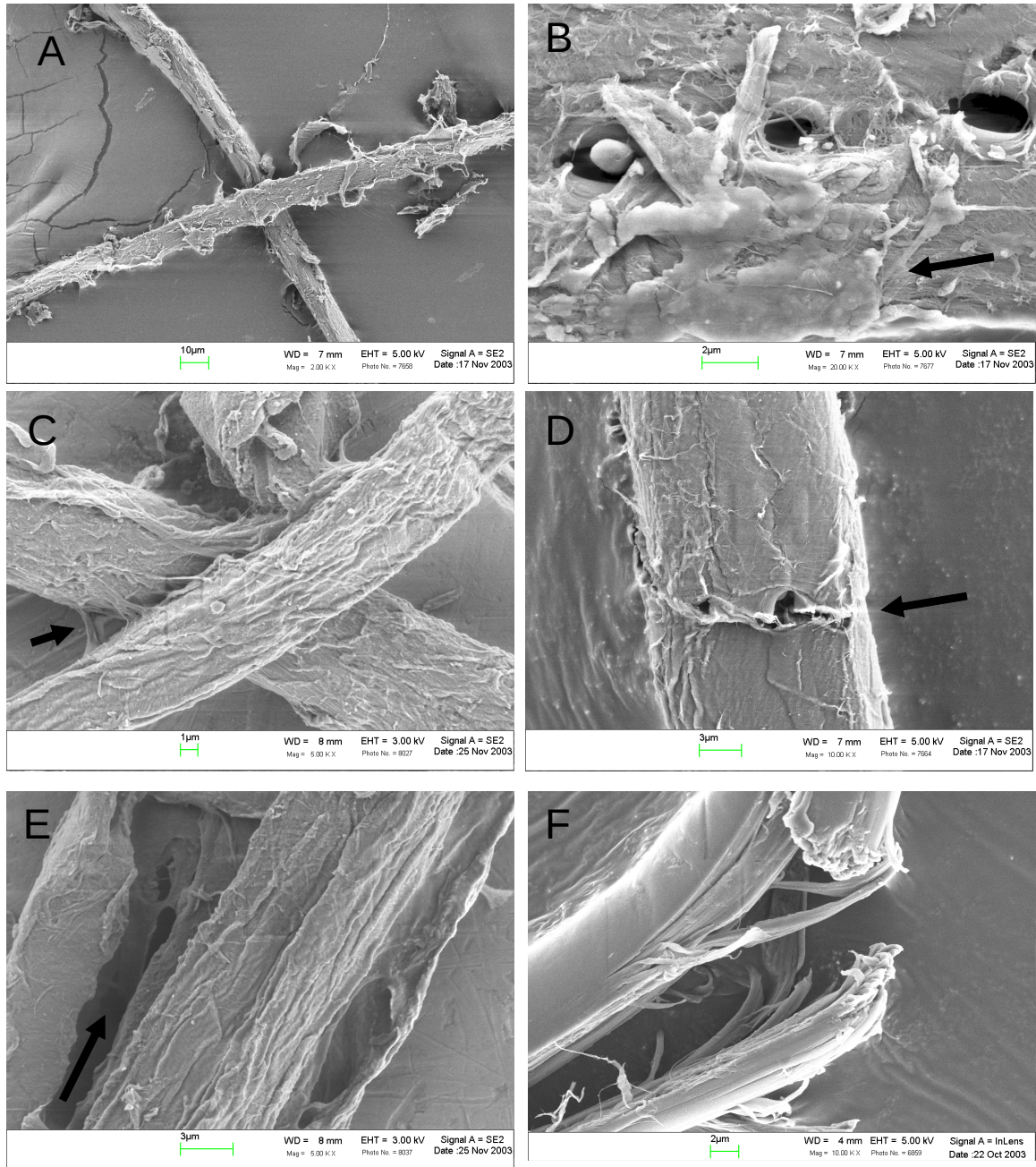


Figure 4.6. Steam-exploded red oak cells A-E (polyolefin free) and lyocell F. (A and B) Characteristic heterogeneous fiber surface. Arrow in B highlights coalesced wood polymer on surface. (C-E) Fiber damage. Arrow in C points to fibrillated cell wall. Arrow in D highlights transverse failure. Arrow in E shows parallel unraveling of wood cell wall. (F) Steam-exploded lyocell fiber with transverse and parallel fracture of the surface.

Co-steam-exploded material with either iPP that has a M_n of 9,500 (Figure 4.7a-c) or PE with a M_n of 1,400 (Figure 4.7d-f) show two unique differences. Co-steam-exploded wood and iPP (M_n 9,500) have fiber bundles of approximately 5 to 10 fibers coated with iPP (Figure 4.7a-b), while micrographs of steam-exploded wood never contained similar fiber bundles. Moreover, co-steam-explosion of wood and iPP (M_n 9,500) veils the surface morphology (cellulose fibril pattern) of the wood cell wall (Figure 4.7c). The distinct fibril pattern is no longer apparent; instead a continuous layer of material is present that contains some submicron sized texture. In contrast, co-steam-exploded wood and PE with a M_n of 1,400 contain individual fibers with a highly fibrillated texture (Figure 4.7d). Coalesced material is found on the fiber surface that appear as 2-6 μ m diameter clusters (Figure 4.7e), or that cover the width of the fiber surface (Figure 4.7f). The SEM images confirm the finding of a difference in polyolefin spreading based on the melt viscosity/molecular weight of the polymer. The iPP with M_n of 9,500 has fiber bundles that are consistently coated, while the lower melt viscosity PE with a M_n of 1,400 do not have a similar response.

The fiber bundles from co-steam-exploded wood and iPP with a M_n of 9,500 are highly representative of the material (Figure 4.3c-d, Figure 4.7a-c). This was evident in washing and recovering the material by vacuum filtration across Whatman filter paper. In the residue, a thin layer of fiber and fines was present on the vacuum filter. Qualitatively, the thin layer of flexible fibers/fines formed a sheet. This was in contrast to the bulk of the material that sat upon that layer and did not have a sheet like property. Most likely, the bundles did not have similar flexibility to come into intimate contact and form a continuous sheet. Spreading of the iPP on the fiber bundles, as documented above, would prevent flexibility to achieve intimate contact.

In order to assist with the determination of polyolefin arrangement on/with the fiber, confocal laser scanning microscopy (CLSM) was employed to distinguish low melt viscosity (<1.0 Pa-s) polyolefin on the fiber surface. CLSM employs a form of fluorescence spectroscopy and as a result, chemically different materials may be separated by the light emitted by fluorescence. A control experiment was used to demonstrate the utility of the method. This was done by dipping a lyocell fiber into a xylene solution containing fluorescent-labeled maleated polyethylene and counter staining the material with rhodamine B (Figure 4.8a-d). The counter stain was used to highlight cellulose rich regions relative to the polyolefin. In other words,

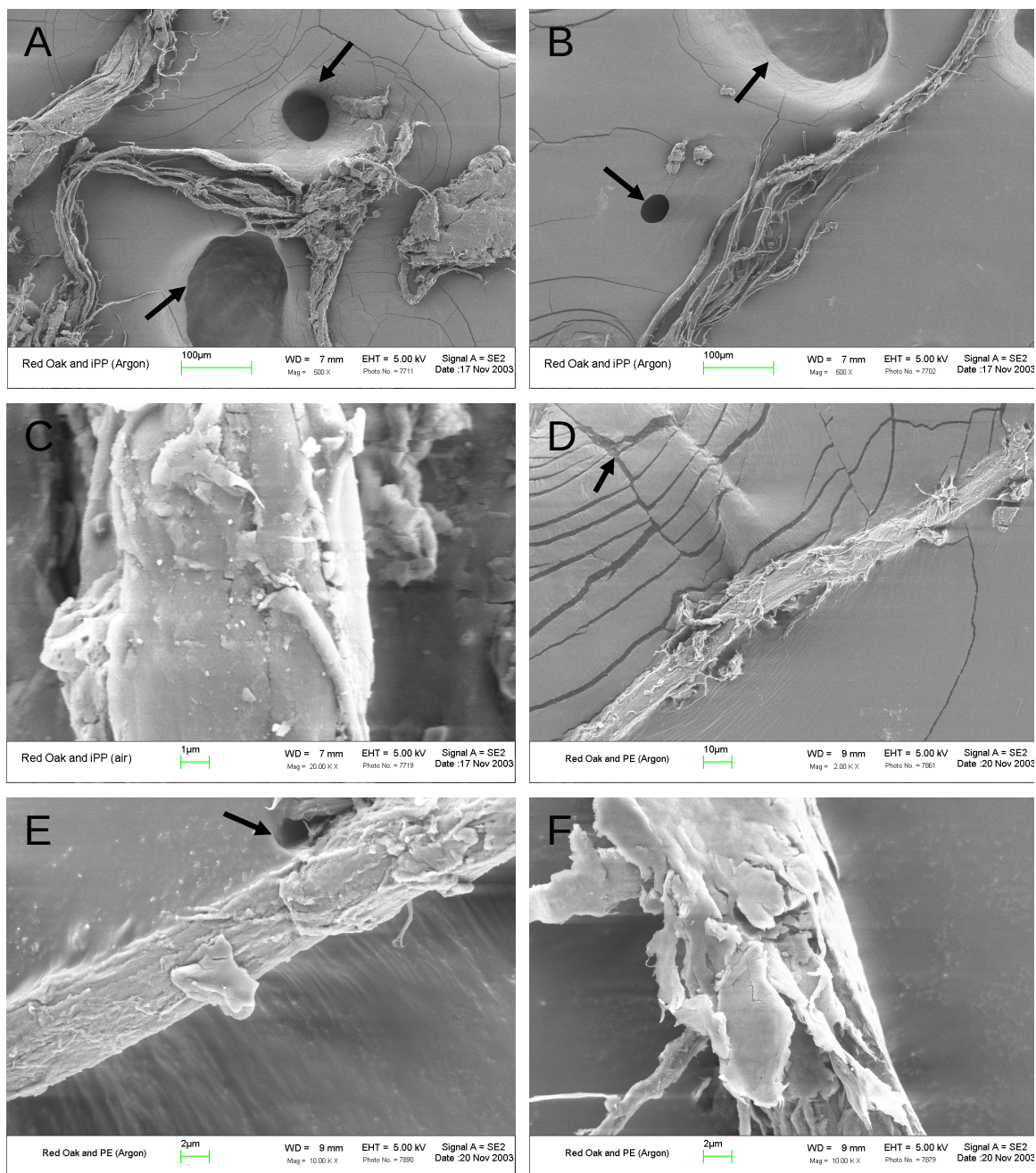


Figure 4.7. Co-steam-exploded wood fiber and polyolefin. (A-C) Co-steam-exploded wood and polypropylene (Mn 9,500), iPP appears to coat fiber bundles. Arrows indicate openings and cracks in mounting medium (C) Magnified view of coated fiber surface. (D-E) Steam-exploded wood and polyethylene (Mn 1400) fiber. Surface is highly heterogeneous making it difficult to distinguish PE.

the areas where there is not overlap of fluorescence are attributed to either cellulose or polyolefin. Fluorescence of the lyocell fiber (cellulose rich component) stained with rhodamine B is shown in Figure 4.8a. The intensity varies across the fiber with both bright and muted areas. This may be explained from concentrated and depleted areas of counter stain. Fluorescence arising from the labeled polyolefin has two distinct fluorescent patterns (Figure 4.8b). There are large clusters that have micron dimensions and smaller clusters that have dimensions in the 100's of nanometers. Figure 4.8c is a transmitted light image of the lyocell fiber with a textured fiber surface. The composite fluorescence image shows a color gradient at the fiber surface with PE-rich regions and cellulose-rich regions (Figure 4.8d). The image makes apparent that the muted fluorescent regions of cellulose (Figure 4.8a) have a corresponding intense fluorescence from the tagged polyolefin.

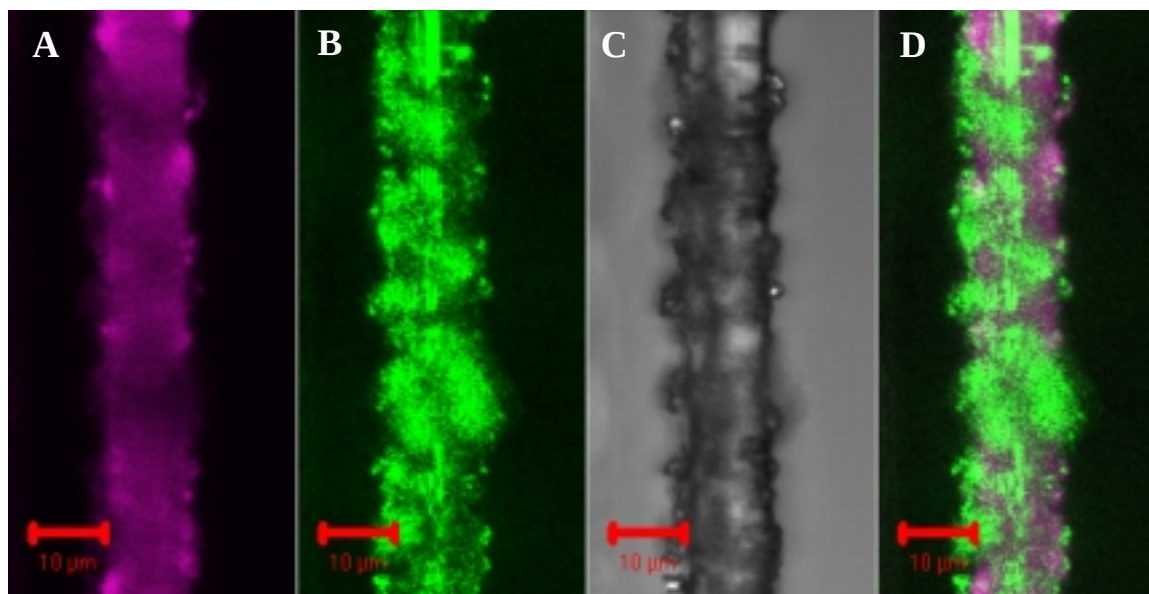


Figure 4.8. Lyocell fiber dipped into fluorescein tagged polyethylene-g-maleic anhydride counter stained with rhodamine B. **A)** Fluorescence from cellulose stain , $\lambda_{\text{ex}}=488\text{nm}$, $\lambda_{\text{em}}=\text{BP } 505\text{-}550\text{nm}$; **B)** Fluorescence from tagged polyolefin, $\lambda_{\text{ex}}=488\text{nm}$, $\lambda_{\text{em}}=\text{LP } 560\text{nm}$; **C)** transmitted light; and **D)** Composite image of A-C. Note cellulose rich and polyolefin rich regions on fiber surface separated by 100's of nm to microns.

Lyocell and the tagged polyolefin were co-steam-exploded and subsequently analyzed with CLSM. A similar methodology was followed of utilizing a counter stain for the cellulose fiber. Lyocell fiber has muted fluorescence in certain areas of the fiber surface (Figure 4.9a). This is similar behavior to what is seen for the lyocell fiber in the control experiment (Figure 4.8a). Additionally, the transmitted light image (Figure 4.9b) contains clusters that have minimal fluorescence in the cellulose-rich image (Figure 4.9a). For this reason the clusters are differentiated from the cellulose/lyocell component. Upon further inspection, the clusters seen in the transmitted light image fluoresce relating to polyolefin fluorescence (Figure 4.9c). Three distinct fluorescent regions are seen in the image (Figure 4.9c): speckled fluorescence, a bright fluorescence streak in the center of the fiber, and areas of continuous fluorescence. The composite image (Figure-4.9d) shows a lightened pinkish-green color resulting from the continuous PO fluorescence (Figure 4.9c) overlapping with the cellulose-rich fluorescence (Figure 4.9a). The speckled fluorescence seen in Figure 4.9c appears independent of the cellulose-rich fluorescence in the composite image. Additionally the bright fluorescent center streak is prominent in the composite image. The fluorescent speckled patches in the composite image have nanometer to micron dimensions. The center streak is evident upon close inspection of the composite images in both the control experiment (Figure 4.9d) and co-steam-explosion experiment (Figure 4.9d). This streak is attributed to be an artifact of the method; other images of lyocell without polyolefin (not shown) demonstrated similar streaks. In both Figure 4.8A and Figure 4.9a there are regions where cellulose related fluorescence has reduced intensity. These regions correspond with fluorescence of the tagged polyolefin in the composite image. The stain cannot fully access the cellulose surface in these regions and therefore does not adsorb to the surface. The modification of the fiber surface by the polyolefin inhibits access of the stain to the fiber surface.

Note that the melt viscosity of the fluorescent-labeled maleated PE is 0.5 Pa-s, which is similar to the values for iPP with a M_n of 5,000 and PE with a M_n of 1,400, (Table 1). Co-steam-explosion of both of these low melt viscosity polyolefins had micron sized particles associated with the wood fiber. This same phenomenon is observed with the micron sized particles for the co-steam-exploded lyocell and tagged polyolefin (figure 4.9D). More importantly, the use of the lyocell and fluorescent-labeled polyolefin demonstrate that there is polyolefin in submicron areas

associated with the fiber surface (Figure 4.9D). This result could not be exclusively determined through scanning electron microscopy because of the heterogeneous nature of the wood fiber surface (Figure 4.7d-e).

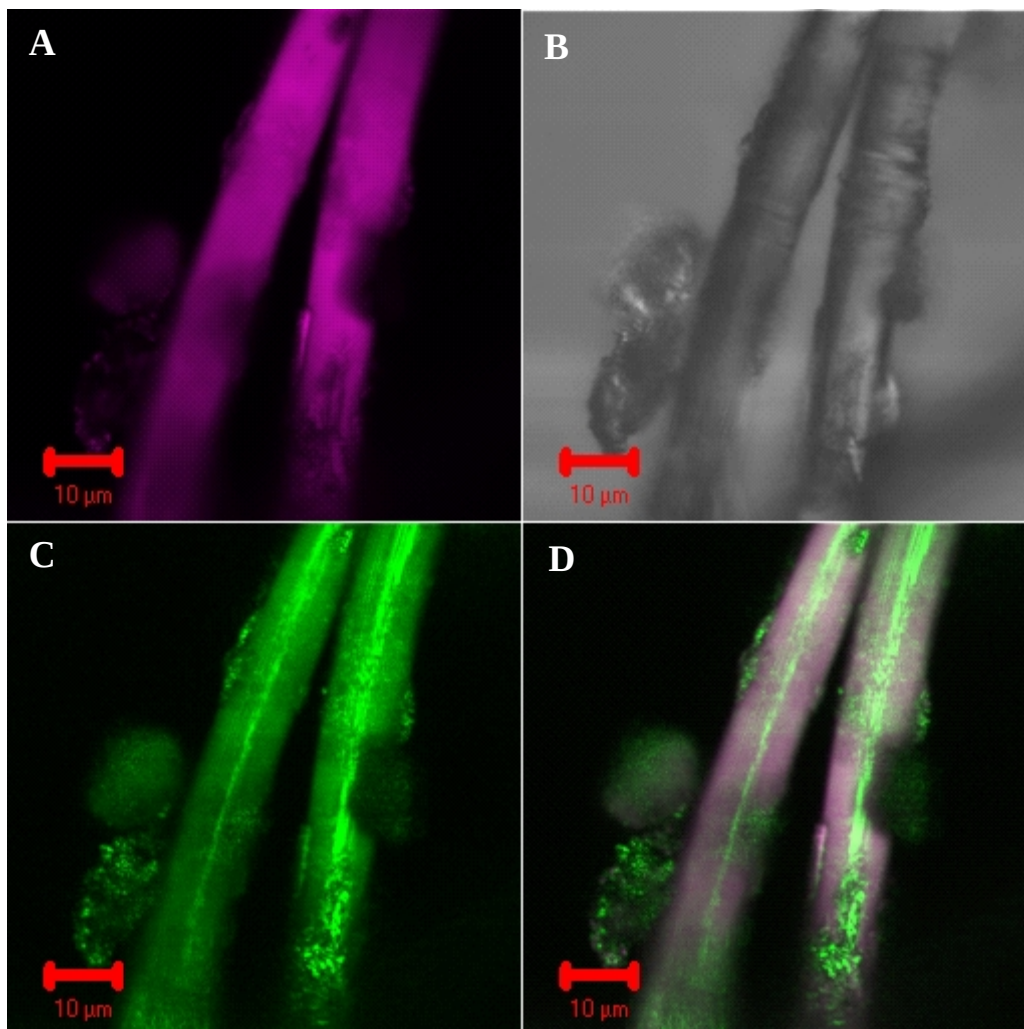


Figure 4.9. Co-steam-exploded lyocell and fluorescein-labeled polyethylene-g-maleic anhydride counter stained. A) Cellulose rich regions, $\lambda_{\text{ex}}=488$ $\lambda_{\text{em}}=\text{BP } 505\text{-}550$ B) $\lambda_{\text{ex}}=488$ $\lambda_{\text{em}}= \text{LP } 560$, C) transmitted light, and D) Composite image.

Autofluorescence of the wood fiber was exploited to further enhance the understanding of the steam-exploded fiber surface. Fluorescence of acetone extracted lignin (in powder form) precipitated by petroleum ether is shown in Figure 4.10a. The image is the composite image from the transmitted light, fluorescence with an excitation wavelength λ_{ex} 364nm and λ_{ex} 633nm. The red fluorescence from the λ_{ex} 633nm laser shows up in the composite image, while there is no sign of fluorescence (blue) from the λ_{ex} 364nm laser (Figure 4.10a). In contrast, the composite image (transmitted light, λ_{ex} 364nm, and λ_{ex} 633nm) of lyocell appears with a uniformly blue fluorescence from λ_{ex} 364nm (Figure 4.10b). From this data it is demonstrated that both lignin and cellulose have distinctive fluorescence with minimal overlap. These excitation wavelengths agree with reported values for alkali extracted lignin and cellulose, respectively [9].

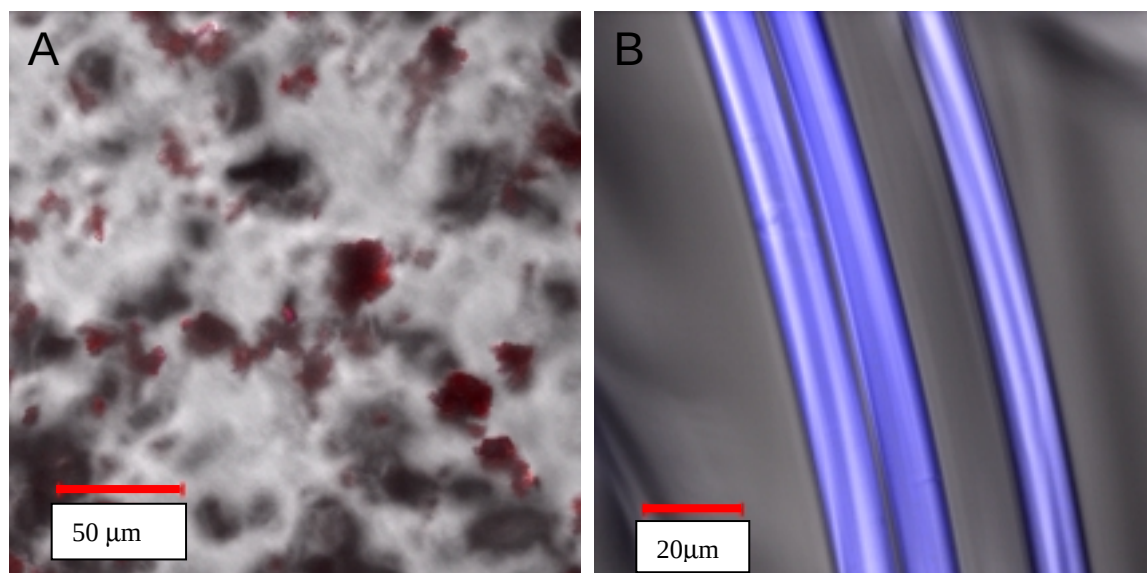


Figure 4.10. CLSM composites images of lignin extract (A) and regenerated cellulose (B). Composite images collected with three channels consisting of fluorescence from 364nm excitation (blue), 633nm excitation (red) and transmitted light image. Lignin extract (A) only fluoresces with the 633nm excitation and cellulose (B) only fluoresces with 364nm excitation.

Steam-exploded wood fiber is presented in Figure 4.11a-d with the same excitation wavelengths used for Figure 4.10a-b. Figure 4.11a shows fluorescence from λ_{ex} 633nm in discrete clusters, while Figure 4.11c has uniform fluorescence from λ_{ex} 364nm. The red fluorescence has nanometer to micron size dimensions throughout the length of the fiber (Figure 4.11a). Unlike the red fluorescence, the blue fluorescence is continuous except for the interruption by some pit structures in the cell wall (Figure 4.11c). Furthermore, the discrete and continuous nature of the fluorescence is conspicuous in the composite image (Figure 4.11d). Attributing the red fluorescence to lignin and blue fluorescence to cellulose illustrates the widely reported reordering of wood polymers caused by steam-explosion [16-18]. The fine distribution of discrete red fluorescence clusters results from the original intimate associate of cellulose and lignin throughout the cell wall. The larger red fluorescent area possibly results from coalescence of lignin or from adsorbed lignin rich middle lamella material.

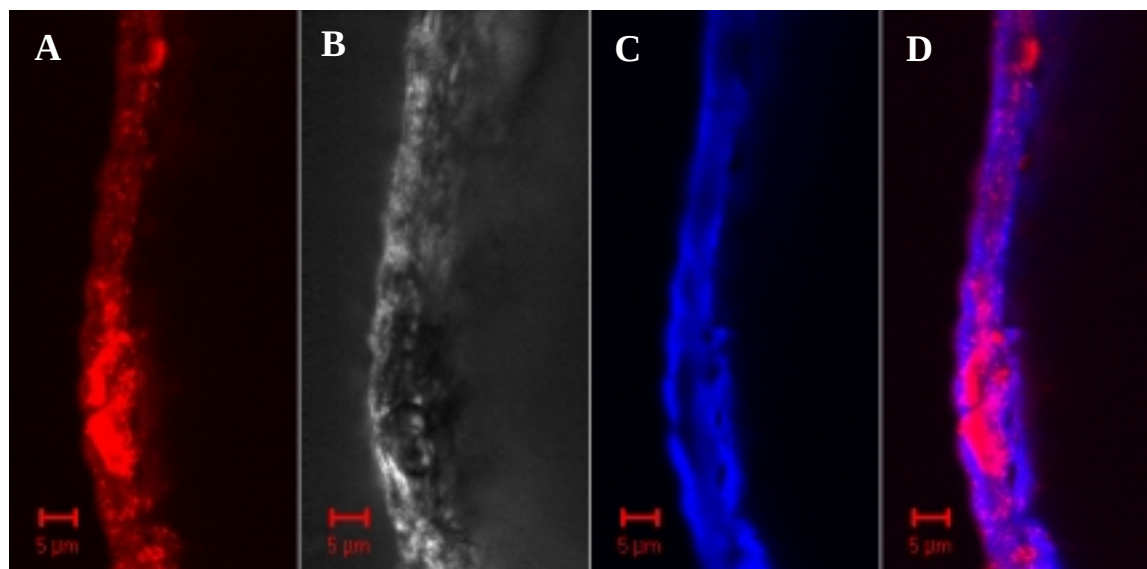


Figure 4.11 CLSM Image of steam-exploded wood fiber. (A) λ_{ex} 633nm, (B)transmitted light, (C) λ_{ex} 364nm, and (D)composite of fluorescent images.

Co-steam-exploded material with either PE that has a M_n of 1,400 (Figure 4.12a-d) or iPP with a M_n of 9,500 (Figure 4.12e-h) was investigated using the same excitation wavelengths from the data in Figure 4.10 and Figure 4.11. The red fluorescence (λ_{ex} 633nm) in Figure 4.12a has both discrete bright spots, near the bottom of the fiber, and areas that are relatively uniform. The transmitted light image shows material adsorbed at the edge of the fiber that was not evident in the red fluorescent image (Figure 12b). The blue fluorescence (λ_{ex} 364nm) no longer appears uniform as previously demonstrated in Figure 4.10b and Figure 4.11c (Figure 12c). The adjacent material seen in the transmitted light image also has blue fluorescence. Furthermore, the composite image still shows areas of blue and red fluorescence that are distinct (Figure 12d). On the other hand, co-steam-exploded wood and iPP (Figure 4.12e-h) has subtle differences. Although there are some bright clusters for the red fluorescence, the submicron sized clusters have disappeared (note different scale) (Figure 4.12e). Furthermore, the distribution of red fluorescence across the fiber bundle is approaching that of the blue fluorescence (Figure 4.12g). The blue fluorescence is not as uniform as seen in the steam-exploded wood sample (Figure-4.11c). A purple hue is seen across the fiber bundle in the composite image indicating the overlap of cellulose and lignin fluorescence (Figure 4.12h).

CLSM indicates an alternative arrangement of wood polymers by co-steam-explosion processing. Moreover, this effect appears to be maximized by the coating of fiber bundle for the co-steam-exploded wood and iPP (M_n 9,500) material. In other words, when the iPP coats the fiber surface, lignin adopts an arrangement that varies from the small discrete clusters seen for the control sample. Also, the bright and continuous fluorescence from cellulose is seen to change because of co-steam-explosion. These results suggest some interaction between the wood components and iPP.

Individual micron sized clusters produced during co-steam-explosion of low melt viscosity PE (M_n of 1,400) and wood were further analyzed with reflected light microscopy and CLSM. The reflected light microscopy shows reddish brown spherical clusters dispersed throughout the steam-exploded fiber (Figure 4.13a). A composite CLSM image (transmitted light, blue fluorescence λ_{ex} 364nm, red fluorescence λ_{ex} 633nm) shows red fluorescence, which was attributed to lignin, predominately at the outer edge of a 50 μ m diameter particle (Figure 4.13b). Additionally, the particle was optically sectioned and 58 images were recorded across a height of 30 microns. Every fourth image is shown in Figure 4.14 with the relative position of

the image displayed in the upper left hand corner. For the images found in the first four microns of depth, the fluorescence predominates at the center of the ball. Red fluorescent inclusions develop maximum fluorescence at 8 at 17 μ m of depth at the outer edge of the particles. From 17 μ m to 30 μ m red fluorescence is reduced although it is still apparent throughout the material. The particle is assumed to be roughly spherical and 30 μ m is near the center of the material. It appears that lignin-rich material is combined with PE mainly at the outer edges of the material.

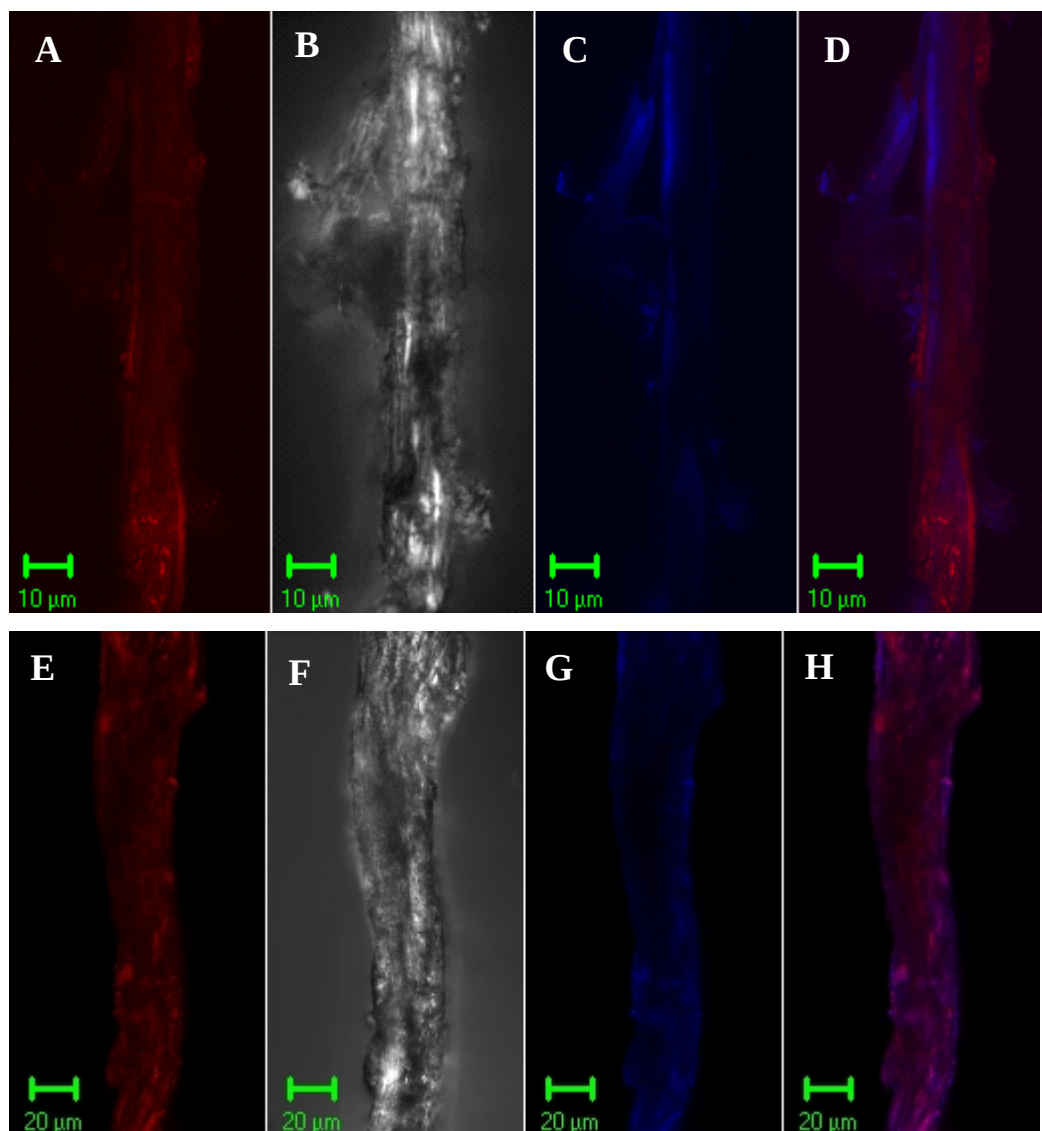


Figure 4.12. CLSM images of co-steam-exploded wood and polyolefin. Images A-D from co-steam-exploded wood and polyethylene. Images E-H from co-steam-exploded wood and polypropylene. A,E (λ_{ex} 633nm); C,G (λ_{ex} 364nm); D,H composite image (λ_{ex} 633nm, λ_{ex} 364nm).

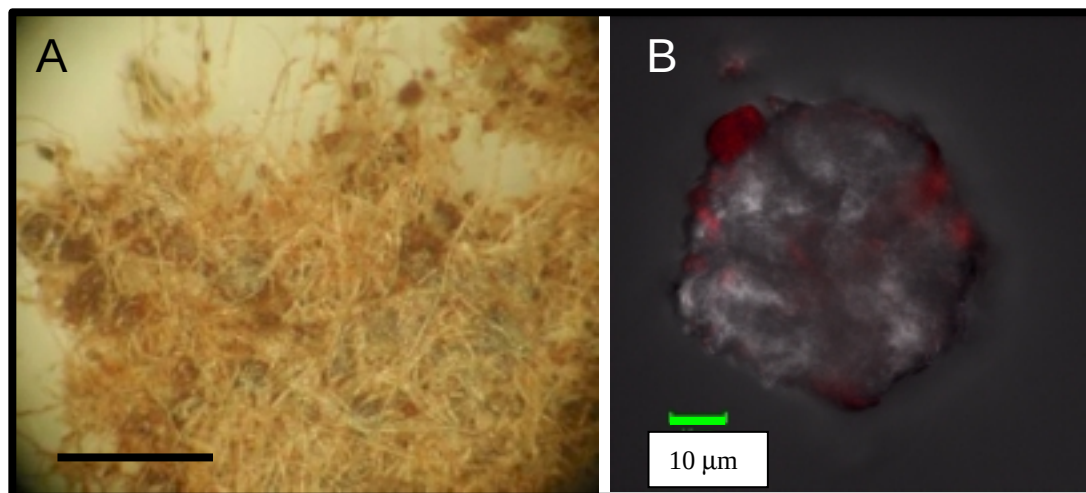


Figure 4.13. Polyethylene-rich clusters found in co-steam-exploded wood and polyethylene. A) Low magnification reflected light image with prominent reddish brown clusters (bar 250μm), B) composite image of polyethylene cluster from CLSM collected with three channels consisting of fluorescence from λ_{ex} 364nm (blue), 633nm λ_{ex} (red) and transmitted light image. Only λ_{ex} 633nm fluorescence is found.

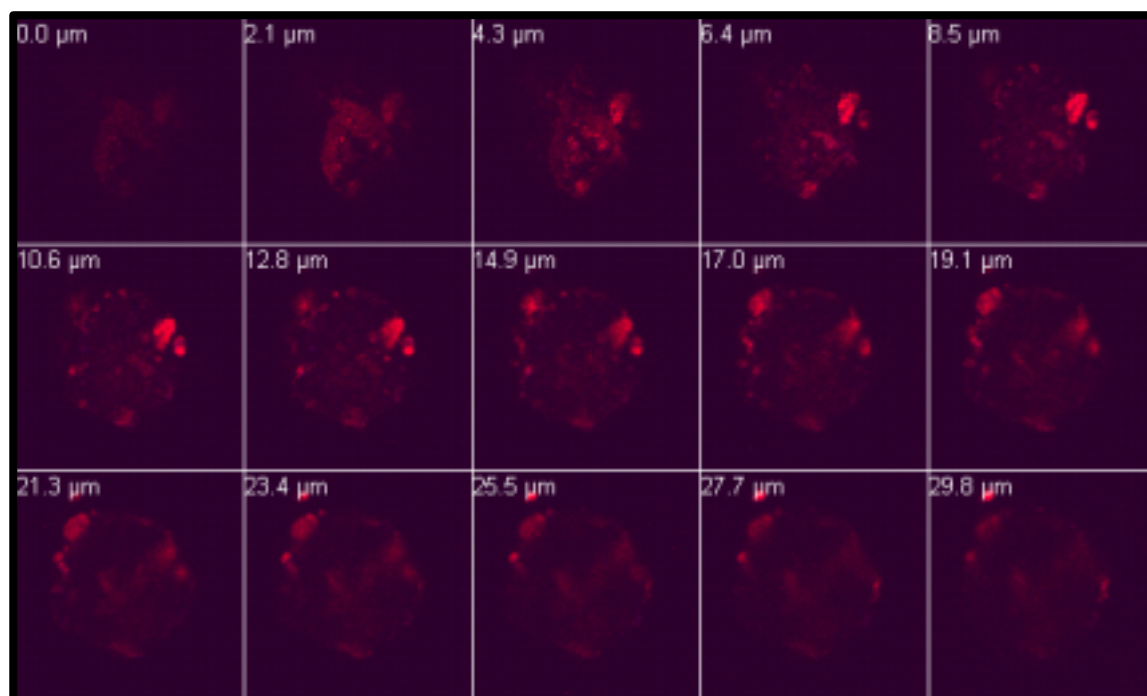


Figure 4.14. Optical depth profiling of PE cluster (from Figure 4.13b). Composite image of fluorescence from laser light λ_{ex} 364 and λ_{ex} 633. Fluorescence only from λ_{ex} 633 is found. Based on these observation it appears that the particle is predominately polyethylene rich (non-fluorescing material) that has inclusion of lignin rich regions that have micron dimensions. The depth profiling provides evidence for the bulk of fluorescence occurring in discrete patches near the surface of the particle.

Conclusions

Molecular weight of the polyolefin plays an important role in the dispersion and coating of the wood fiber by the polyolefin. Although the range of molecular weight to achieve fiber bundle coating is not defined in this study, it does give three examples that show three unique outcomes. Low molecular weight iPP and PE (M_n 5,000 and 1,400, respectively) does not offer significant coating of the wood fiber and forms distinct micron sized clusters. iPP with a M_n of 9,500 coats fiber bundles of steam-exploded wood. Finally, iPP with M_n of 50,000 does not coat wood fibers and separates from the wood material in macroscopic clusters interconnected by

strings. Additionally, polyolefin form was shown to have a negligible effect on changing the dispersion of the higher molecular weight iPP.

Scanning electron microscopy revealed the heterogeneous nature of the fiber surface along with typical damage occurring from steam-explosion. Polypropylene with a M_n of 9,500 could readily be identified spread across the fiber bundle's surface. Arrangement of lower molecular weight polyolefin was elucidated by CLSM in a model study using a regenerated cellulose fiber and fluorescent labeled maleated polyethylene. This co-steam-exploded material showed evidence of low molecular weight polyolefin present on the fiber surface in sub-micron sized patches. Additionally, CLSM was used to confirm the aggregation of lignin on the steam-exploded fiber's cellulose surface by autofluorescence. Lignin was shown to autofluoresce at an excitation wavelength of 633nm while cellulose autofluoresced at an excitation wavelength of 364nm. Co-steam-explosion of wood and polypropylene had a change in autofluorescence patterns. Lignin and cellulose no longer had distinct regions of fluorescence. It is suggested that the polypropylene coating the wood fiber is changing the redistribution of lignin during steam-explosion.

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