

CHAPTER 5

Fiber Surface Modification by Steam-Explosion. II. Sorption Studies with Co-Refined wood and polyolefins.

Abstract

Steam-explosion was investigated as a reactive processing method to create a modified wood fiber by simultaneously co-refining wood chips and polyolefins (polyethylene and polypropylene). Sorption studies along with infrared spectroscopy and scanning electron microscopy were utilized to determine changes in physical and chemical properties. Co-steam-exploded wood fiber had reduced weight gain for humidity in the isotherm swelling region as compared to control. The reduction in weight gain for the co-steam-exploded samples was a function of polyolefin loading, atmosphere (argon, air, and oxygen), and polyolefin type. Additionally, the rate of sorption of the fibers was reduced for the co-steam-exploded wood with polypropylene (argon atmosphere). With polyethylene, however, the rate of sorption increased for the co-steam-exploded mixtures. This phenomenon arose from an increase in the initial diffusion constant for the wood cell wall. Although, co-steam-exploded wood and polypropylene had a similar increase in diffusion constants, a difference of polyolefin interaction with wood fiber is attributed to slowing the rate of moisture penetration into the fiber for the iPP samples. The increase in diffusion constant for all co-steam-exploded material indicates modification within the cell wall. The proposed agents for interior cell wall modification are oxidized polyolefin degradation products that migrate into the cell wall during processing.

Introduction

Plant fibers from wood, flax, hemp and other biological sources are used to fill and reinforce thermoplastics creating stiff composite materials. Applications range from paneling in car interiors to decking for commercial and residential properties [1]. The incorporation of plant fiber into thermoplastic materials is justified from the increased stiffness, reduced cost, reduced processing equipment wear, low density, and renewability when compared with synthetic and inorganic fibers and fillers [2, 3]. However, thermal stability and ultimate and impact strengths decline with the incorporation of unmodified wood and plant fibers into thermoplastic composites [4, 5].

Scientists indicate that incompatibility between the cellulose-based wood fiber and the thermoplastic matrix hinders adhesion between the two components [6, 7]. The high surface energy of cellulose based plant fibers is often cited as the property that inhibits strong wood fiber interaction with polyolefin thermoplastic matrices due to a large interfacial surface energy between the two components. A direct consequence is the reduction in stress transfer across the interface [8] while generating voids in the matrix where crack propagation initiates and leads to composite failure. Coupling and compatibilizing agents have been used to improve interfacial adhesion between wood fibers and thermoplastic matrices, while also increasing performance by influencing dispersion of fiber [9], orientation of fiber [10], and thermoplastic morphology [11]. Block copolymers like maleic anhydride grafted polypropylene (MAPP) have proved the effectiveness in achieving interfacial compatibilization [12]. Yet, some communications report the efficacy of MAPP is negated with commercial lubricants or with certain conditioning [13].

Traditional processing of wood-filled thermoplastic composites involves extrusion or injection molding with the materials added to the processing equipment in pellet form. Wood fiber is added to the thermoplastic in the melt and undergoes severe agitation during extrusion and the aspect ratio of the fiber can be reduced by more than half [14]. An alternative method involving steam-explosion processing for wood fiber thermoplastic composites is currently under investigation. This method involves co-refining wood chips and thermoplastic together; wood chips are reduced to wood fibers and fiber bundles while the thermoplastic is distributed among the fibers. This material is then used in a random wetlay process forming mats of wood fiber “spot-welded” together with thermoplastic that can be compression molded [15]. Advantages of

combining co-steam-explosion with random wetlay process include the step reduction of refining chips while simultaneously dispersing the thermoplastic and maintaining fiber aspect ratio.

Previous work established that co-steam-explosion processing is a viable method to co-refine polyolefin and wood chips [16-18]. Other work demonstrated that thermoplastic material was evenly distributed with the wood fiber on a milligram scale [19]. However, it was not known if the thermoplastic formed a uniform polymer coating. If PO forms a uniform coating, this should influence sorption and rate of sorption. Therefore, the objective of this study is to examine the sorption properties of co-steam-exploded wood and polyolefin materials as a function of environment reactivity and polyolefin loading. It is hypothesized that co-steam explosion is a reactive processing technique and the degree of modification can be controlled through these two factors. Chemical spectroscopy and microscopy methods along with sorption behavior of the fibers are used to evaluate sorption properties and relate it to the mechanism controlling the sorption rate and modification.

Methods and Materials

Materials

The materials used in steam-explosion processing were red oak chips, polyethylene (PE) powder, and isotactic polypropylene (iPP) beads. Air-dried red oak chips were obtained from a local saw mill and were sorted through a screen with hole diameters of 5/8" and retained by the screen with hole diameters of 3/8". PE with a number average molecular weight of 1400 and density of 0.9 g/cm³ was obtained from Scientific Polymer Products. iPP with a melt flow index of 1000 was obtained from Sigma-Aldrich. Dissolving grade cellulose pulp was obtained from Rayonier Corporation of Jessup, GA.

Steam-Explosion Processing

Red oak chips were co-refined with either polyethylene powder or isotactic polypropylene beads by steam-explosion processing. The steam-explosion vessel was a converted 1-gallon Parr reactor fitted with an exit ball valve and cyclone to separate the steam and material. Prior to filling the vessel with steam, the atmosphere was evacuated and replaced with argon, air, or an 1:1 argon/oxygen mixture. Table-1 contains the loading conditions and atmospheres for all experiments. After steam-explosion the material was placed in water in an Erlenmeyer flask and

stirred for 1 hour on a magnetic plate. The material was then recovered by vacuum filtration and additionally rinsed with water (twice the volume of the Erlenmeyer flask) in a Buchner funnel. Subsequently, the material was dried in a desiccator over phosphorous pentoxide.

Table 5.1 Steam-Explosion Materials and Conditions

Materials	Atmosphere			Temperature	Time
	air	argon	O ₂ /argon	°C	Minutes
red oak chips		X		230	5
red oak chips and PE 20% loading		X		230	5
red oak chips and PE 33% loading	X	X	X	230	5
red oak chips and PE 50% loading		X		230	5
red oak chips and iPP 50% loading	X	X		230	5

Fourier Transform Infrared Spectroscopy

A Midac Fourier Transform infrared (FT-IR) spectrometer with an attenuated total reflectance attachment was used to obtain the infrared spectra of the samples. Five spectra were recorded for each treatment with an average of 64 scans and 8cm⁻¹ resolution.

Sorption Isotherms

Method

Test specimens were dried in an evacuated desiccator containing phosphorous pentoxide until there was no change in the sample weight. Five specimens from each treatment were weighed and placed in each desiccator with a saturated salt solution. Lithium chloride, calcium carbonate, sodium nitrate, potassium carbonate, potassium chloride, and water were used to regulate the relative humidity of each desiccator. The specimens were left in each desiccator for 30 days and periodically weighed until an equilibrium weight gain was achieved.

Sorption Kinetics

Test Procedure

A thermogravimetric analyzer was modified in order to introduce water vapor into the chamber to measure rate of water sorption at a constant temperature. Nitrogen gas was passed through a bubbler filled with distilled water at a rate of 55 cm³ per second to generate water vapor which was subsequently mixed with dry nitrogen. The modified instrument measured weight gain with a sensitivity of 1 µg as a function of time for 60 minutes. Five tests were performed for each treatment of fiber that was dried in a desiccator across vacuum containing phosphorus pentoxide.

Initial Sorption Rate Determination

The initial rate of sorption (K_1), a time period of less than five minutes ($t < 5$ min), was determined for all treatments by the slope of a linear regression model. The average fraction of the wood fiber present in the co-steam-exploded samples was determined previously by thermogravimetric analysis [19]. The normalized initial sorption rate (K_1^*) was calculated by dividing K_1 by the average fiber fraction (Equation 1).

$$K_1^* = K_1 / \text{wood fraction} \quad \text{Equation 1}$$

The percentage change (K_c) of K_1^* for the co-steam-exploded wood and polyolefin compared to the control was calculated based on K_1^* of the steam-exploded wood (Equation 2).

$$K_c = \frac{(K_1^*_{co-stex} - K_1^*_{wood})}{K_1^*_{wood}} \quad \text{Equation 2}$$

When using this method to normalize the sorption rate, the assumption is made that the fraction of wood will dominate the rate of weight gain by only the wood fraction contributing to water sorption.

Initial Diffusion Coefficient Determination

According to Crank, the initial unsteady-state moisture diffusion (D_1) may be determined from Equation 3 [20],

$$D_1 = \frac{\pi \left(\frac{w(t)}{w_\infty} \right)^2 (L)^2}{16t} \quad \text{Equation 3}$$

where $w(t)$ is the weight gain at a given time t , w_∞ is the equilibrium weight gain, L is the thickness of the cell wall. [Note w_∞ values were determined from first calculating the relative humidity from the sorption kinetic graph. This was performed by running three samples (each sample duplicated) to 300 minutes (Figure 5.4 inset). The maximum weight gains for the 300 minute time (w_∞) were then compared to the weight gain at varying relative humidity from the sorption isotherm graph. The relative humidity with the same w_∞ for the three samples was then used to determine the w_∞ for the other treatments.] Furthermore, the kinetic data [$w(t)$ vs. t] was transformed to [$w(t)/w_\infty$ vs. $t^{0.5}$] and the slope (S) of the graph is described in Equation 4 [21],

$$S = \frac{w(t)/w_\infty}{\sqrt{t}} \quad \text{Equation 4}$$

The slope value was then placed in Equation 3 to determine (D_1), Equation 5;

$$D_1 = \pi * S^2 * L^2 / 16 \quad \text{Equation 5}$$

The values involved in the graphical solutions are approximate with the following assumptions: the diffusion coefficient is constant, the initial moisture is uniform within the specimen, there is instantaneous equilibrium with the relative humidity at the cell surface, and there is symmetrical transport of moisture through the cell wall [21].

Field Emission Scanning Electron Microscopy

Desiccator dried fibers were placed on scanning electron microscopy stubs and coated with a 2 nanometer layer of gold palladium. The fibers were then scanned in a LEO 1550 field emission scanning electron microscope at low accelerating voltages (<5kV).

Confocal Laser Scanning Electron Microscopy

Steam-exploded red-oak fibers were made into fiber bundles by drawing fibers from a slurry with a disposable pipette. Fiber bundles attached to the tip of the pipette were removed and allowed to air dry. Fiber bundles were then embedded in a commercial soft epoxy and 25 μm sections were cut with a microtome. The cut sections were then mounted on glass microscope slides and viewed in a Zeiss 510 laser scanning microscope. Autofluorescence of the wood excited with 488nm laser light was used to contrast the wood fiber from the surrounding background. The resulting images were analyzed using Zeiss image examining software.

Results

Chemistry of Fiber

Wood is composed of three polymeric components: cellulose, lignin, and hemicellulose [22]. In addition to these constitutive bio-polymers, wood has extractives and pectin rich substances. Together these substances give rise to an infrared spectrum with a variety of absorbance bands: hydroxyl stretching and bending, methylene stretching, carbonyl stretching, and aromatic bending and breathing (Figure 5.1). Polyethylene (PE) and isotactic polypropylene (iPP) absorb radiation due to methyl, methylene, and methine groups. While methyl and methylene groups occur in wood, the presence of added polyethylene and polypropylene to wood fiber is conspicuous in the infrared spectrum (Figure 5.1).

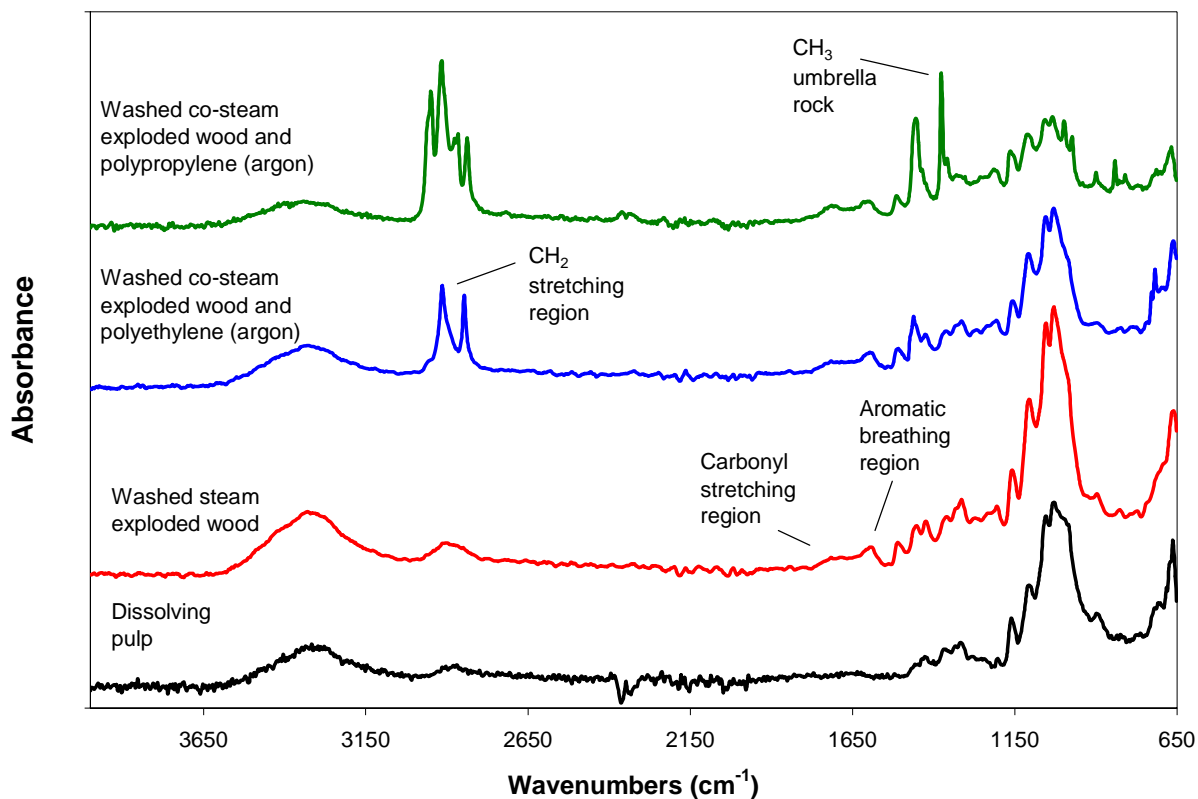


Figure 5.1 FT-IR spectra of pulp and steam-exploded fiber.

Reflectance FT-IR spectroscopy must rely on relative absorbance intensity through the use of band ratios for quantitative comparisons among treatments. The ratio of specific group frequency bands to the cellulose in-phase ring stretching (1107 cm^{-1}) were used to find the relative quantity of components for lignin, hemicellulose, polyethylene, and polypropylene. The corresponding group frequencies utilized were aromatic stretch (1604 cm^{-1}), carbonyl stretch (1728 cm^{-1}), methylene asymmetric stretch (2916 cm^{-1}), and methyl umbrella rock (1377 cm^{-1}) to describe the chemical make-up of the material among treatments (Table 5.2). The increase of the band intensity ratios of the asymmetric methylene stretching and methyl umbrella rock for the co-steam-exploded samples indicate a polyolefin (PO) enrichment of the fiber relative to the dissolving pulp fiber and steam-exploded red oak fiber. From this data it is apparent that the co-steam-exploded fiber has polyolefin associated with it.

Table 5.2. IR absorbance band intensity ratio of specific frequency groups to cellulose glucose ring stretch (1107cm^{-1}). Standard deviation listed below the average value.

Treatment	Asymmetric Methylene Stretch (2916 cm^{-1})	Xylan Carbonyl Stretch (1728 cm^{-1})	Aromatic Skeletal Vibration (1604 cm^{-1})	Methyl Umbrella Rock (1377 cm^{-1})
Dissolving pulp	0.20	0.12	0.14	0.31
	0.015	0.013	0.016	0.015
Stex red oak fiber	0.27	0.18	0.26	0.351
	0.011	0.016	0.010	0.008
Co-stex red oak and iPP (argon)	1.70	0.31	0.39	1.53
	0.126	0.023	0.025	0.135
Co-stex red oak and iPP (air)	0.90	0.23	0.31	0.87
	0.170	0.015	0.022	0.130
Co-stex red oak and PE (argon)	0.76	0.22	0.29	0.39
	0.085	0.004	0.007	0.003
Co-stex red oak and PE (air)	0.95	0.18	0.26	0.38
	0.036	0.017	0.020	0.009
Co-stex red oak and PE (O_2/Ar)	0.73	0.20	0.26	0.39
	0.049	0.006	0.006	0.003

The band ratio for the methyl umbrella rock of polypropylene is greater for the co-steam-exploded mixture in an argon atmosphere relative to co-steam-explosion in an air atmosphere for the two polypropylene containing samples (Table 5.2). Additionally, the band ratios for the other chemical groups increased as well for the co-steam-exploded wood and polypropylene in the argon atmosphere. This may be a sign of the cellulose component having a decreased signal relative to the other chemical groups instead of an enrichment of the other components. Otherwise, the signals for the lignin and hemicellulose components remained unchanged for the steam-exploded samples. Also, the intensity band ratios reveal a lower lignin and hemicellulose content for dissolving pulp than the washed steam-exploded wood samples.

Fiber Water Sorption Properties

Sorption Isotherm

The chemistry of the material dictates its interaction with water vapor. At a given partial pressure of water vapor in relation to the total pressure of a system a number of secondary bonding sites on the fiber are occupied by water molecules increasing the sample weight (Figure 5.2). The fiber samples follow a typical BET type II isotherm when exposed to rising relative humidity levels. There is an initial weight increase, followed by a gradual rise in slope until higher RH where swelling of the material occurs, increasing water sorption [23].

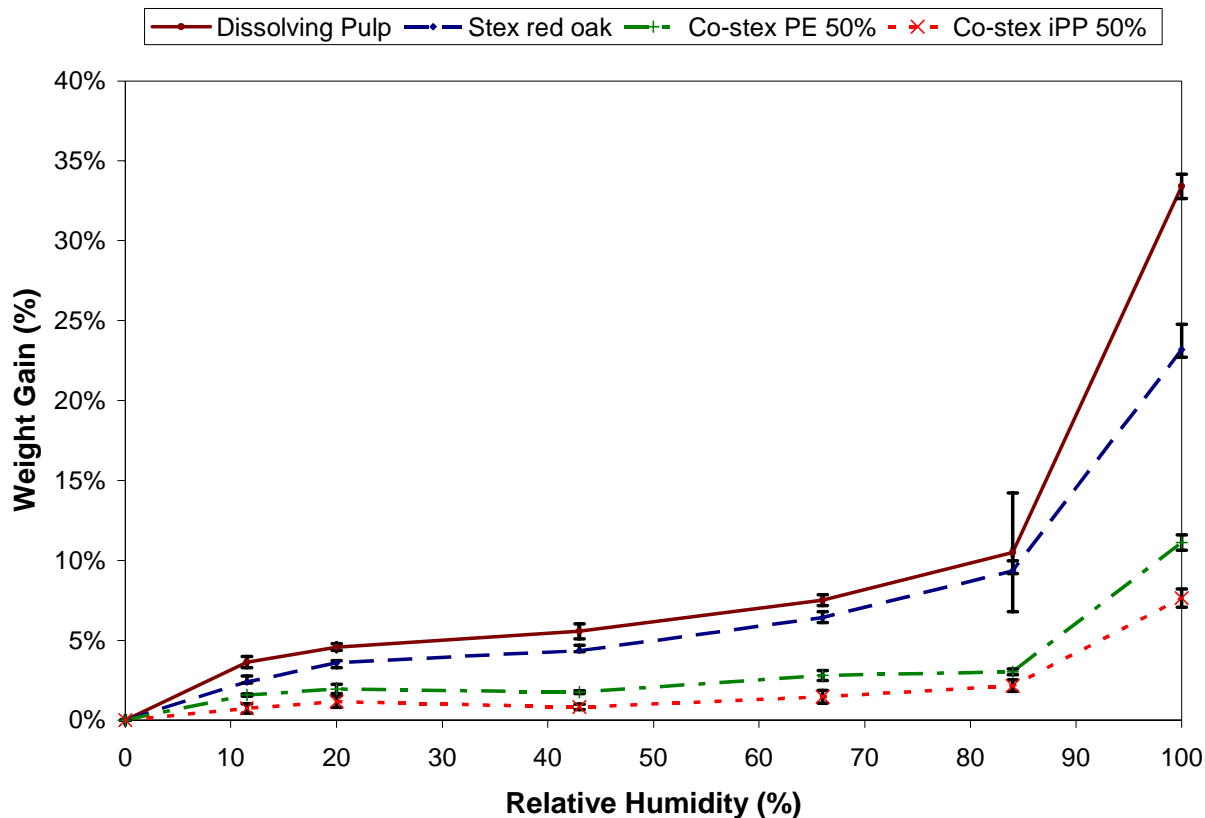


Figure 5.2. Sorption isotherm of fiber samples ($T=295^{\circ}\text{K}$). Weight gain is based on total mass.

Even with a greater relative hemicellulose content (determined from the IR band ratio for the carbonyl group) the steam-exploded fiber sorbed less water than the dissolving pulp fiber used as a control (Figure 5.2). Higher lignin concentration and possibly higher crystallinity in the steam-exploded samples are most likely the causes for the reduced sorption. Lignin contains fewer water binding moieties per unit weight than disordered cellulose, while heat treatment at high humidity is known to increase the crystallinity index of cellulose for wood samples [24]. Crystalline order reduces interaction with moisture. Additionally, it is evident that the introduction of polyethylene and polypropylene reduces the overall weight gain (based on total mass).

It is assumed that wood fiber contributes to all water-vapor sorption. For this reason, the sorption isotherms were normalized by the fraction of wood. The normalized values for the co-steam-exploded wood with PO were compared directly to the steam-exploded sample and the difference of weight gain (Δ) was plotted against polyolefin loading (Figure 5.3). There was a

varying response based on the relative humidity. Average Δ values were greater for the swelling region of the isotherm (86 and 100 RH) relative to the non-swelling region (12 to 66 RH). In the non-swelling region of the isotherm for co-steam-exploded wood and PE samples, Δ remains at zero for all polyolefin loadings. However, Δ for the swelling region increases in magnitude for the PE containing material. At the highest PE loading in the swelling region Δ is -2.9%. This value corresponds with a decrease in weight gain by almost 18% relative to the weight gain of the steam exploded fiber. In other words, this decrease is the ratio of Δ to the average weight gain of the steam exploded fiber in this region. Co-steam-exploded wood with iPP have Δ values of -2% and -7% for the non-swelling and swelling regions, respectively (Figure 5.3). The Δ value relative to the average weight gain of the control value is a decrease by 12% for the non-swelling region and decreased by 44% for the swelling region. From these observations there appears a trend that co-processing wood with PO impacts sorption at higher RH. However, while co-processing wood and PE did not affect the sorption at low RH, there was reduced water vapor sorption for co-processed wood and iPP material within the non-swelling region. In addition, the co-processed wood and PE in an oxygen containing atmosphere has no significant deviation in Δ for the non-swelling region (Figure 5.3). However, Δ for the PE containing material does increase in magnitude relative to the oxygen-starved atmosphere for the swelling region of the isotherm. In contrast, co-processing with iPP in an oxygen containing atmosphere (air) does not show significant deviation in Δ for either section of the isotherm (Figure 5.3).

Additional study of the fractionation of co-steam-exploded mixtures demonstrated increased water extractable material for the co-steam-exploded wood and PE mixture compared to that of mixtures with iPP [25]. This is important because the normalization of the co-steam-exploded wood and iPP is based on earlier experimentation with PE [19]. Therefore, it is likely less wood material was removed for the iPP containing material during water washing relative to the PE containing samples. Because of this, the true polyolefin fraction may be less for the iPP relative to PE. This would increase the magnitude of the slope in Figure 5.3 by shifting the values of the polypropylene containing samples to the left.

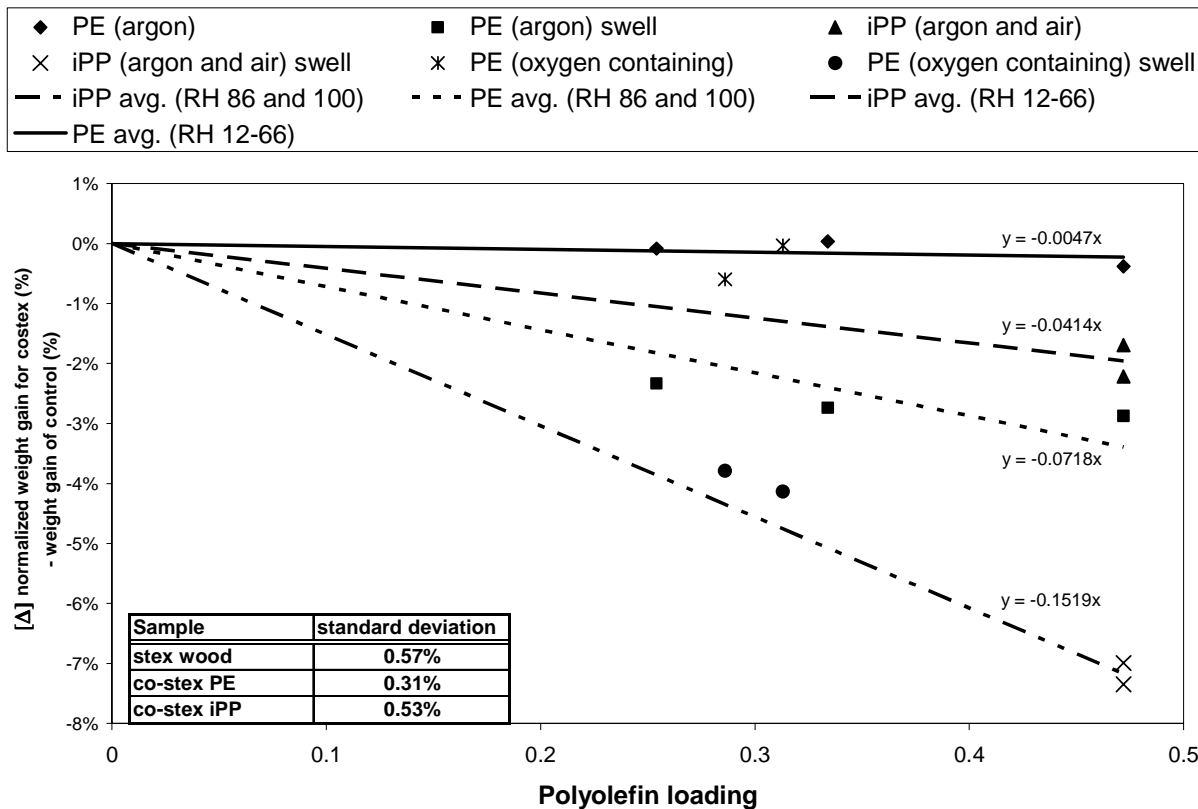


Figure 5.3. Weight gain for steam-exploded wood subtracted from the normalized weight gain for co-steam-exploded material as a function of polyolefin loading. Average values determined for non-swelling (RH of 12, 20, 43, and 66) and swelling (RH of 86 and 100) isotherm regions.

Kinetics of Water Sorption

Initial Sorption Rate

Not only does the quantity of the hygroscopic chemical groups influence the sorption, but access to these groups is important for product performance. Kinetic data of water sorption show an initial rapid weight gain, which declines until a final plateau value is reached (Figure 5.4). Note that a true equilibrium state was not achieved for the samples in the monitored time. Instead, the equilibrium value was calculated by determining the RH of the chamber and using the isotherm graph (Figure 5.2) to locate the equilibrium value for the same RH. The RH was determined by using three different materials that were run for extended times of up to 300 minutes (Figure 5.4 inset). Using these three equilibrium weights, the RH of the chamber was estimated to be 85.3%.

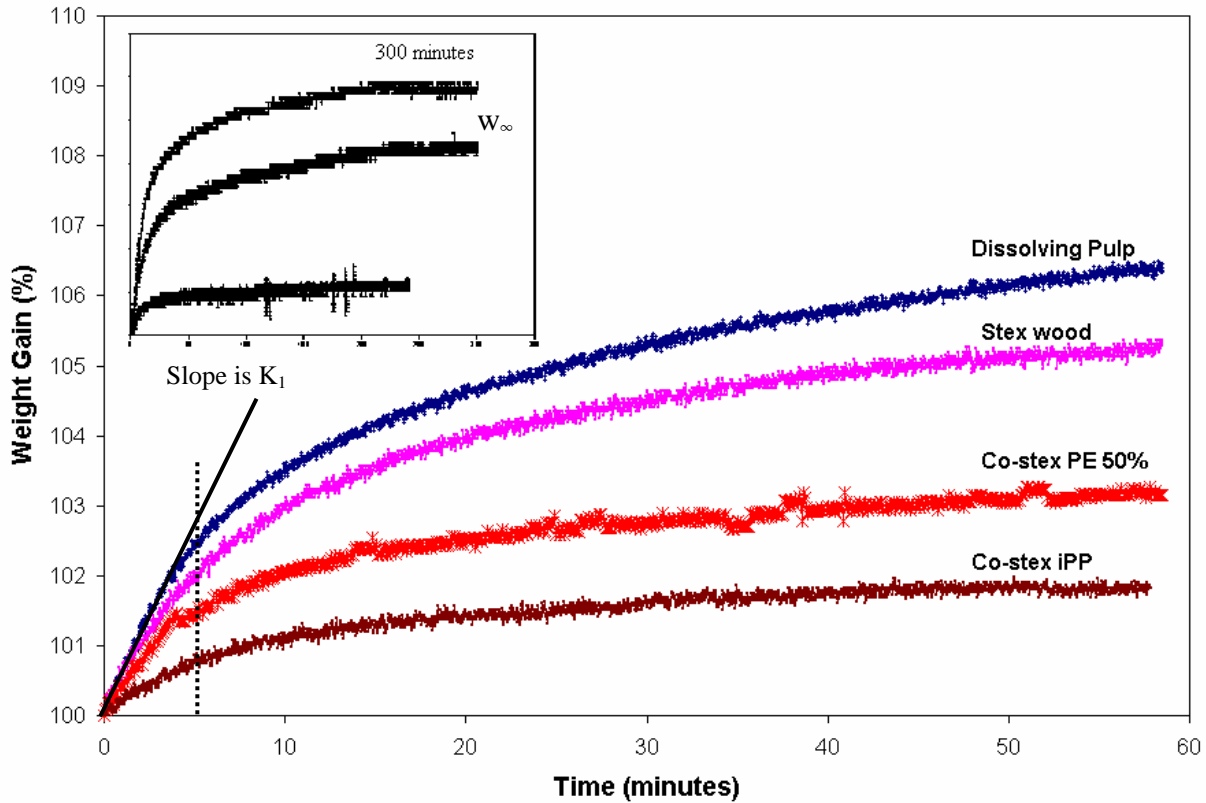


Figure 5.4. Water sorption kinetics for fiber samples. (estimated RH=85.3%)

Sorption rates and diffusion rates are listed in Table 5.3. The initial sorption rate based on total mass (K_1) is greater for the dissolving pulp relative to the steam-exploded wood sample (Table 5.3). The initial sorption rates were normalized by fiber fraction (K_1^*) for the co-steam-exploded wood and PO. K_1^* shows a change in the rate of sorption for the co-processed wood and polyolefin when compared to the steam-exploded wood sample (Table 5.3). Except for co-steam-exploded wood and iPP in an argon atmosphere ($K_1^*=0.27$), all co-steam-exploded materials show an increase in K_1^* values. This is noted by the sign of K_c , which shows the change over the steam-exploded wood K_1 value (Table 5.3). Although K_c for co-processed wood and iPP in an air atmosphere is positive, it is lower than all PE containing material. It is apparent that the K_1^* is reduced for co-steam-exploded wood and iPP relative to co-steam-exploded wood and PE. Moreover, K_c increases from -30% to 10% when air is present during co-processing of wood and iPP (Table 5.3). A similar increase in K_c is observed for co-processed wood and PE in an oxygen containing atmospheres. K_c values increase from 30% for the oxygen starved

atmosphere to 92% and 76% for the air and enhanced oxygen atmospheres. From this it is suggested that the presence of oxygen during co-processing of wood and PO increases K_1^* .

Table-5.3. Water sorption kinetic data and diffusion constants for fiber samples for initial sorption rate only (standard deviation in parenthesis).

Treatment	Polyolefin fraction from [19]	(K_1) Initial sorption rate (%/min)	(K_1^*) Normalized rate (rate/wood fraction) from eq. 1	(K_c) Change in K_1^* (%) from eq. 2	(D_1) Initial diffusion coefficient $\text{cm}^2\cdot\text{s}^{-1}$ ($\times 10^{-12}$) from eq. 5	Increase in D_1 (%) over control
Dissolving Pulp	0	0.49 (0.06)	0.49	x	6.51 (1.71)	x
Stex red oak	0	0.38 (0.03)	0.38	0%	7.32 (1.59)	x
Co-stex PE 20%	0.254	0.40 (0.07)	0.54	41%	15.69 (3.28)	114
Co-stex PE 33%	0.334	0.33 (0.07)	0.50	30%	13.52 (4.15)	85
Co-stex PE 50%	0.472	0.27 (0.08)	0.51	35%	19.71 (6.45)	169
*Co-stex iPP 50%	0.472	0.14 (0.02)	0.27	-30%	13.86 (3.34)	89
*Co-stex iPP 50% Air	0.472	0.22 (0.05)	0.42	10%	28.53 (10.55)	290
Co-stex PE 33% Air	0.286	0.52 (0.04)	0.73	92%	33.51 (4.47)	358
Co-stex PE 33% O ₂ /Ar	0.313	0.46 (0.06)	0.67	76%	33.70 (7.2)	360

* For same initial loading polypropylene content assumed equal to polyethylene content.

Note iPP and PE have distinct molecular weight differences: iPP Mn=9,500 and PE Mn=1,400.

The rate of sorption (K_1) reveals the speed of water molecules being sorbed to the fiber sample. One aspect of K_1 is the diffusion rate (D_1) at which moisture moves through the cell wall. Both dissolving pulp and steam-exploded wood have diffusion coefficients less than $10 \times 10^{-12} \text{ cm}^2 \cdot \text{sec}^{-1}$ (Table 5.3). Upon co-steam-explosion of wood with PO the diffusion coefficients increase for all samples (Table 5.3). The increase ranges from 90% to 360% with no significant differences for polyolefin type: co-processing with PE and iPP give rise to similar values of D_1 in relation to the variance of the data (Table 5.3). Furthermore, the presence of oxygen gas increases the diffusion coefficient for the co-processed material. Using a Fisher's least significant difference comparative means analysis, with a significance level (α) of 0.05, the D_1 values (28 to $34 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$) for co-steam-exploded wood and polyolefin material in an air or oxygen/argon atmosphere mixture are significantly greater than for all other treatments (Table 5.3).

The diffusion coefficient is influenced by the cell wall thickness measurement. The cell wall thickness was measured from the cross-sections of epoxy embedded wood fibers (Figure 5.5). Cross sections of the wood cells are both round and rectangular. Four measurements of

each cross section were made and a 5 μm average value for the thickness of the wood cell wall was derived from 28 fibers. The average cell wall thickness values ranged from 2 to 6.5 μm (Figure 5.6). It is noted that the D_1 values for the control materials (steam-exploded wood and dissolving pulp fiber) are lower than other reported diffusion values (3 to 6 $\times 10^{-11} \text{cm}^2 \cdot \text{s}^{-1}$) for cotton fibers [26]. Cell wall collapse during drying may cause the apparent thickness of the cell wall to increase (instead of hollow rectangle, cell becomes flattened and filled). Increasing the thickness from 5 μm to 10 μm would result in the diffusion coefficients increasing to $2.5 \times 10^{-11} \text{cm}^2 \cdot \text{s}^{-1}$, which is within range of the reported value. Regardless of the absolute value of the diffusion coefficients, the measurements among all the steam-exploded material used the same cell wall thickness and so provides for a relative measure of diffusion among the treatments.

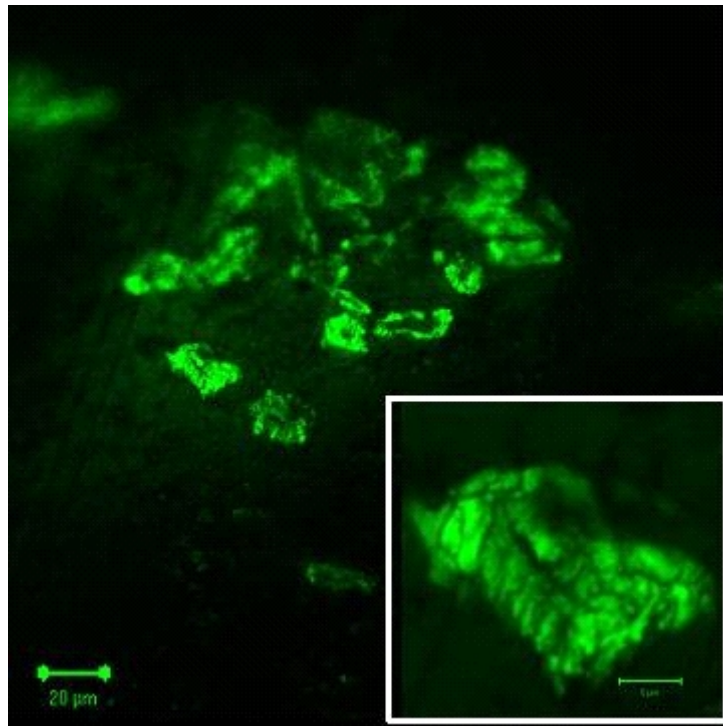


Figure-5.5. Autofluorescence of steam-exploded red oak fiber cross sections viewed by laser scanning microscopy ($\lambda_{\text{ex}}=488\text{nm}$).

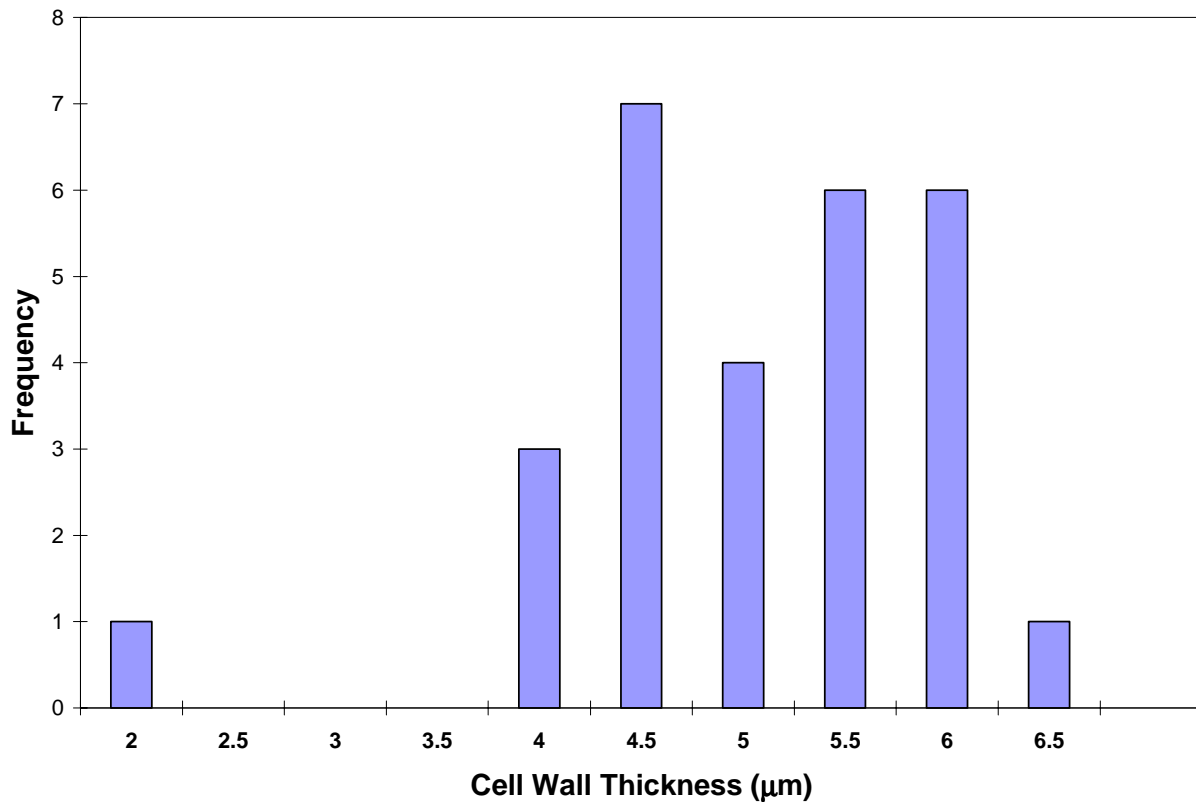


Figure 5.6. Histogram of cell wall thickness measurements for steam-exploded material.

Using the data from Table 5.3, K_c is plotted against D_1 and compared to the control steam-exploded wood sample (Figure 5.7). For co-steam-exploded wood and polyethylene, there is an increase in initial sorption rate as D_1 increases. This relationship includes the control steam-exploded wood fiber. Hence, an increase in sorption rate from the control is directly related to the diffusion of water-vapor. Furthermore, co-steam-explosion of wood and iPP has a decrease in the initial sorption rate compared to the control steam-exploded wood sample and then increases with an increase in D_1 . The increase in K_c (in relation to D_1) for the co-steam-exploded wood and iPP has the same slope as found for co-steam-exploded wood and PE samples. It is evident from the graph that diffusion plays an important role in increasing initial sorption rate for both samples. However, the graph reveals that diffusion is not the only influence on K_c for co-steam-exploded wood and iPP material.

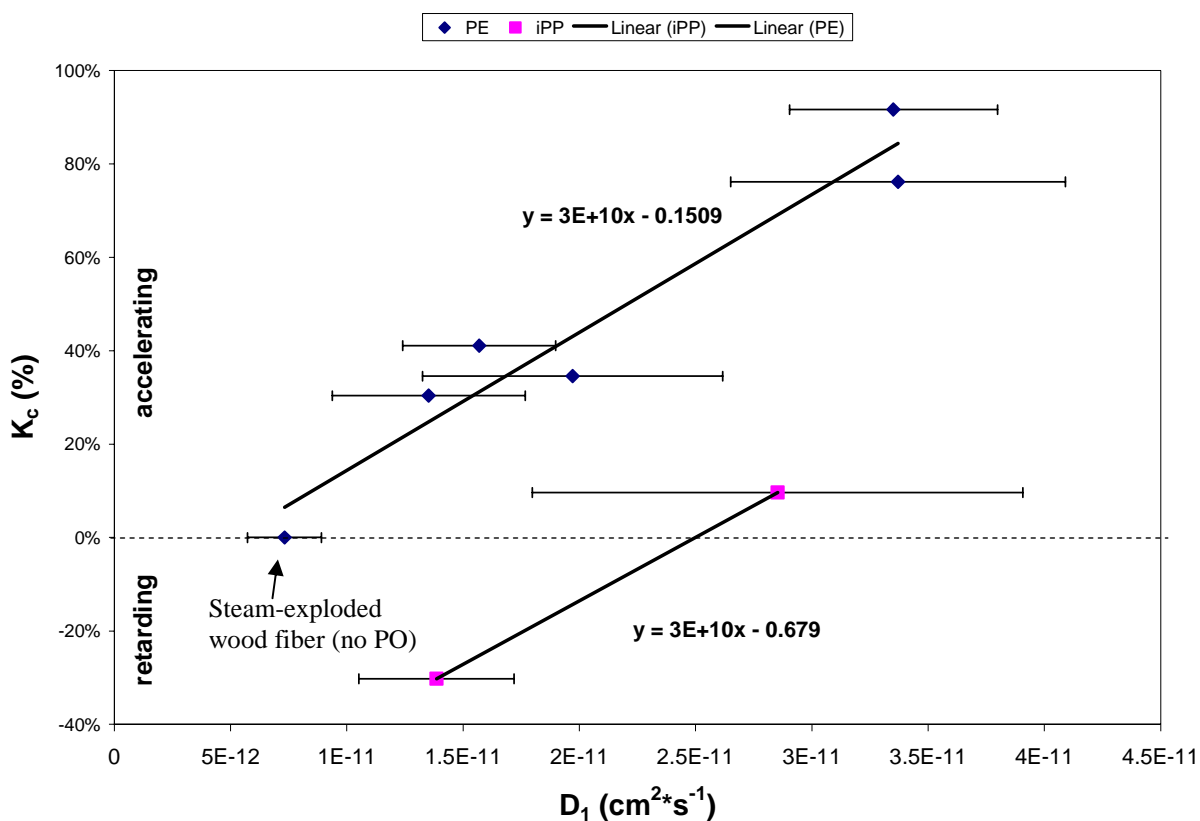


Figure 5.7. Initial sorption rate change of wood fiber fraction due to co-steam-explosion processing (K_c from eq. 2) vs. the initial diffusion coefficient (D_1 from eq. 5).

High resolution microscopy was used to examine the cell wall of co-steam-exploded samples. The surfaces of both steam-exploded wood and co-steam-exploded wood and PE contain microfibrils and agglomerations (Figure 5.8ab). In contrast, co-steam-exploded wood and iPP has a relatively uniform surface with the microfibril pattern covered, most likely by iPP (Figure 5.8c). This is in agreement with previous experimentation that found melt viscosity of the polyolefin to control the coating and uniformity of the co-steam-exploded wood fiber (iPP with Mn of 9,000 showed coated fiber bundles, while PE with Mn of 1,400 did not) [27]. From the micrographs it appears that the surface of co-steam-exploded wood with iPP has a distinct difference in surface structure. It is suggested that the retarding effect that is found by co-steam-

explosion of wood with iPP in an argon atmosphere arises from moisture having limited access to the interior of the fiber wall.

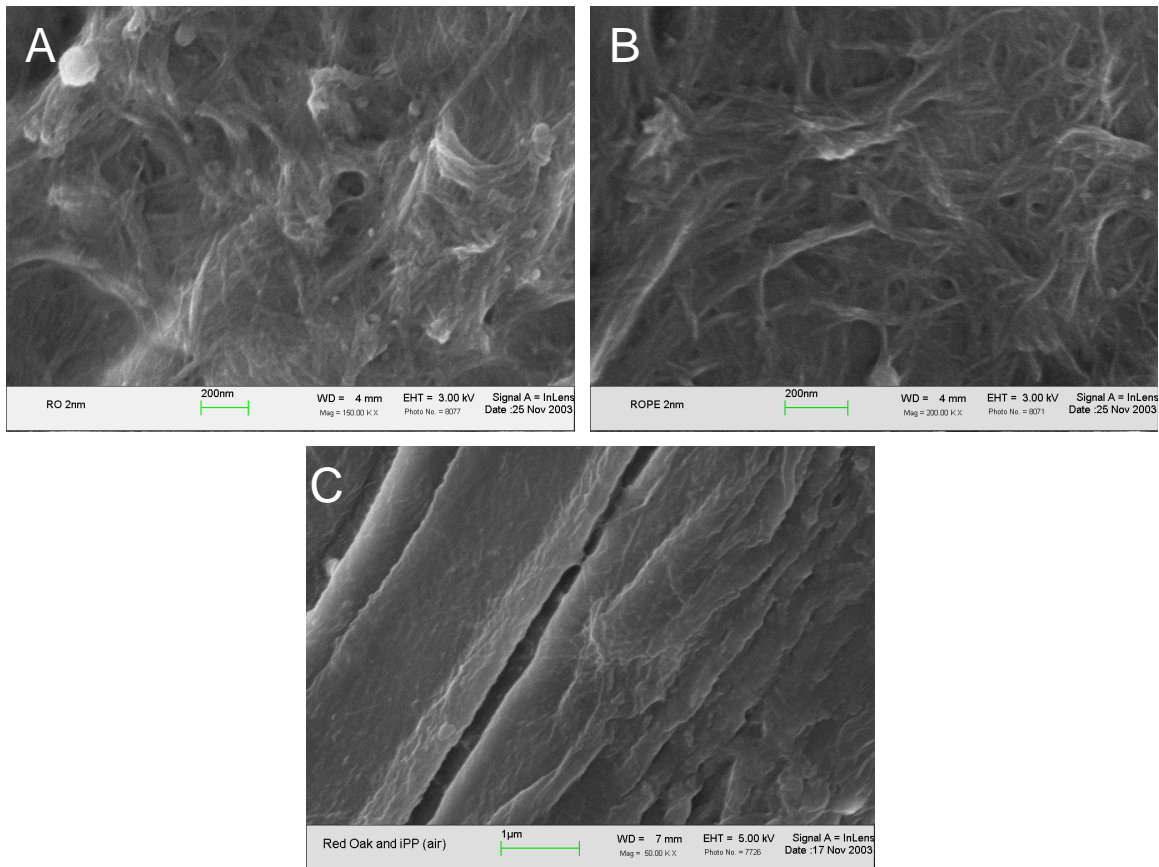


Figure 5.8. Field-emission scanning electron micrographs of steam-exploded material. A) steam-exploded wood fiber at 150Kx magnification; B) co-steam-exploded wood fiber and PE (50% loading) at 200Kx magnification; C) co-steam-exploded wood and iPP (50%, argon loading) at 50Kx magnification.

Inhibited access of moisture to the wood cell wall is demonstrated by comparing advancing contact angles of the steam-exploded wood and co-steam-exploded wood and iPP (Figure 5.9). Water is wetting the steam-exploded wood fiber surface, illustrated by the advancing contact angle which is less than 90° . The co-steam-exploded wood fiber and iPP has

an advancing contact angle greater than 90° indicated by the depression in the water surface. The contact angle for co-steam-exploded wood and PE behaved similar to the control steam-exploded wood fiber. The non-wetting phenomenon for the co-steam-exploded wood and iPP samples demonstrates how the surface structure elucidated in Figure 5.8 influences its interaction with moisture.

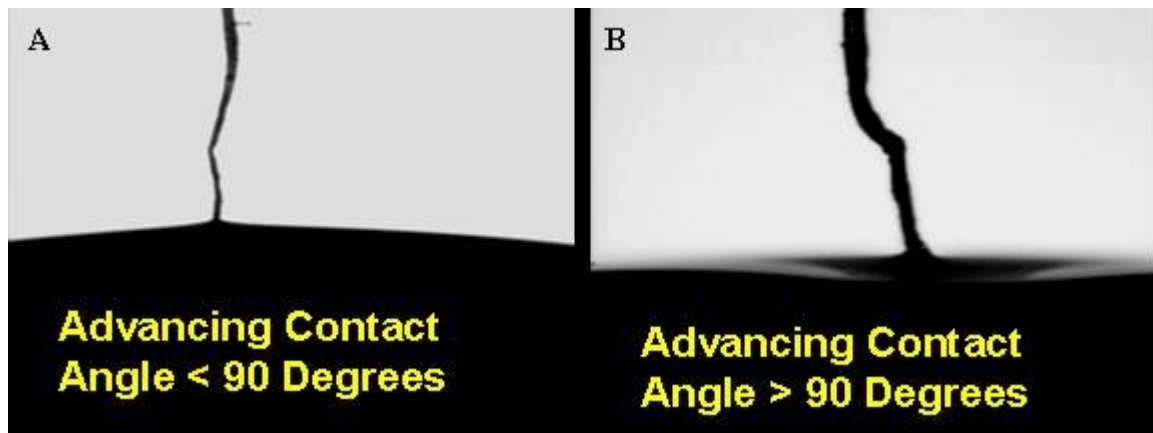


Figure 5.9. Wetting and non-wetting of fiber observed through the advancing contact angle. A) steam-exploded red oak fiber and B) co-steam-exploded red oak and polypropylene

DISCUSSION

The diffusion coefficient measurement is sensitive to the passage of vapor through the cell wall and is a measure of both the paths or channels that vapor can move and interaction of moisture with chemical groups within the wall. Denying access to molecular scale passages would change the vapor path. A change of morphology or the addition of other chemical components within the cell wall would influence the path of vapor movement. Examples of these changes would be an increase in the crystalline component of the amorphous cellulose or the addition of non-polar chemical groups expediting the movement of vapor. In other words, hydroxyl groups of amorphous cellulose would be interacting with themselves in a crystal structure or covered by non-polar moieties; both cases would make them unavailable to form H-bonds with water vapor reducing the interaction.

In order for the change in diffusion coefficients to occur, co-steam-explosion must alter the hierarchical arrangement of order within the cell wall. It is unlikely that bulky polymeric substances penetrate into the interior of the wood cell wall; a plausible explanation is that migration of PO degradation products into the wood cell wall causes the increase in the diffusion coefficients. Moreover, oxygen atmospheres cause increased thermal instability of the PO while moisture reduces the activation energy (E_a) of thermo-oxidative degradation [28]. These factors would increase the yield of polyolefin degradation products. An increased amount of decomposition products produced in the oxygen containing steam-explosion atmospheres may be responsible for the higher diffusion coefficients (Table 5.3), and hence an increase in the degree of modification (chemical or morphological) of the cell wall. These degradation products of thermo-oxidation and wet air thermo-oxidation may range from oligomeric polyolefin species to degradation acid by-products such as formic, acetic, and glycolic acid [29]. The oligomeric species migration may occur during the swollen state of the wood fiber wall under the high pressure of the steam-explosion vessel. The presence of acidic polyolefin degradation by-products is evident by the distinct odorific acid volatiles detected during processing (between batch samples). The migration and adsorption of degraded polyolefin products may be similar to the inactivation of wood during drying, where the surface becomes inactive from adsorbing species [30].

If the polymer degradation products migrate into the cell wall, possibly changing the porosity, they must limit the number of possible interaction sites (directly by masking hygroscopic groups or indirectly by causing a change in the morphology). Although initial rate of water sorption increases for all co-refining treatments except for co-steam-exploded wood and iPP (argon) relative to the control steam-exploded fiber (Table-5.3), the total water vapor sorption remains unchanged or decreases (Figure 5.2 and Figure 5.3). This observation indicates that the change in rate of sorption cannot result from a greater quantity of water bonding sites. Instead, the water binding capacity remains unchanged or is decreased (Figure 5.3) and the remaining sites are being occupied at a faster rate.

Conclusions

Co-steam-explosion processing of wood chips with polyolefin creates a fiber with modified sorption properties. Equilibrium weight gain at varying RH, initial rate of sorption, and the initial diffusion coefficient for the co-steam-exploded fiber are changed depending upon both polyolefin loading and reactivity of the atmosphere within the vessel prior to the introduction of steam.

Infrared absorbance intensity band ratios indicate that all steam-exploded samples had a similar quantity of lignin and hemicellulose associated with the fibers at the fiber surface. Co-steam-explosion with iPP and PE caused an enhancement in the methylene and methyl absorbance bands establishing PO presence with the fiber.

Sorption isotherms contained lower water vapor gain for the co-steam-exploded wood and polyolefin samples. Moreover, the water vapor gain for the fraction of wood present in the sample was reduced as a function of polyolefin loading for the swelling region of the isotherm. Co-steam-explosion of wood and iPP with a M_n of 9,500 had lower weight gain than the co-steam-explosion of wood and PE with a M_n of 1,400.

Comparing the rate of sorption for the fiber fraction of the steam-exploded samples to the initial diffusion coefficient indicates a close relationship for the rate of water sorption. For the co-steam-exploded wood and polyethylene samples, the diffusion of the vapor within the cell wall is a controlling factor for the increase in the rate of sorption. In contrast, rate of sorption was depressed for the co-steam-explosion of wood and iPP (argon) relative to the control fiber. This may indicate that surface penetration of moisture was important in retarding the sorption rate for the co-steam-exploded wood and iPP. Both microscopy and fiber wetting support a difference in surface structure for the co-steam-exploded fiber.

The diffusion coefficient increased for all the co-steam-exploded wood and polyolefin samples compared to that of the steam-exploded wood. This is an indication of the modification of the sample within the wood cell wall. The greatest increase in the diffusion coefficient was for the material produced in an oxygen containing atmosphere. It is suggested that polyolefin degradation products may be the modifying agent. This work proposes that co-steam-explosion is a reactive processing technique that causes enhanced interaction between wood polymers and polyolefin. Changes in diffusion constants of wood fiber walls provide supporting evidence.

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