

# FIBER SURFACE MODIFICATION BY STEAM-EXPLOSION: SORPTION STUDIES WITH CO-REFINED WOOD AND POLYOLEFINS

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## 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, were utilized to determine changes in physical and chemical properties to assess the degree of modification. From the isotherm sorption studies, it was found that co-steam-exploded wood fiber had reduced weight gain for the swelling region of the isotherm as compared to steam-exploded fiber without polyolefin (normalized by fiber mass). The reduction in weight gain for the co-steam-exploded samples was a function of polyolefin loading and polyolefin type. Additionally, the sorption rate of the fibers was reduced for the co-steam-exploded wood with polypropylene (in oxygen gas-deficient reaction conditions). 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 all the materials. 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 sample (in oxygen gas-deficient reaction conditions). 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.

*Keywords:* Sorption, diffusion, reactive processing, wood plastic composites (WPC), moisture.

## INTRODUCTION

Plant fibers from wood, flax, hemp, and other 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 proper-

ties (Clemons 2002). 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 (Joly et al. 1996a; Bledzki and Gassan 1999). However, thermal stability and ultimate and impact strengths decline with the incorporation of un-

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modified wood and plant fibers into thermoplastic composites (Saheb and Jog 1999; Matias et al. 2000).

Scientists indicate that incompatibility between the cellulose-based wood fiber and the thermoplastic matrix hinders adhesion between the two components (Oksman et al. 1998; Mahlberg et al. 2001). 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 (George et al. 2001), 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 (Raj and Kokta 1989), orientation of fiber (Wilkes 2002), and thermoplastic morphology (Qiu et al. 2003). Block copolymers like maleic anhydride grafted polypropylene (MAPP) were effective in achieving interfacial compatibilization (Felix and Gatenholm 1991). Yet, some communications report the efficacy of MAPP is negated with commercial lubricants or with certain conditioning (Chowdhury et al. 2002).

Traditional processing of wood-filled thermoplastic composites involves extrusion or injection molding with the materials added to the processing equipment in pellet form. Wood flour 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 (Clemons et al. 1999). 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

(Johnson 2004). 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 (Brooks et al. 2002; Brooks 1999). Other work demonstrated that thermoplastic material was evenly distributed with the wood fiber on a milligram scale (Rennecker et al. 2004). Coating of the wood fiber bundle with polyolefin was achieved as a function of the melt rheology of the thermoplastic. A uniform coating should influence sorption and rate of sorption of the wood fiber. Therefore, the objective of this study is to examine the sorption properties of co-steam-exploded wood and polyolefin materials as a function of environmental 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 two factors: oxygen content within the reactor and polyolefin loading. Chemical spectroscopy and microscopy methods along with sorption behavior of the fibers are used to evaluate sorption properties and relate them to the mechanism controlling the degree of modification.

## MATERIALS AND METHODS

### *Materials*

The materials used in steam-explosion processing were *Quercus rubra* 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 16 mm and retained by the screen with hole diameters of 10 mm. PE with a number average molecular weight of 1400 and density of 0.9 g/cm<sup>3</sup> 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 at 230°C for 5 min. 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 101 KPa of argon, air, or a 1:1 argon/oxygen mixture. Table-1 contains the loading and atmospheric conditions for all experiments. After steam-explosion, the material was placed in water in an Erlenmeyer flask and stirred for 1 h 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.

### 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<sup>-1</sup> resolution.

### Sorption isotherms

Test specimens were dried in an evacuated desiccator containing phosphorous pentoxide until there was no change in the sample weight ( $\pm 0.0001$ ). Five specimens from each treatment were randomly selected, weighed (approx. 0.1 g per sample), 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 (RH) of each desiccator at room temperature 21°C (note: fluctuation within 5°C alters the RH by only less than 1%). The specimens were left in each desiccator for 30 days and periodically weighed until an equilibrium weight gain was achieved ( $\pm 0.0001$ ).

### 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 cm<sup>3</sup> per s to generate water vapor, which was subsequently mixed with dry nitrogen. The modified instrument measured weight gain with a sensitivity of 1  $\mu$ g as a function of time for 60 min. 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 min ( $t < 5$  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 (Rennekar et al. 2004). The normalized initial sorption rate ( $K_1^*$ ) was calculated by dividing  $K_1$  by the average fiber fraction (Eq. 1).

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

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 (Eq. 2).

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

When using this method to normalize the sorption rate, the assumption is made that the fraction of wood will dominate the rate of weight

TABLE 1. Materials and conditions for steam-explosion.

Materials	Mixture w/w (wood:plastic)	Atmosphere		
		Argon	Air	O <sub>2</sub> /Argon
Red oak chips	(100:0)	×		
Red oak chips and PE	(80:20)	×		
Red oak chips and PE	(67:33)	×	×	×
Red oak chips and PE	(50:50)	×		
Red oak chips and iPP	(50:50)	×	×	

gain with only the wood fraction contributing to water sorption.

*Initial diffusion coefficient determination.*—According to Crank (1956), the initial unsteady-state moisture diffusion ( $D_1$ ) may be determined from Eq. (3):

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

where  $w(t)$  is the weight gain at a given time  $t$ ,  $w_\infty$  is the equilibrium weight gain,  $L$  is the thickness of the cell wall.  $w_\infty$  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 min. Equilibrium weight gains for the 300-min time ( $w_\infty$ ) were then compared to the weight gain at varying relative humidity from the sorption isotherm graph. The relative humidity with the same  $w_\infty$  for the three samples was then used to determine the  $w_\infty$  for the other treatments. Furthermore, the kinetic data [ $w(t)$  vs.  $t$ ] were transformed to [ $w(t)/w_\infty$  vs.  $t^{0.5}$ ] and the slope ( $S$ ) of the graph is described in Eq. (4) (Siau 1984):

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

The slope value was then placed in Eq. (3) to determine ( $D_1$ ), Eq. (5):

$$D_1 = \pi * S^2 * L^2 / 16 \quad (5)$$

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 (Siau 1984).

#### *Cell-wall thickness determination*

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- $\mu$ m sections were cut with a microtome. 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 software. Four measurements of each cross section were made from 28 fibers.

#### *Contact angle measurement*

Individual wood cells were mounted on the tip of a glass capillary tube with "5-minute Epoxy." Epoxy was mixed and applied to the glass tube and allowed to set for 25 min. Under a stereo microscope, individual fibers were laid out with tweezers and then attached to the glass capillary by touching the tacky epoxy to the fiber. A First Ten Angstroms DCA 2000 was used to lower the attached fiber into HPLC grade water. Eight fibers from each treatment were used in this method.

## RESULTS

### *Chemistry of fiber*

Wood is composed of three polymeric components: cellulose, lignin, and hemicellulose (Fengel and Wegener 1989). 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 (Fig. 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 (Fig. 1).

Reflectance FT-IR spectroscopy must rely on

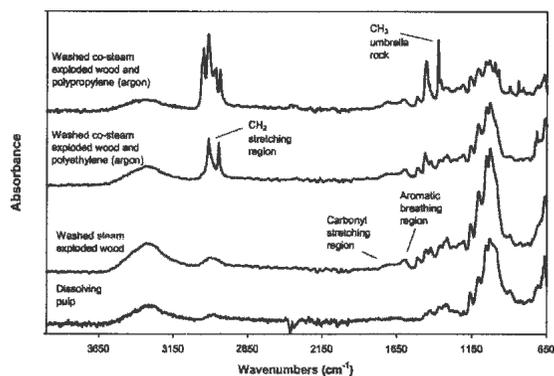


FIG. 1. FT-IR spectra of pulp and steam-exploded fiber.

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 ( $1107\text{ cm}^{-1}$ ) was used to find the relative quantity of components for lignin, hemicellulose, polyethylene, and polypropylene. The corresponding group frequencies utilized were aromatic stretch ( $1604\text{ cm}^{-1}$ ), carbonyl stretch ( $1728\text{ cm}^{-1}$ ), methylene asymmetric stretch ( $2916\text{ cm}^{-1}$ ), and methyl umbrella rock ( $1377\text{ cm}^{-1}$ ) to describe the chemical make-up of the material among treatments (Table 2). The increase of the band intensity ratios of the asymmetric methylene stretching and methyl um-

rella rock for the co-steam-exploded samples indicates a polyolefin (PO) enrichment of the fiber relative to the dissolving pulp fiber and steam-exploded red oak fiber. From these data, it is apparent that the co-steam-exploded fiber has polyolefin associated with it.

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 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.

### Sorption isotherm

The chemistry of the material dictates its interaction with water vapor. At a given partial

TABLE 2. IR absorbance band intensity ratio of specific frequency groups to cellulose ring stretch ( $1107\text{ cm}^{-1}$ ).<sup>a</sup>

Treatment	Asymmetric methylene stretch $2916\text{ cm}^{-1}$	Carbonyl stretch $1728\text{ cm}^{-1}$	Aromatic skeletal vibration $1604\text{ cm}^{-1}$	Methyl umbrella rock $1377\text{ cm}^{-1}$
Dissolving pulp fiber	0.20 (0.02)	0.12 (0.01)	0.14 (0.02)	0.31 (0.02)
Red oak	0.27 (0.01)	0.18 (0.02)	0.26 (0.01)	0.351 (0.01)
Red oak and iPP (argon)	1.70 (0.13)	0.31 (0.02)	0.39 (0.02)	1.53 (0.13)
Red oak and iPP (air)	0.90 (0.17)	0.23 (0.02)	0.31 (0.02)	0.87 (0.13)
Red oak and PE (argon)	0.76 (0.08)	0.22 (0.004)	0.29 (0.01)	0.39 (0.003)
Red oak and PE (air)	0.95 (0.04)	0.18 (0.02)	0.26 (0.02)	0.38 (0.01)
Red oak and PE (O <sub>2</sub> /AR)	0.73 (0.05)	0.20 (0.01)	0.26 (0.01)	0.39 (0.003)

<sup>a</sup> Standard deviation in parentheses.

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 (Fig. 2). The fiber samples follow a typical Brunauer, Emmett, and Teller (BET) type II isotherm when exposed to rising relative humidity (RH) 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 (Labuza 1984).

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 (Fig. 2). Higher lignin concentration and possibly increased 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 (Debzi et al. 1991). The result of the 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 ( $\Delta$ ) was plotted against polyolefin loading (Fig. 3). There was a varying response based on the relative humidity. Average  $\Delta$  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,  $\Delta$  remains at zero for all polyolefin loadings. However,  $\Delta$  for the swelling region increases in magnitude for the PE-containing material. At the highest PE loading in the swelling region  $\Delta$  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  $\Delta$  to the average weight gain of the steam-exploded fiber in this region. Co-steam-exploded wood with iPP has  $\Delta$  values of  $-2\%$  and  $-7\%$  for the non-swelling and swelling regions, respectively (Fig. 3). The  $\Delta$  value relative to the average weight gain of the control value indicates a decrease by 12% for the non-swelling region and 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

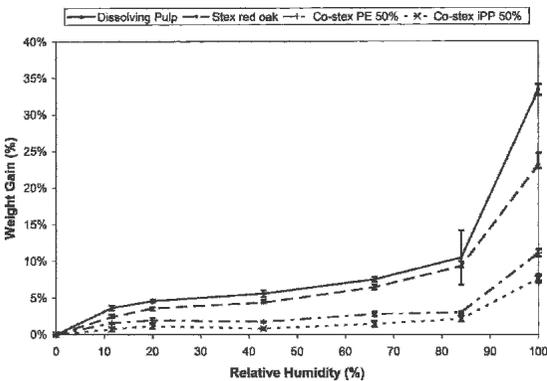


FIG. 2. Sorption isotherm of fiber samples (T = 290°K). Weight gain is based on total material mass.

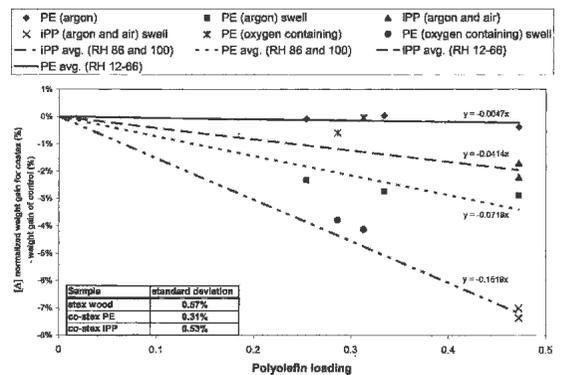


FIG. 3. Weight gain for steam-exploded wood subtracted from the normalized weight gain for co-steam-exploded material as a function of polyolefin loading. Average values determined for non-swelling (RH of 12, 20, 43, and 66) and swelling (RH of 86 and 100) isotherm regions.

the non-swelling region. In addition, the co-processed wood and PE in an oxygen-containing atmosphere have no significant deviation in  $\Delta$  for the non-swelling region (Fig. 3). However,  $\Delta$  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  $\Delta$  for either section of the isotherm (Fig. 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 (Rennekar 2004). This is important because the normalization of the co-steam-exploded wood and iPP is based on earlier experimentation with PE (Rennekar et al. 2004). Therefore, it is likely that 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 Fig. 3 by shifting the  $\Delta$  values of the polypropylene-containing samples to the left on the x-axis.

#### 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 moisture sorption show an initial rapid weight gain, which declines until a final plateau value is reached (Fig. 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 (Fig. 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 min. (Fig. 4, inset). Using these three equilibrium weights, the RH of the chamber was estimated to be 85.3%.

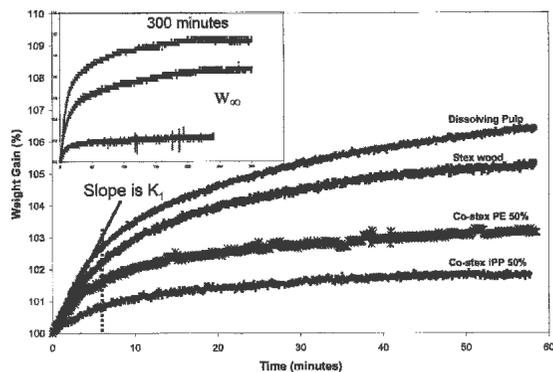


FIG. 4. Water sorption kinetics for fiber samples (estimated RH = 85.3%). Inset shows three samples for extended times to find equilibrium values.

Sorption rates and diffusion rates are listed in Table 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 3). The initial sorption rates were normalized by fiber fraction ( $K_1^*$ ) for the co-steam-exploded wood and polyolefin.  $K_1^*$  shows a change in the rate of sorption for the co-processed wood and polyolefin when compared to the steam-exploded wood sample (Table 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 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 3). A similar increase in  $K_c$  is observed for co-processed wood and PE in 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  $K_1^*$ .

The rate of sorption ( $K_1$ ) reveals the speed of water molecules being sorbed to the fiber

TABLE 3. Water sorption kinetic data and diffusion constants for fiber samples.

Treatment	Polyolefin fraction from [19]	(K <sub>1</sub> ) initial sorption rate (%/min)	(K <sub>1</sub> *) normalized rate (rate/wood fraction) from Eq. 1	(K <sub>c</sub> ) change in K <sub>1</sub> * (%) from Eq. 2	(D <sub>1</sub> ) initial diffusion coefficient cm <sup>2</sup> *s <sup>-1</sup> (×10 <sup>-12</sup> ) from Eq. 5	Increase in D <sub>1</sub> over control (%)
Dissolving pulp	0	0.49 (0.06) <sup>a</sup>	0.49	×	6.51 (1.71) <sup>a</sup>	×
Stex red oak	0	0.38 (0.03)	0.38	0%	7.32 (1.59)	×
Co-stex PE 20% (Ar)	0.254	0.40 (0.07)	0.54	41%	15.69 (3.28)	114
Co-stex PE 33% (Ar)	0.334	0.33 (0.07)	0.50	30%	13.52 (4.15)	85
Co-stex PE 50% (Ar)	0.472	0.27 (0.08)	0.51	35%	19.71 (6.45)	169
<sup>b</sup> Co-stex iPP 50% (Ar)	0.472	0.14 (0.02)	0.27	-30%	13.86 (3.34)	89
<sup>b</sup> 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 <sub>2</sub> /Ar)	0.313	0.46 (0.06)	0.67	76%	33.70 (7.2)	360

<sup>a</sup> Standard deviation in parentheses.

<sup>b</sup> For same initial loading polypropylene content assumed equal to polyethylene content.

sample. One aspect of K<sub>1</sub> is the diffusion rate (D<sub>1</sub>) at which moisture moves through the cell wall. Both dissolving pulp and steam-exploded wood have diffusion coefficients less than 10\*10<sup>-12</sup>cm<sup>2</sup>\*sec<sup>-1</sup> (Table 3). Upon co-steam-explosion of wood with PO, the diffusion coefficients increase for all samples (Table 3). The increase ranges from 90% to 360% with no significant differences for polyolefin type: co-processing with PE and iPP gives rise to similar values of D<sub>1</sub> in relation to the variance of the data (Table 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<sub>1</sub> values (28 to 34\*10<sup>-11</sup>cm<sup>2</sup>\*s<sup>-1</sup>) 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 3).

The diffusion coefficient is influenced by the cell-wall thickness measurement. The cell-wall thickness values ranged from 2 to 6.5 μm with a 5 μm average value (Fig. 5). It is noted that the D<sub>1</sub> values for the control materials (steam-exploded wood and dissolving pulp fiber) are lower than other reported diffusion values (3 to 6 \*10<sup>-11</sup>cm<sup>2</sup>\*s<sup>-1</sup>) for cotton fibers (Joly et al. 1996b). Cell-wall collapse during drying may cause the apparent thickness of the cell wall to increase (instead of hollow rectangle, cell

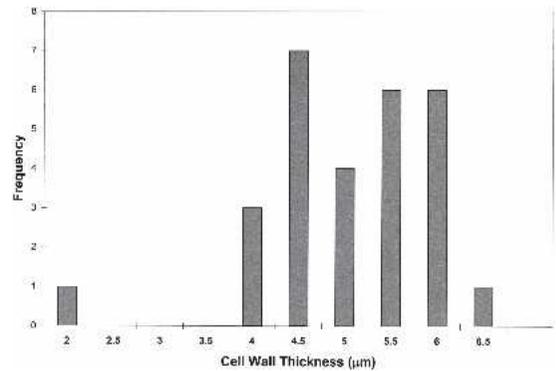


FIG. 5. Histogram of cell-wall thickness measurements for steam-exploded material.

becomes flattened and filled). Increasing the thickness from 5 μm to 10 μm would result in the diffusion coefficients increasing to 2.5\*10<sup>-11</sup>cm<sup>2</sup>\*s<sup>-1</sup>, 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 provide for a relative measure of diffusion among the treatments.

Using the data from Table 3, K<sub>c</sub> is plotted against D<sub>1</sub> and compared to the control steam-exploded wood sample (Fig. 6). For co-steam-exploded wood and polyethylene, there is an increase in initial sorption rate as D<sub>1</sub> increases. This relationship includes the control steam-exploded wood fiber. Hence, an increase in sorp-

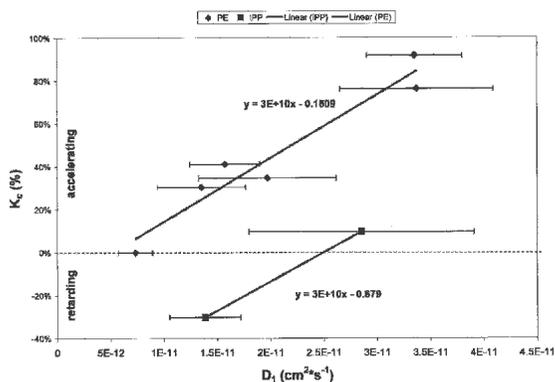


FIG. 6. Initial sorption rate change,  $K_c$  (from Eq. 2), of wood fiber fraction due to co-steam-explosion processing vs. the initial diffusion coefficient,  $D_1$  (from Eq. 5) for co-refined samples with polyethylene (PE) or polypropylene (iPP).

tion 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.

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 (Fig. 7). Water is wetting the steam-exploded wood fiber sur-

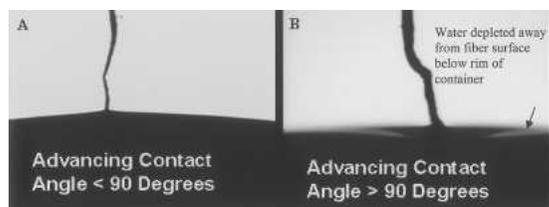


FIG. 7. Wetting and non-wetting of fiber observed through the advancing contact angle. A) steam-exploded red oak and B) co-steam-exploded red oak and polypropylene.

face, illustrated by the advancing contact angle which is less than  $90^\circ$ . The co-steam-exploded wood fiber and iPP has an advancing contact angle greater than  $90^\circ$  indicated by the depleted water at the fiber surface. The contact angle for co-steam-exploded wood and PE behaved similarly to the control steam-exploded wood fiber. Previous experimentation found melt viscosity of the polyolefin controlled 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) (Renneckar 2004). The surface of co-steam-exploded wood with iPP has a distinct difference in surface structure. The non-wetting phenomenon for the co-steam-exploded wood and iPP samples demonstrates how the surface structure may influence its interaction with moisture vapor. 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.

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 (Kotoyori 1972). 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 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 by-products such as formic, acetic, and glycolic acid (Bjerre and Sorenson 1994). 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 (Sernek et al. 2004).

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 3), the total water vapor sorption remains unchanged or decreases (Fig. 2 and Fig. 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

(Fig. 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 (control by oxygen gas content) 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 reduced 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. Fiber wetting supports a difference in surface structure for the co-steam-exploded fiber.

Initial diffusion coefficients increased for all

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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