

CHAPTER 6

Fiber Surface Modification by Steam-Explosion. III. Chemical Changes in Co-refined Wood and Polyolefins.

Abstract

Steam-explosion processing was used to co-refine wood and polyolefin into material for use in wood-reinforced thermoplastic composites. During steam-explosion a number of reactions occur that may promote chemical modification of wood fiber with polyolefin material. A stepwise fractionation was performed on the co-steam-exploded mulch in an effort to analyze chemical changes in the hemicellulose and lignin biopolymers of wood as well as the polyolefin. The amount of oxygen within the reaction vessel was regulated to influence degree of modification of material. While the quantity of soluble hemicellulose-rich fraction changed, no polyolefin enrichment was noted for this portion. Lignin did show enhancement with polyethylene by FT-IR spectroscopy. The polyolefin that was exposed to steam-explosion in presence of wood demonstrated fluorescence from oxidation; a change in methyl content for the experiments with the highest O₂-concentration; as well as indications for an uptake of methoxy groups. A hypothetical scheme is discussed for the chemical changes that involve thermo-oxidation of the polyolefin and free radical reactions with the wood components.

INTRODUCTION:

The manufacturing process of composite materials is critical in determining composite performance and the importance is not always realized when attempting to improve composite properties. Orientation, thermal history, and reaction of components are influenced by composition, processing conditions, and process type. Maximizing the efficiency of the manufacturing process balances the desired material properties with cost of materials, cost of processing, and cost of waste disposal.

Traditional processing for wood and agrofiber filled thermoplastics involves the extrusion of material into pellet form and then injection or compression molding the desired product [1]. In this process wood must be reduced to either particulate or fiber form, which involves milling or pulping, respectively. Wood flour is seen to have a role as a filler (offering limited mechanical support), while pulp fibers may offer reinforcement depending upon the interaction between the thermoplastic and fiber [2]. In addition, the importance of wood fiber aspect ratio was demonstrated for reinforcement, unfortunately, the extrusion process can decrease the aspect ratio of wood fiber by more than half [3]. Wood material is typically added with the thermoplastic pellets to an extruder along with a variety of additives, such as lubricants, coupling agents, and plasticizers. In addition to increasing the adhesion between filler and thermoplastic there are other challenges inherent to this processing method such as increasing filler distribution and reducing fiber damage during extrusion. The amount of wood was shown to impact orientation of fiber [3], while the surface treatment influences the morphology of the interfacial region [4].

Extrusion technology is well established and commonly used with particulate fillers such as talc and inorganic fibers such as glass [5]. While this methodology is currently accepted, an alternative is suggested for the processing of wood and thermoplastic materials by steam-explosion processing. Steam-explosion has gained scientific interest over the years in its ability to process biomass for a variety of uses such as pulping, animal feed, and enzyme production [6-8]. Nevertheless, it is an underutilized technology that could play a larger role in the refining of biomass.

Currently, wood chips from deciduous species can be processed into wood fiber bundles and wood fiber depending upon steam temperature and residence time. The reactive process involves thermal energy, plasticization and explosive decompression. As a result a number of

chemical and morphological changes occur during processing that are well documented, such as glycosidic bond breakage, hydrolysis of the lignin carbohydrate bond complex, increase in cellulose crystallinity, and lignin rearrangement in larger domain structures [9]. These changes involve both radical or acid catalyzed reactions.

Moreover, steam-explosion processing was utilized in an attempt to co-refine wooden pallets and polypropylene gas tanks [10]. It was noted that “binderless” panels from this material offered better performance than other similar fiber board panels in water boil durability tests. In order to understand and characterize the co-refined wood plastic material by steam-explosion, a number of studies were conducted to investigate composition [11], fiber sorption properties [12], and distribution of thermoplastic with the fiber [13]. These studies indicate that co-steam-explosion processing creates a modified fiber. Furthermore, the molecular weight/melt rheology of the thermoplastic was shown to be an important parameter in the distribution of the thermoplastic with the fiber. The advantage of the co-processing technique is that it reduces wood chips to wood fiber while simultaneously distributing thermoplastic with the wood fiber. While this process is novel, it has the additional potential of increasing interaction between the thermoplastic and wood fiber without the addition of coupling agents. This is due to the variety of reactions occurring during steam-explosion processing that may provide an opportunity for individual wood components to become chemically modified by the thermoplastic. The objective of this paper is to determine if chemical modification of the material occurs by investigating fractionated components. Specifically, extracted hemicellulose, lignin, and polyolefin from co-steam-exploded wood and polyolefin (PO) are investigated to determine chemical changes in the material.

METHODS AND MATERIALS:

Steam-Explosion Processing

Materials

Air dry *Quercus rubra* chips were obtained from a local sawmill and sorted through a circular diameter sorter to obtain the fraction that passed through 5/8” diameter hole screen but retained by the 3/8” hole diameter screen. The polyethylene and polypropylene that was co-refined with the wood chips were obtained from Scientific Polymer Products Inc. and Sigma-Aldrich, respectively. The polyethylene powder had a density of 0.92 and a number average

molecular weight (M_n) of 1,400. The isotactic polypropylene beads had a M_n of 9,500. Argon, air, and a 50:50 oxygen/argon compressed gas cylinders (Linde Gas) were used to regulate the atmosphere within the steam-explosion vessel prior to the introduction of steam.

Procedure

The reaction vessel was heated internally to 230 °C prior to any work. The wood chips and polyolefin were added to the reactor on either a 67:33 wood-polyethylene or 50:50 wood-polypropylene dry matter basis, but used as air-dry. Next, the reactor was closed and the air atmosphere was immediately evacuated by a vacuum pump. Upon emptying the air atmosphere, compressed gas was introduced back into the reaction vessel until 1 bar of gas pressure was achieved. Steam at a temperature of 230°C was introduced into the reaction vessel for a 5 minute period. After the five minute residence time, the exit ball valve was opened decompressing the reaction vessel and ejecting the material into a collection container. The delay time from loading the material into the reactor to the introduction of steam was approximately 150 seconds. After steam-explosion the material was dried and stored until further examination.

Fractionation

Procedure

A stepwise fractionation procedure was used to remove hemicellulose-rich material, lignin-rich material, and polyolefin from the co-steam-exploded fiber. The steps and solvent/non-solvents used in the extraction procedure are detailed in Figure 6.1. Co-steam-exploded material was placed in hot water and stirred for 2 hours in an Erlenmeyer flask and subsequently filtered across Whatman (1) qualitative filter paper. The solutions were then freeze dried to recover the water-soluble material and were stored in a desiccator until further analysis. Water washed co-steam-exploded material was then transferred to a Soxhlet extraction apparatus and extracted with acetone for 24 hours. By the end of that time, the solution around the thimble was clear. Acetone filtrate was subsequently poured into petroleum ether and further fractionated by precipitation. The dark brown precipitate was filtered from the solution, dried, and stored in a desiccator. Next, the co-steam-exploded material was Soxhlet extracted with tetrahydrofuran (THF) for 48 hours. The resulting extract was poured into acetone and filtered to remove polyolefin-rich material. The filtrate was then poured into petroleum ether and filtered to remove lignin-rich material. The resulting filtrate was then vacuum dried leaving a highly

viscous liquid. Finally, the co-steam-exploded material was Soxhlet extracted with xylenes for 48 hours. The resulting solution was poured into acetone and filtered, removing the precipitated polyolefin from the solution. The white polyolefin powder was then dried in a vacuum oven and stored until further analysis. Note that all solutions were precipitated with equal volumes except for the xylene/acetone solution where a 2:1 excess of acetone was used to precipitate the polyolefin in the xylene solution. In order to ensure the fractionation procedure was not modifying the materials relative to a control, the procedure was repeated for a dry mixture of neat polyolefin and steam-exploded wood. During every stage of the fractionation process polyolefin was in the presence of steam-exploded wood and any modification of the components during extraction would have been carried through all samples.

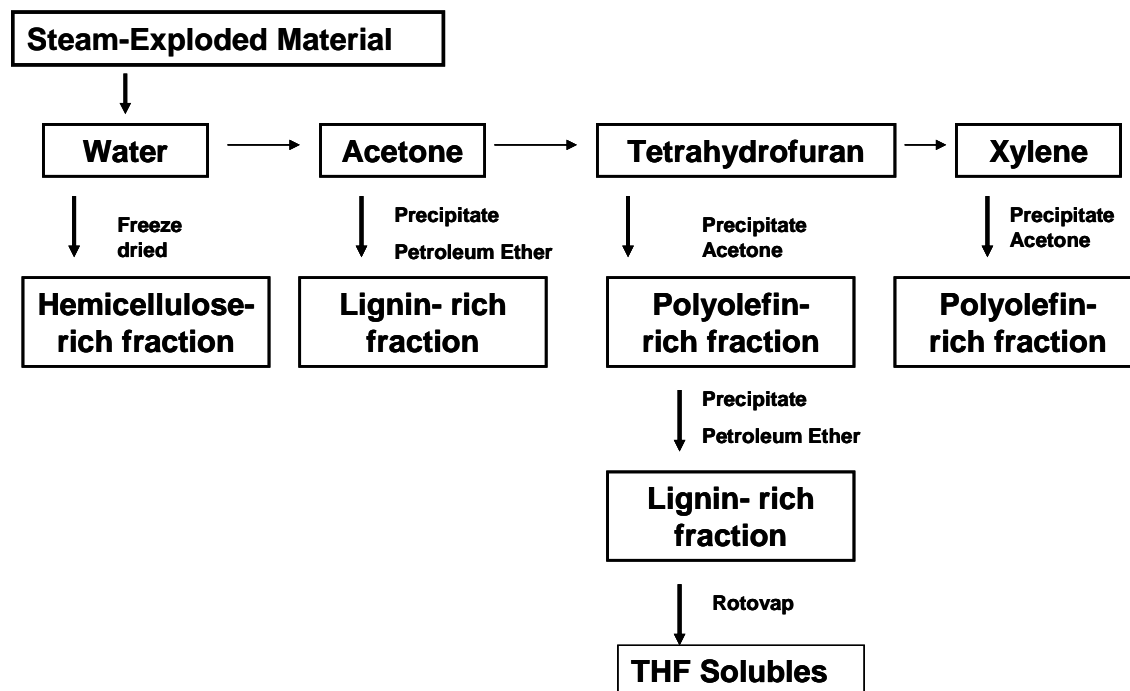


Figure 6.1. Stepwise fractionation procedure for steam-exploded material.

Infrared Spectroscopy

A Midac M series Fourier Transform Infrared (FT-IR) spectrometer equipped with a Durascope attenuated total reflectance (ATR) attachment was used to make all measurements. The ATR FT-IR spectrometer was set to a single bounce mode and 64 absorbance spectra with a resolution of 8 cm^{-1} were recorded for each sample. The reproducibility of the spectra was confirmed by recording IR spectra for each sample in triplicate.

Ultraviolet-Visible Spectroscopy

Solutions of extracted lignin were prepared using absolute ethanol with a maximum concentration of 40 mg/L. UV measurements were recorded by a Hewlett Packard 8453 UV-Visible Spectrophotometer.

Confocal Laser Scanning Microscopy

Polyolefin film samples were prepared by compression molding polyolefin directly between microscope slides and cover slips at 170°C . The films were then analyzed with a Zeiss LSM510 confocal microscope with a 40x objective lens. Laser light of wavelengths 364 nm and 633 nm were used to irradiate the films and both the fluorescence and transmitted light images were recorded. The relative intensity of fluorescence was then determined from pixel brightness.

Gel Permeation Chromatography

Chalmers University of Technology provided the molecular weight analysis of the extracted polypropylene. A refractive index detection unit was used to determine the number average (M_n) and weight average (M_w) molecular weights on a Waters alliance GPCV 2000. The solvent used was 1,2,4-trichlorobenzene that was at 135°C . Prior to experimentation 1 mg/ml iPP was prepared, heated for 15 hours and filtered through a 0.45micron filter. The equipment was calibrated with polystyrene standards.

Differential Scanning Calorimetry

TA instruments 2920 Modulated DSC was used to determine the melting temperature of the polyolefins. Hermetic aluminum pans were used for the experimentation with a heating rate of 5°C/minute. Nitrogen purge gas used in the experimentation.

RESULTS AND DISCUSSION:

Fractionation

Reported in the literature is the hydrolysis of the lignin carbohydrate complex during steam-explosion disrupting the hierarchical order of the wood fiber wall [9, 14-16]. As a consequence, hemicellulose becomes hot water soluble [15]. Steam–exploded material was fractionated removing hemicellulose-rich and lignin-rich components with hot water and acetone, respectively. The fraction of water extracted material removed from the “control” steam-exploded material, based on wood content, is within range of the reported values for other carbohydrate fraction of red oak (Table 6.1) [Glasser]. Moreover, water soluble values for co-steam-exploded wood-iPP were lower than the reported water extracted values of red oak, while the water soluble values from co-steam-exploded wood-PE are higher (Table 6.1). Using Fisher’s LSD multiple mean comparison method with $\alpha=.05$ significance level, the water soluble fractions from the co-steam-exploded wood-iPP and co-steam-exploded wood-PE are significantly different from each other. By comparing the extraction quantity for co-steam-exploded material to the reported value, it is evident that co-steam-explosion wood-PE enhances hydrolysis and extraction of wood components and co-steam-explosion wood-iPP inhibits hydrolysis and extraction of wood components. Besides the structural chemical difference between the two polyolefins, the molecular weight was different for the two polyolefins which caused a variation in the coating of the fiber by the polyolefin [13]. The complete coating of the fiber by iPP would inhibit water access, possibly retarding the extraction of wood components. Additionally, the iPP inhibited some reorganization of lignin limiting its flow and separation into its own domain [13].

Table 6.1. Water and acetone extracted quantity (shown as fraction of wood fiber material)

Solvent	Red Oak ^a	Polyolefin Type (atmosphere)					
		Control (air)	PE (argon)	PE (air)	PE (O ₂ /argon)	iPP (argon)	iPP (air)
Water	0.19	0.17	0.24	0.24	0.26	0.11	0.14
Acetone	0.29	0.23	0.23	0.21	0.17	0.23	0.25
Total	0.48	0.40	0.47	0.45	0.43	0.34	0.39

^a Values reported in Ibrahim and Glasser, (Used alkali instead if acetone)

The quantities of acetone extracted material are lower in yield than reported alkali extracted yield (consisting of lignin, tannins, and furans) of red oak (Table 6.1) [16]. Both co-steam-explosion of PE and iPP do not offer significant difference from each other for a given atmosphere. However, the molar absorptivity coefficient of the lignin (see below) confirms the choice of acetone as a good solvent for the removal of lignin in steam-exploded wood.

Water Extracted Fraction

Infrared Spectroscopy

The major component of red oak's hemicellulose fraction, 4-O-methyl β -D glucuronoxylan, has its chemical structure well defined in the literature. In addition to the absorbance bands assigned to xylan, there are also absorbance bands due to lignin within the steam-exploded wood water extract (Figure 6.2ab) [15,18]. The spectrum from the water soluble fraction of steam-exploded red oak (Figure 6.2) appears to be similar to reported xylan spectra that contain between 2 and 8% Klason lignin [19]. Specific absorption regions found in Figure 6.2a are attributed to the following: a broad hydroxyl stretching band (3400cm^{-1}); methyl and methylene stretching ($2950\text{-}2850\text{ cm}^{-1}$); carbonyl stretching ($1740\text{-}1700\text{ cm}^{-1}$); aromatic modes ($1600\text{-}1200\text{ cm}^{-1}$); and secondary alcohol stretches, glycosidic ether stretch, and xylan ring stretching ($1200\text{-}1000\text{ cm}^{-1}$). It should be highlighted that xylan's most intense absorbance occurs at 1047cm^{-1} arising from both the C-C ring stretching and C-OH bands [19,20]. However, the control sample from steam-exploded wood has its most intense absorption occurring at $1029\text{-}1034\text{cm}^{-1}$ (Figure 6.2b). Most likely this shift arises from a cellulose component that may be present from the breakage of glycosidic bonds within the amorphous cellulose region [9]. A cellulose component in the water extracted fraction has been previously reported by Tanahashi [21]. However, it should be noted that the ATR crystal can cause a shift in the group frequency of specific bands because of the optical physics of the system [22]. For example, the carbonyl peak found for xylan at 1732 cm^{-1} is shifted to lower wavenumbers.

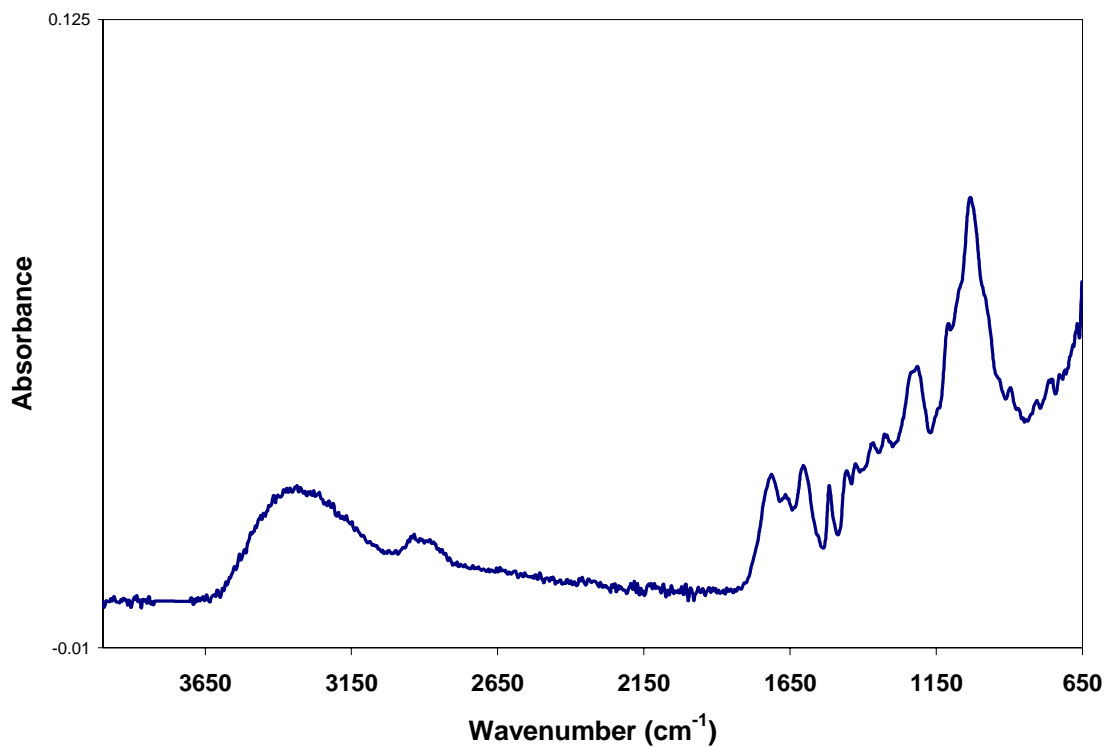


Figure 6.2a. FT-IR spectrum of freeze-dried water extract from steam-exploded wood.

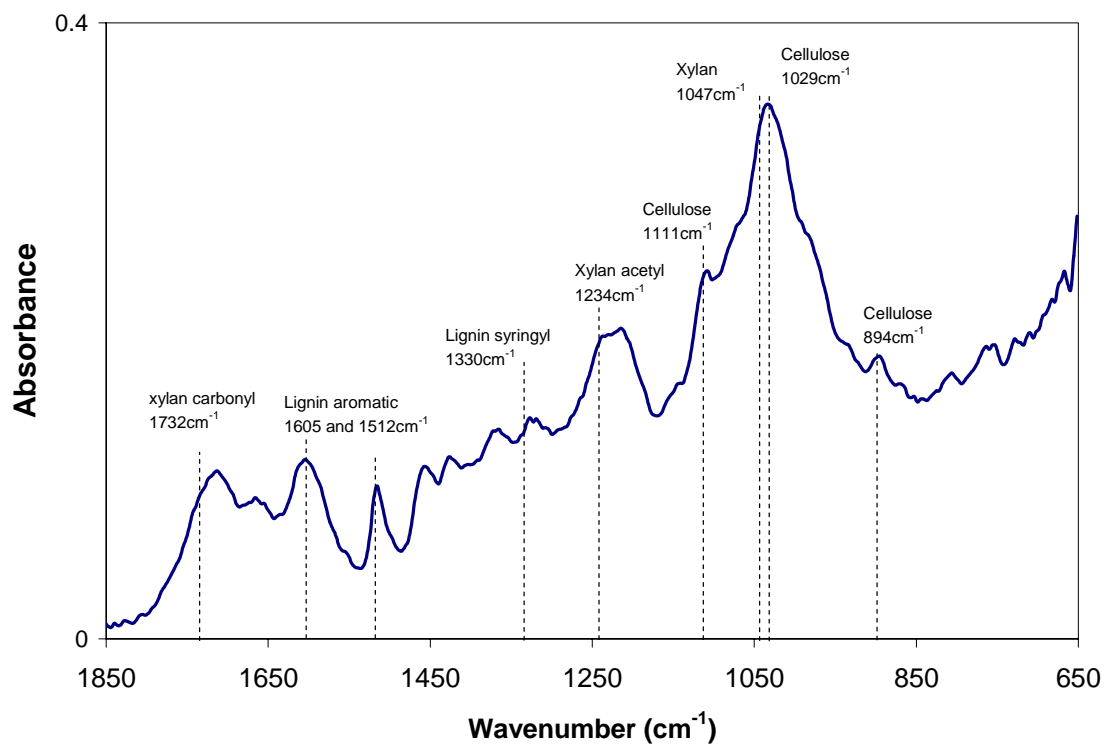


Figure 6.2b. FT-IR spectrum of freeze-dried water extract from steam-exploded wood.

The spectra for the water extracted fractions for co-steam-exploded wood-polyolefin material have similar absorbing group frequencies to the control sample (Figure 6.3a-b). The spectra were normalized with a carbohydrate ring in-phase stretching peak (1108 cm^{-1}), which also made the carbohydrate carbonyl (1720 cm^{-1} to 1750 cm^{-1}) have similar absorption intensities for all the samples. Under the assumption of a given beam path length and constant sample-ATR crystal contact, the relative concentrations of the carbohydrate components are similar for all samples. Furthermore, there is a decrease in absorption between 1700 and 1500cm^{-1} for co-steam-exploded wood and PE samples (Figure 6.3a). This region contains group frequencies that have been attributed to aromatic carbonyl/carboxyl groups and aromatic ring breathing groups. In the same region for co-steam-exploded wood and iPP, there is not any deviation from the control spectrum (Figure 6.3b). From these observations it is suggested that there is a difference in relative lignin concentration for the water extracted material between co-steam-exploded wood-PE and the control. It is also evident that the relative concentrations of lignin and carbohydrate are similar for the control and co-steam-exploded wood and iPP.

Although the extraction quantity (Table 1) is not statistically significant for the control and co-steam-exploded wood and PE samples, there is a statistical difference between the quantity of water extracted material for co-steam-exploded wood-PE and co-steam-exploded wood and iPP. The quantity and the chemistry indicate a lignin, carbohydrate and polyolefin interaction that may be polyolefin dependent (see Discussion section). However, there is no evidence of PO enrichment of the spectra in the methyl or methylene stretching regions 3000 - 2800cm^{-1} (not shown). In other words, there is no polyolefin intimately associated with the water soluble solids.

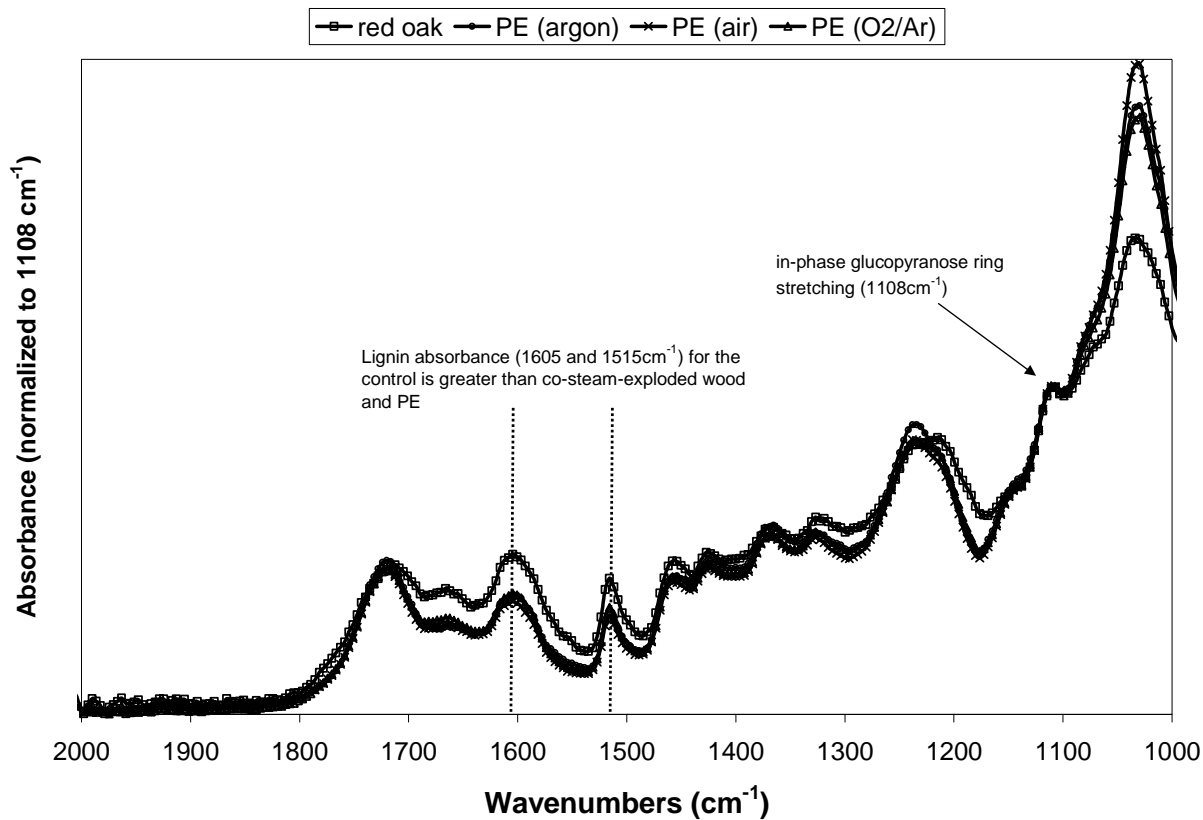


Figure 6.3a FT-IR spectra for freeze-dried water extract from co-steam-exploded wood and PE and steam-exploded wood fiber (control). Note all co-steam-exploded wood and PE spectra overlap.

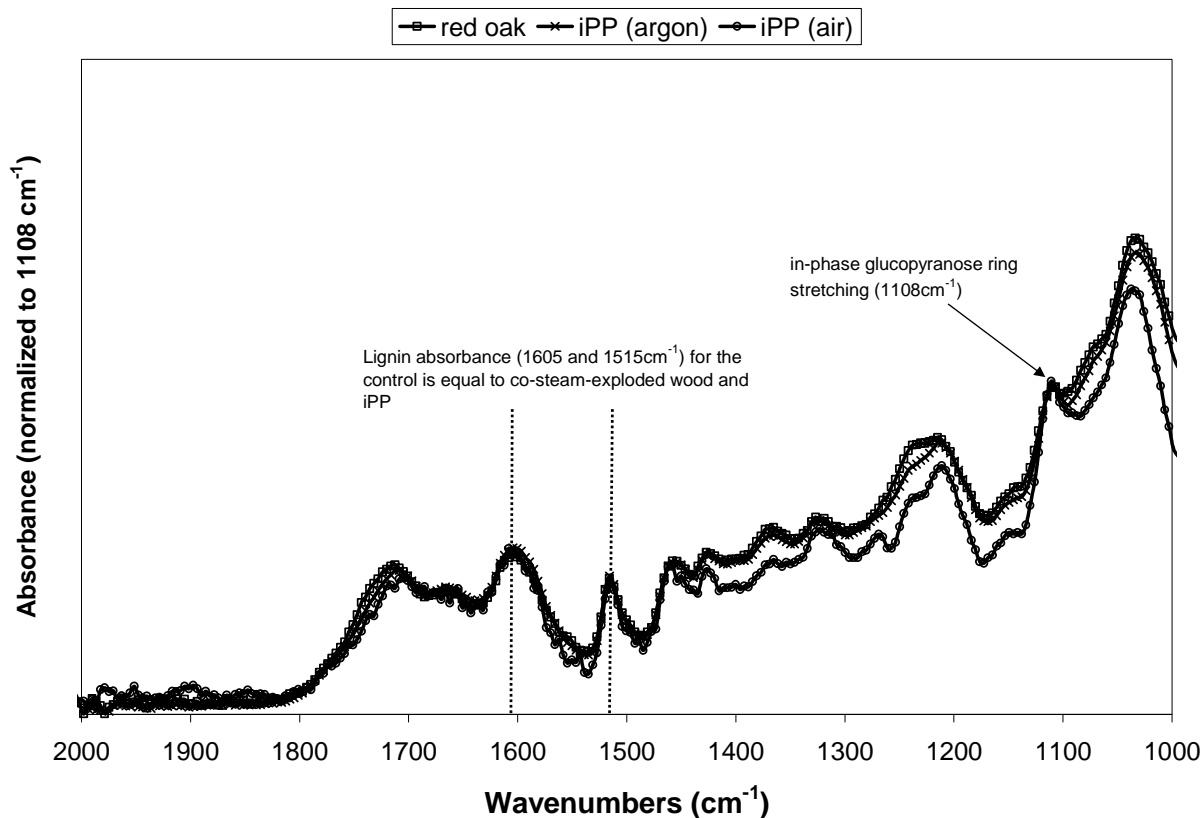


Figure 6.3b FT-IR spectra for freeze-dried water extract from co-steam-exploded wood and iPP and steam-exploded wood fiber (control). Note overlap of spectra.

Acetone Extracted Fraction

UV-Visible Spectroscopy

Acetone extracted fraction (precipitated in petroleum ether) from steam-exploded red oak has a UV-visible molar absorptivity coefficient value in ethanol of 18.8 mg/L at the wavelength 273 nm (Figure 6.4). There is some scatter in the data, but the R^2 value of the regression is 0.94 with the line going through the origin. This is in good agreement with the molar absorptivity coefficient of lignin reported in the literature [23]. Moreover, the UV-visible spectra for co-steam-exploded wood-polyolefin are similar to the control (Figure 6.5). From this observation, the UV-visible absorbing chromophores within the acetone extracted/petroleum ether precipitated samples may not be modified by the co-steam-explosion process.

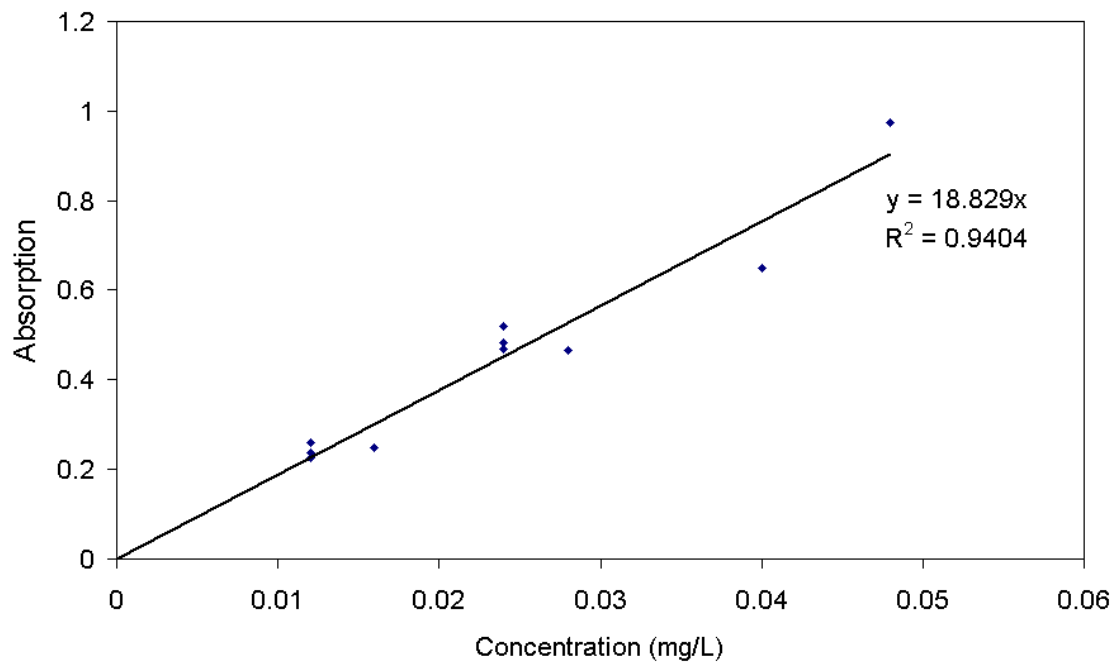


Figure 6.4. UV-vis absorbance vs. concentration for acetone extracted and petroleum ether precipitated solids from steam-exploded wood. λ 273nm, in ethanol.

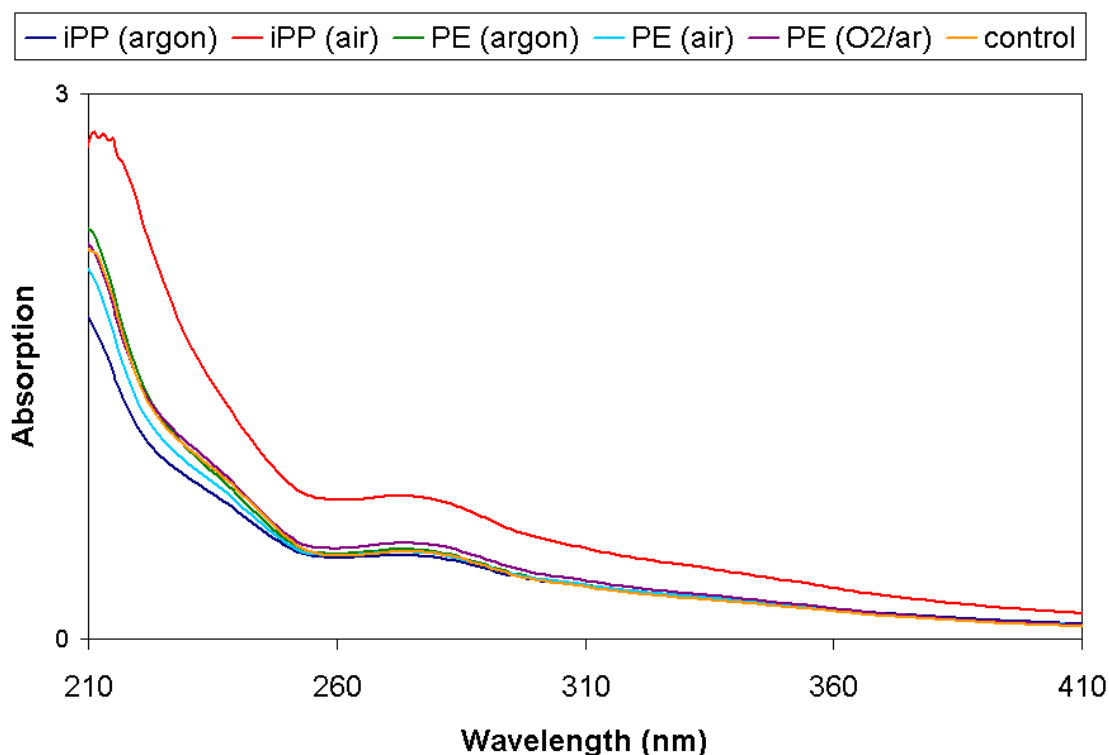


Figure 6.5. UV spectra for lignin component extracted from steam-exploded material in ethanol.

Fourier Transform Infrared Spectroscopy

Infrared spectra were used to determine chemical and conformational changes of the acetone-soluble fraction that were not detected by UV-visible spectroscopy. The control spectrum from steam-exploded wood absorbs IR radiation in the hydroxyl stretching, methyl and methylene stretching, carboxylic acid, carbonyl, aromatic, and primary/secondary hydroxyl stretching regions (Figure 6.6ab). The aromatic peaks at 1600 cm^{-1} and 1511 cm^{-1} are prominent, as well as with the carbonyl peak at 1700 cm^{-1} , 1211 cm^{-1} , and carbohydrate related peaks at 1111 cm^{-1} and 1029 cm^{-1} . Capretti and Focher describe changes found in the spectra for lignin arising from steam-explosion such as shifts from 1596 cm^{-1} to 1608 cm^{-1} (caused by carbonyl/carboxyl group induced by steam-explosion) and an increase in 1511 cm^{-1} compared to 1504 cm^{-1} (caused by increase in G lignin over GS lignin) [24]. It is interesting that the aromatic breathing mode shift caused by steam-explosion at 1608 cm^{-1} is less pronounced (most likely

convoluted in the 1596 peak) while the other aromatic breathing mode shift at 1511 cm^{-1} is evident (Figure 6.6b). Tanahashi reports that steam-explosion degradation of lignin does not follow strong acidolysis and as a result the amount of carbonyl groups attached to aromatic structure is lower for the steam-explosion process when compared with acidolysis [21].

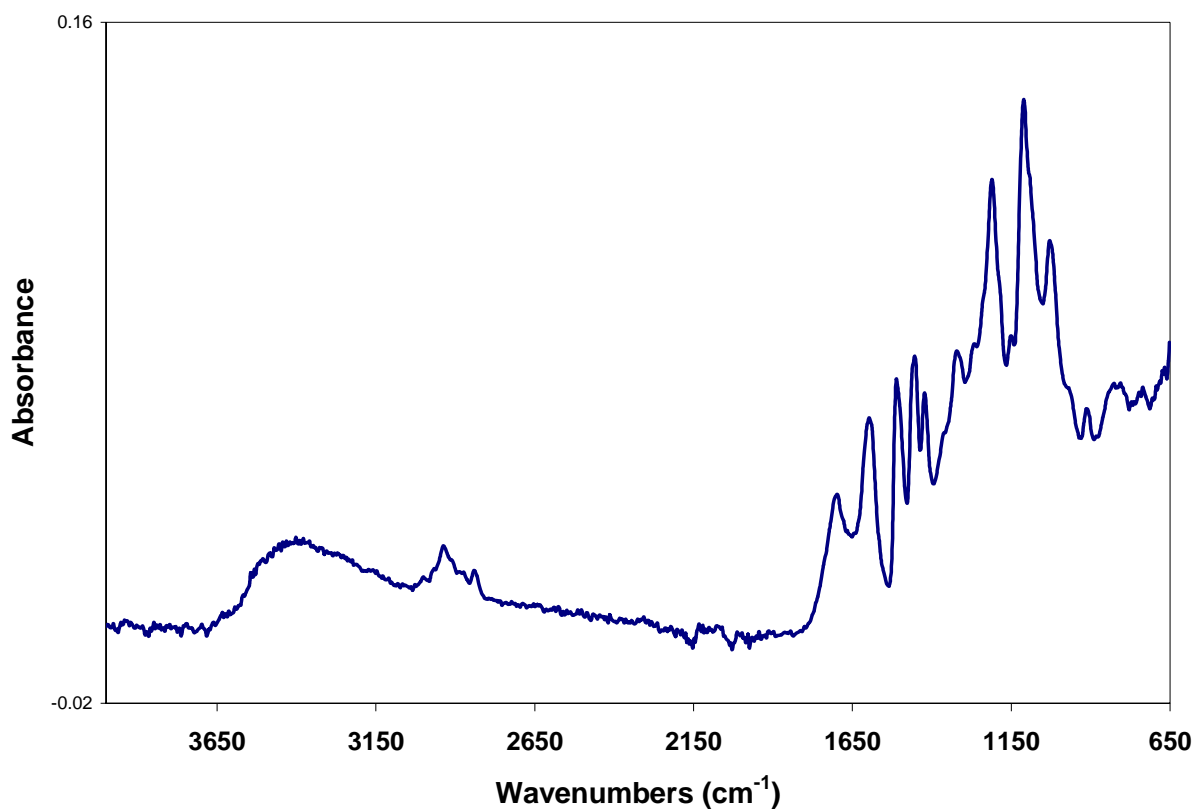


Figure 6.6a. FT-IR spectrum for acetone extracted lignin from steam-exploded wood.

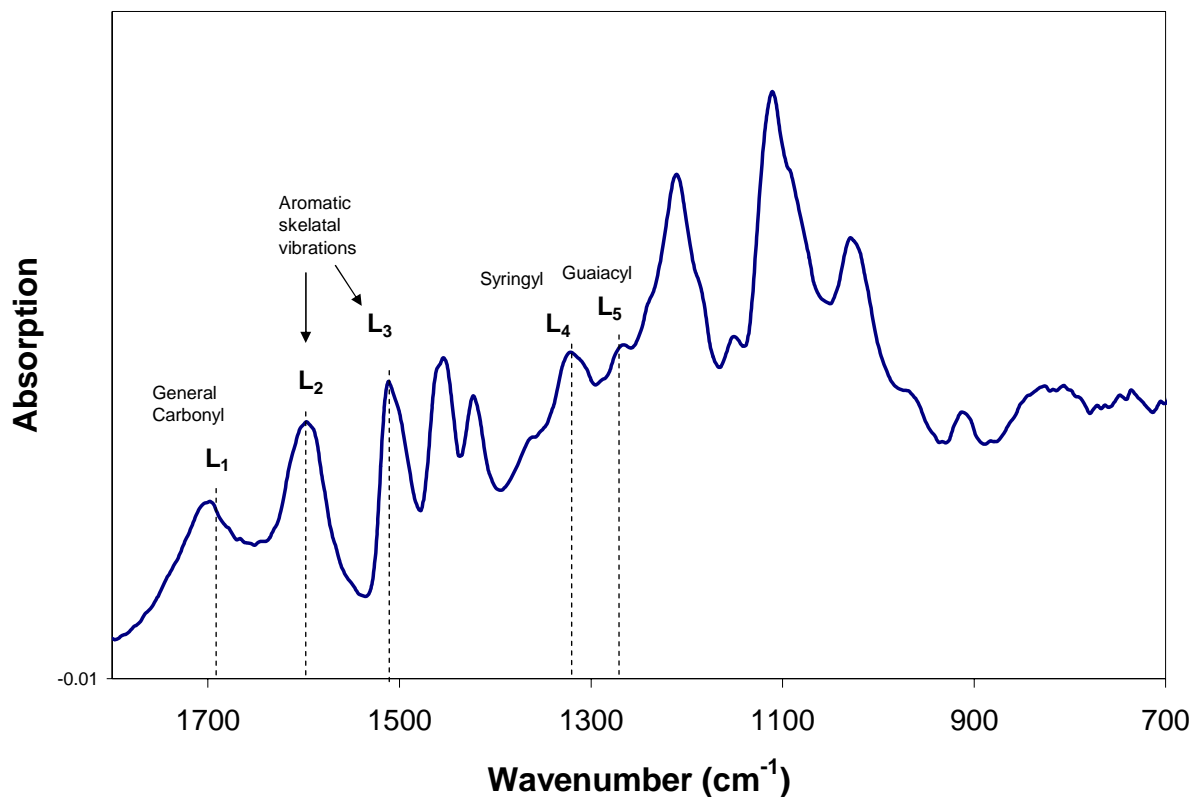


Figure 6.6b. FT-IR spectrum for acetone extracted lignin from steam-exploded wood.

Like the water-soluble fraction of the co-steam-exploded wood and polyolefin, the acetone-soluble fraction is similar to the control sample from the steam-exploded wood. However, spectra for the extracted lignin from the co-steam-exploded wood-PE samples show increased absorbance at the 2916 cm^{-1} and 2846 cm^{-1} bands (Figure 6.7a). These bands are the asymmetric and symmetric methylene stretching for polyethylene (Figure 6.7a). The values are assigned to polyethylene because the methylene stretches found in wood polymers are shifted. Furthermore, the peaks are more defined for the co-steam-exploded wood-PE in an oxygen containing atmosphere. In contrast, the co-steam-explosion wood-iPP shows minimal change in the methylene and methyl stretching region for the acetone soluble spectra (Figure 6.7b). Steam-explosion in an argon containing atmosphere for both iPP and PE has increase absorption relative to the other samples in the hydroxyl stretching region (Figure 6.7a,b). In the fingerprint region, the spectra predominately overlap each other (Figure 6.7b and Figure 6.8). This may indicate

relative homogeneity among the carbonyl portion, aromatic skeletal concentrations, and syringyl and guaiacyl ratios for the acetone soluble material.

From the FT-IR data it is suggested that co-steam-explosion of wood-PE causes enhancement of the lignin with PE species. It is not known if the two species are covalently linked together. There is a possibility that some low molecular weight fraction of PE is contaminating the lignin. However, the following reasons would favor an increased association between lignin and PE and not contamination: (1) acetone is a non-solvent for polyethylene and acetone extracted material is further purified by precipitation with petroleum ether and recovered by filtration before FT-IR analysis, (2) there was plenty of water soluble extract and that extract was lignin-starved.

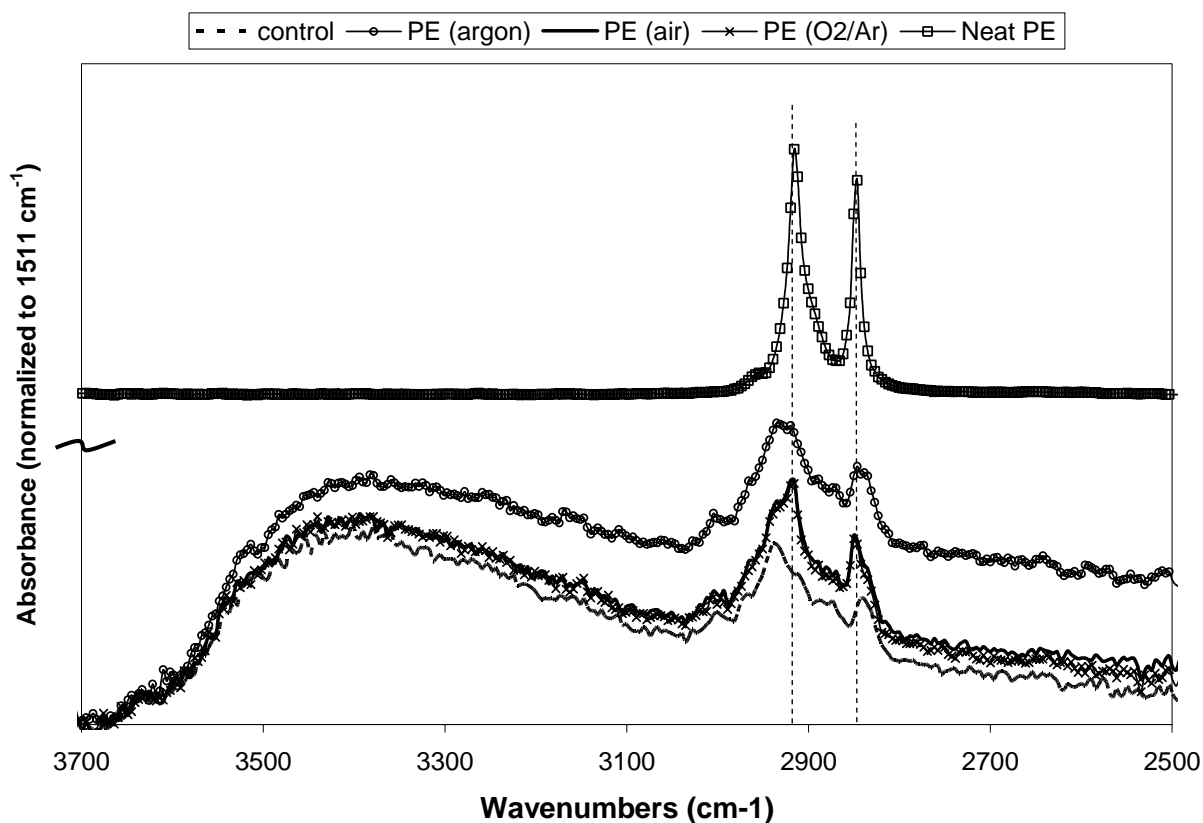


Figure 6.7a. FT-IR spectra for acetone extracted lignin from co-steam-exploded wood and PE, steam-exploded wood fiber (control), and neat PE. Note PE (air) and PE (O₂/Ar) overlap.

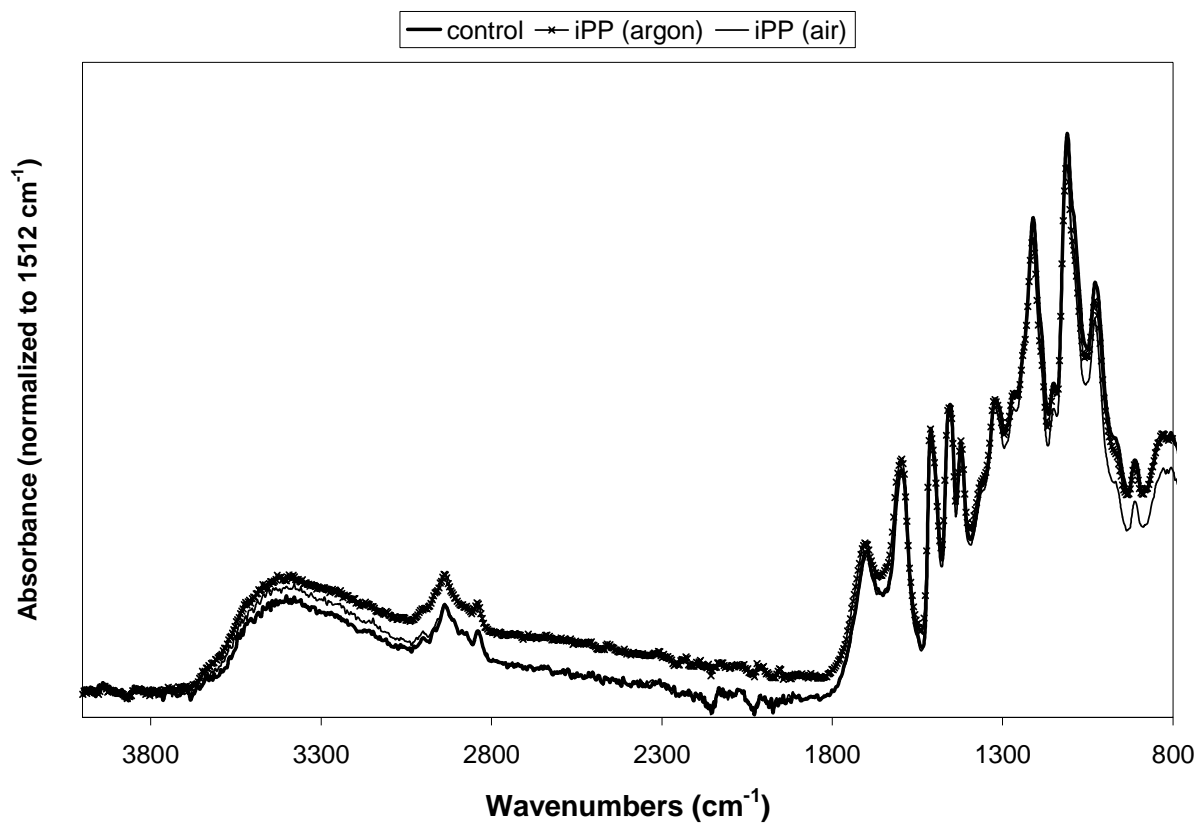


Figure 6.7b. FT-IR spectra for acetone extracted lignin from co-steam-exploded wood and iPP and steam-exploded wood (control).

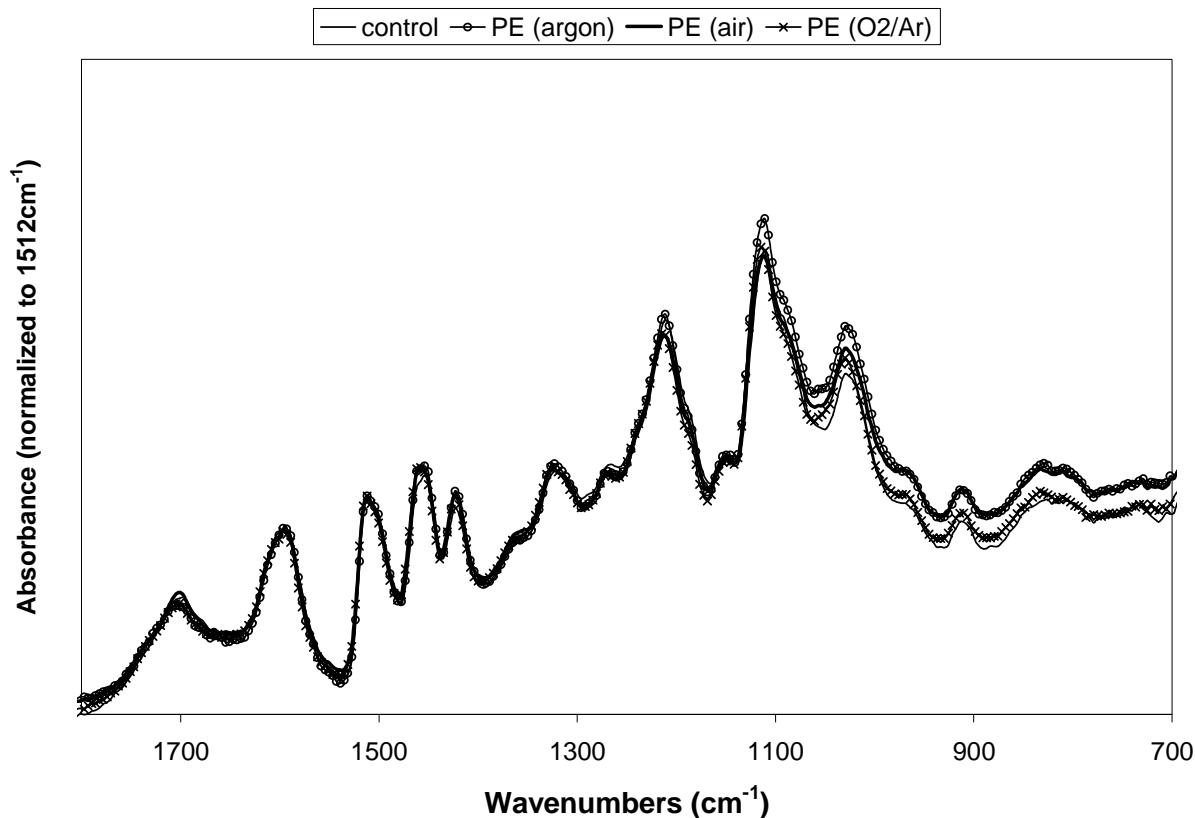


Figure 6.8. FT-IR spectra for acetone extracted lignin from steam-exploded wood (control) and co-steam-exploded wood and PE.

Xylene Soluble Fraction

Fourier Transform Infrared Spectroscopy

Nearly colorless polyolefin powder was recovered from the acetone precipitated xylene soluble fraction after extraction with water, acetone, and tetrahydrofuran for both the control (binary mixture of polyolefin and steam-exploded wood) and co-steam-exploded wood-polyolefin samples. Spectra from both isotactic polypropylene and polyethylene control samples are similar to reported spectra for the two polyolefins (Figure 6.9) [25]. This demonstrates that the extraction process is not causing any changes in the non-steam-exploded polyolefin. Peaks relating to oxidation, such as carbonyl groups, are not visible in the spectra for the co-steam-exploded wood-polyolefin (Figure 6.10a). However, the spectra indicate an increase in the methyl (2965cm^{-1} and 1367cm^{-1}) component for co-steam-exploded wood-PE (O_2/Ar) (Figure

6.10ab). This is confirmed when the ratio of peak intensities of methylene to methyl stretching is analyzed. The average intensity ratio is reduced from 10.03 to 8.32 which is significant ($\alpha=.05$ level), while the co-steam-exploded wood-PE in argon or air did not decrease significantly from the control polyethylene. Also, the intensity of the methylene symmetrical stretching peak is increased in relation to the methylene asymmetrical stretching peak for the co-steam-exploded wood-PE species (O_2/Ar) (Figure 6.10b). The presence of oxygen within the molecule can increase the intensity of the symmetric stretch relative to the asymmetric stretch and cause a shift in peak location [25]. Although, specific absorption bands related to oxygen groups are not seen in the spectra, the effect of oxidation is apparent in the polyethylene for co-steam-exploded wood-PE (O_2/Ar).

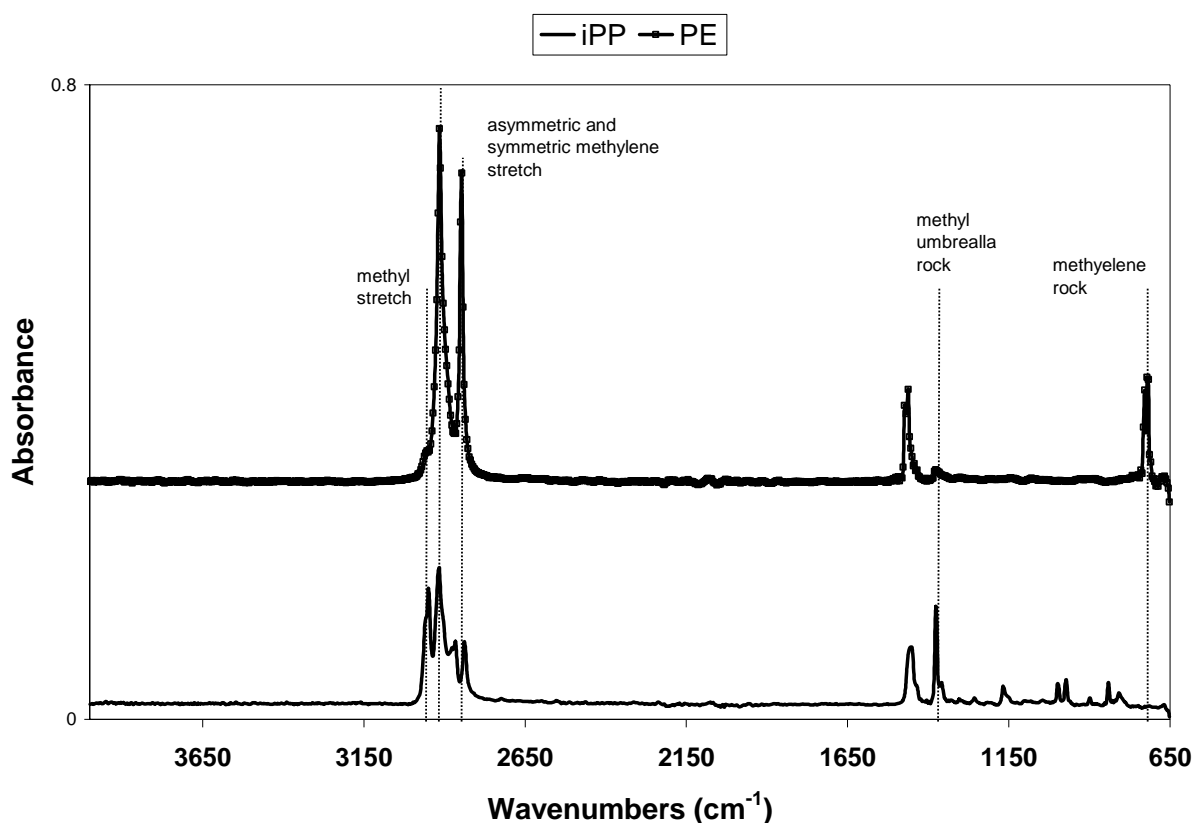


Figure 6.9. FT-IR spectra for neat polyethylene and polypropylene.

Spectra for co-steam-exploded wood-iPP(argon) indicate an increase in methylene absorption (2915cm⁻¹, 2846cm⁻¹) (Figure 6.11) without indication of a change in carbonyl containing groups. This increase in methylene absorption is attributed to contamination of sample within the steam-explosion vessel by polyethylene from previous experiments. The spectrum for co-steam-exploded wood-iPP (air) contains an increase in the methyl symmetric stretching (Figure 6.11). This change can be caused by the presence of oxygen in the molecule [25].

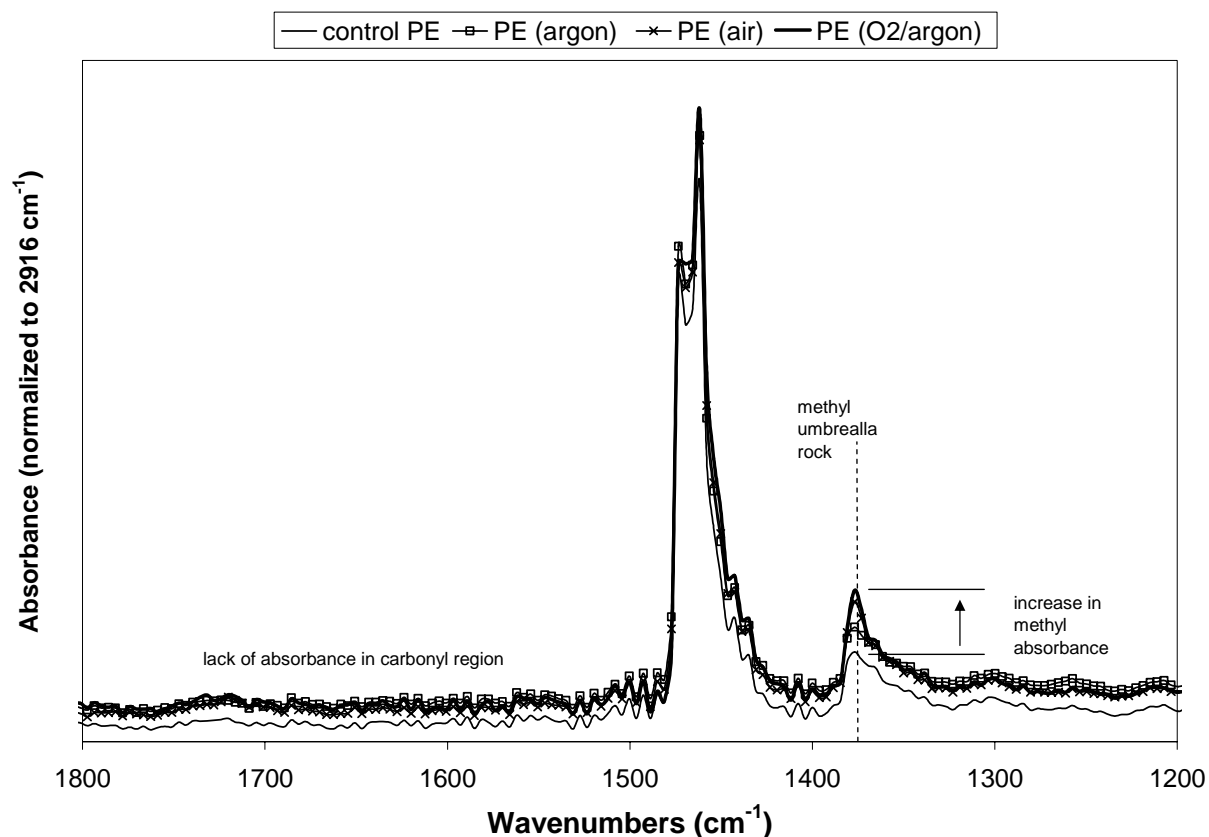


Figure 6.10a. FT-IR spectra for xylene extracted polyethylene from co-steam-exploded wood and PE (extracted neat PE from dry binary mixture of steam-exploded wood fiber and PE is the control).

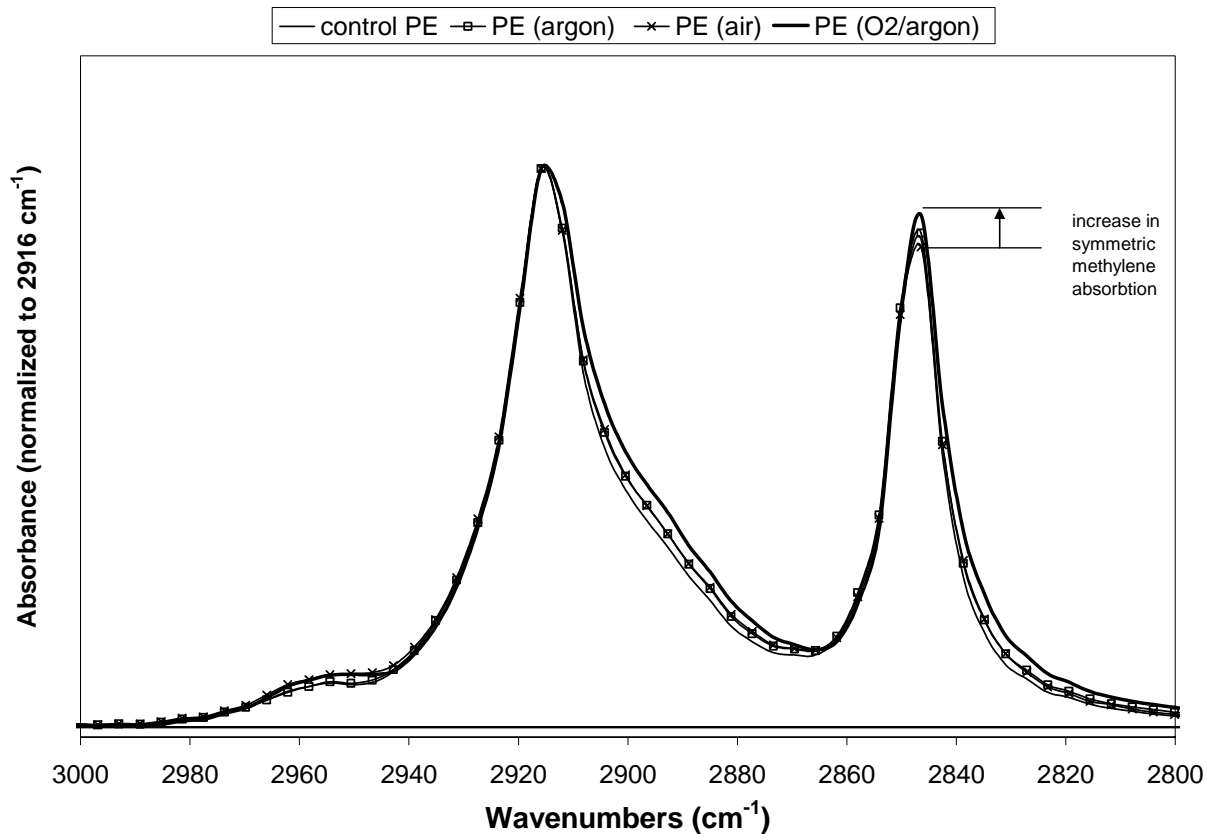


Figure 6.10b. FT-IR spectra for xylene extracted polyethylene from co-steam-exploded wood and PE (extracted neat PE from dry binary mixture of steam-exploded wood fiber and PE is the control).

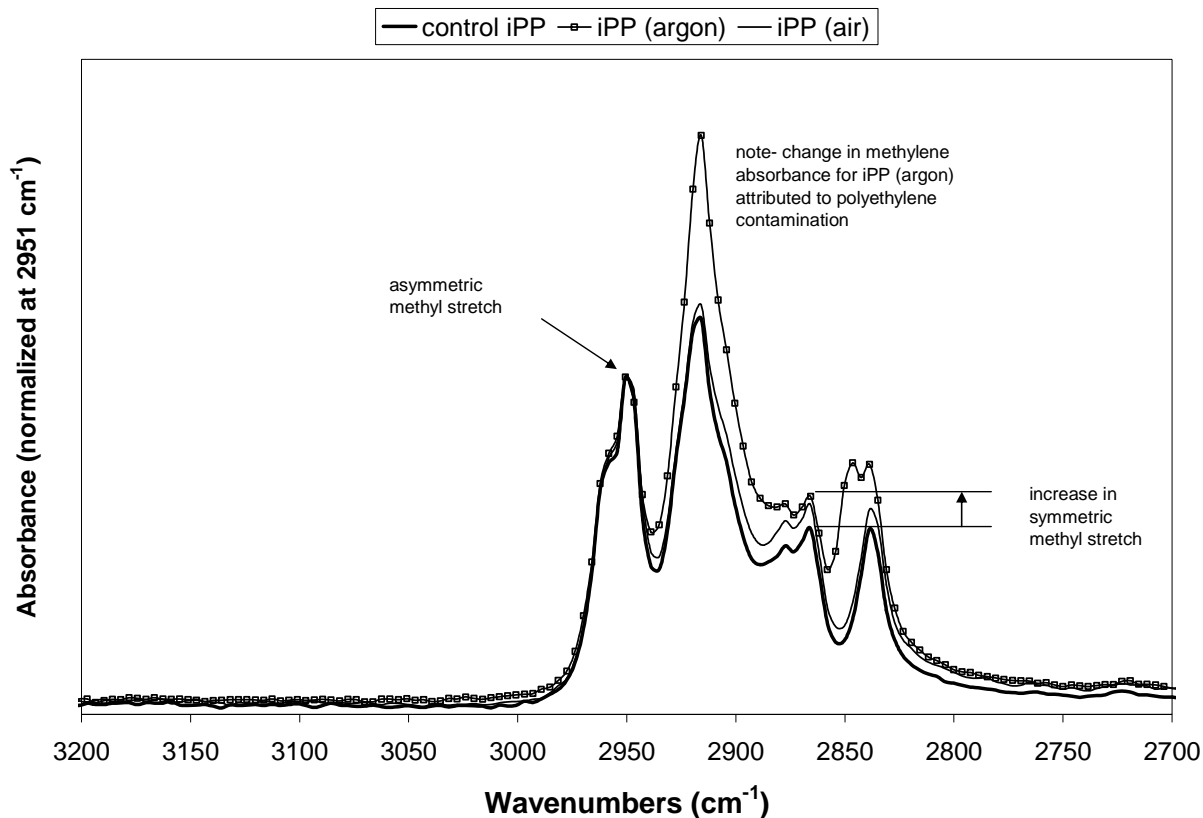


Figure 6.11. FT-IR spectra for xylene extracted polypropylene from co-steam-exploded wood and polypropylene (extracted neat iPP from dry binary mixture of steam-exploded wood fiber and iPP is control). Note polyethylene contamination evident in increased in methylene absorbance for co-steam-exploded wood and iPP (argon).

A thermal scan by differential scanning calorimetry shows the crystalline melting for both polyethylene and polypropylene extracted from co-steam-exploded wood and PO samples (Figure 6.12). There is a single melting peak for polyethylene located at 107 °C. Polypropylene contains a double melting peak centered at 149 and 157 °C. These melting peaks correspond to α and β crystal structures within the iPP. Additionally, a less intense peak is found at 105 °C that corresponds well with the melting peak of PE. Based on the spectroscopy and thermal analysis, co-steam-exploded wood and iPP (argon) has some contaminating PE species.

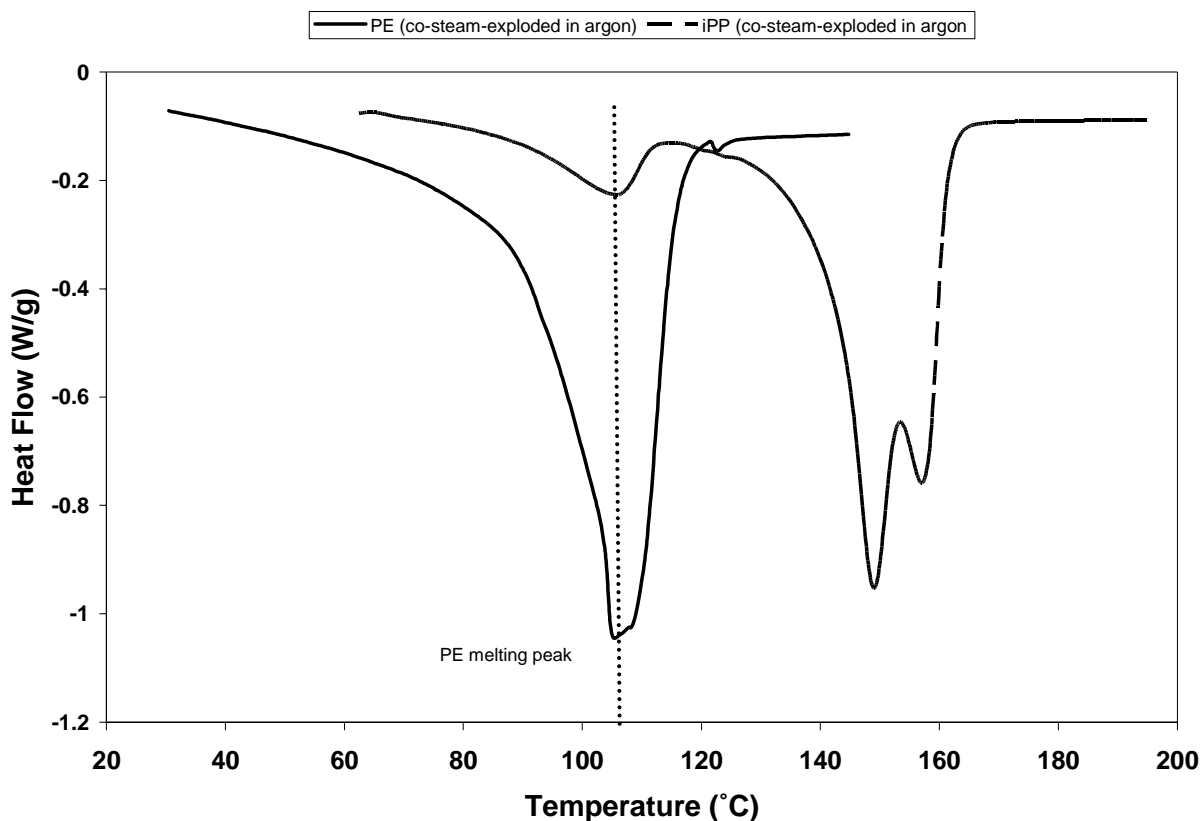


Figure 6.12. DSC heating ramp for extracted polyolefin from co-steam-exploded wood with PE and co-steam-exploded wood with iPP (argon). Note evidence of contamination of iPP with PE by overlapping melting peak at 107°C.

Confocal Laser Scanning Microscopy

The chemiluminescence of polyethylene and polypropylene caused by thermo-oxidation is well documented [26-30]. Compression molded films of extracted PE from co-steam-exploded wood-PE demonstrate fluorescence when excited with the 364nm laser (Figure 6.13a-d). The films have a gradient of fluorescence with the most intense fluorescence at the center of the film. The fluorescence was recorded using a scanning head and as a result there is the least amount of exposure at the edge. In other words, because of some overlap of the scanning, the edges are irradiated the least. This phenomenon occurs equally for all samples. Furthermore, the analysis of the relative intensity uses an average of values across the film to determine relative intensity of the pixel brightness.

The control sample (Figure 6.13a) underwent a similar extraction process (see Methods section), and there is some fluorescence for this sample. PE extracted from material that was co-steam-exploded in argon has greater fluorescent intensity (Figure 6.13b). This intensity increases for the samples that were co-steam-exploded in an oxygen containing atmosphere (Figure 6.13c-d). The average intensity of the fluorescence is compared among the control and three sample treatments with the fluorescence changing as a function of steam-explosion vessel oxygen gas content (Figure 6.14). The higher oxygen content in the steam-explosion vessel increases the degree of fluorescence of the extracted material. The intensity of the fluorescence is related to the concentration of byproducts produced by thermo-oxidation. Most literature cites decomposition of hydroperoxides into carbonyl compounds as the source of chemiluminescence.

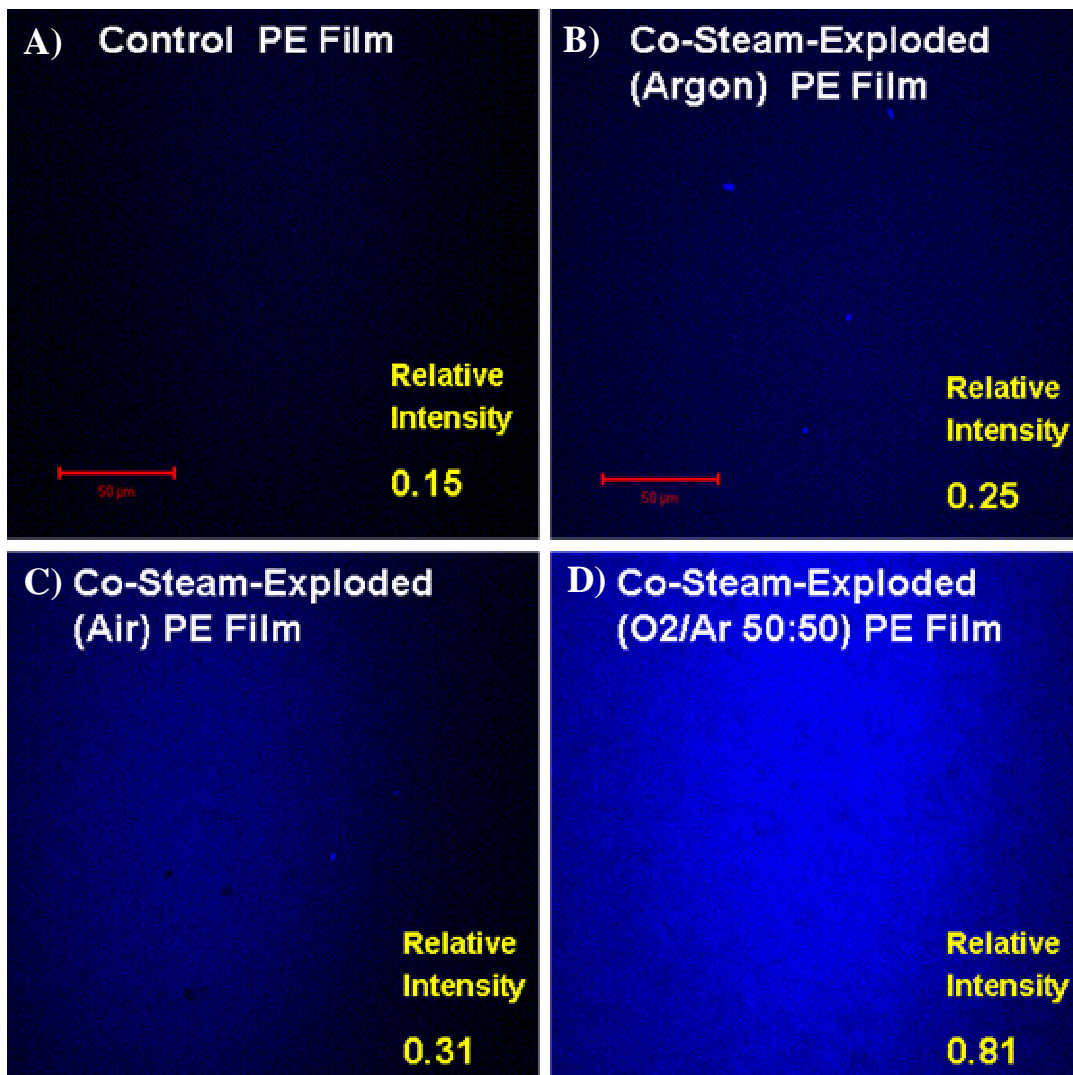


Figure 6.13. Fluorescence from oxidation of extracted PE films monitored by CLSM, λ_{ex} 364nm. A) Control, extracted neat PE (non-steam-exploded); B) PE extracted from co-steam-exploded wood and PE (argon); C) PE extracted from co-steam-exploded wood and PE (air); and D) PE extracted from co-steam-exploded wood and PE (O₂/argon). Relative intensity is determined from the average pixel brightness of image.

Co-steam-exploded wood-iPP also demonstrated fluorescence; however, the polypropylene film that was extracted from co-steam-exploded wood-iPP (argon) had greater fluorescence intensity than the co-steam-exploded wood-iPP (air) (Figure 6.15). In addition to the 364nm excitation laser, fluorescence is also noted with excitation of the 633nm laser for the co-steam-exploded wood-iPP samples (Figure 6.15). The cause of the fluorescence is most likely two-fold. The first is the chemical structural difference of iPP relative to PE, creating additional chemical groups that fluoresce with excitation at higher wavenumbers. Uniform fluorescence along the folded spherulite chains and along the outer edge of the spherulite is evident (upon slowly annealing spherulites contaminating species nucleate crystallization and are moved to spherulite interfaces). In addition to this fluorescence caused by oxidation, there are bright spots that have micron dimensions. Previous work established that the steam-exploded lignin fluoresced at the red wavelength. Moreover, CLSM only detects fluorescence in a given plane. It is likely that the discrete fluorescence seen arises from lignin.

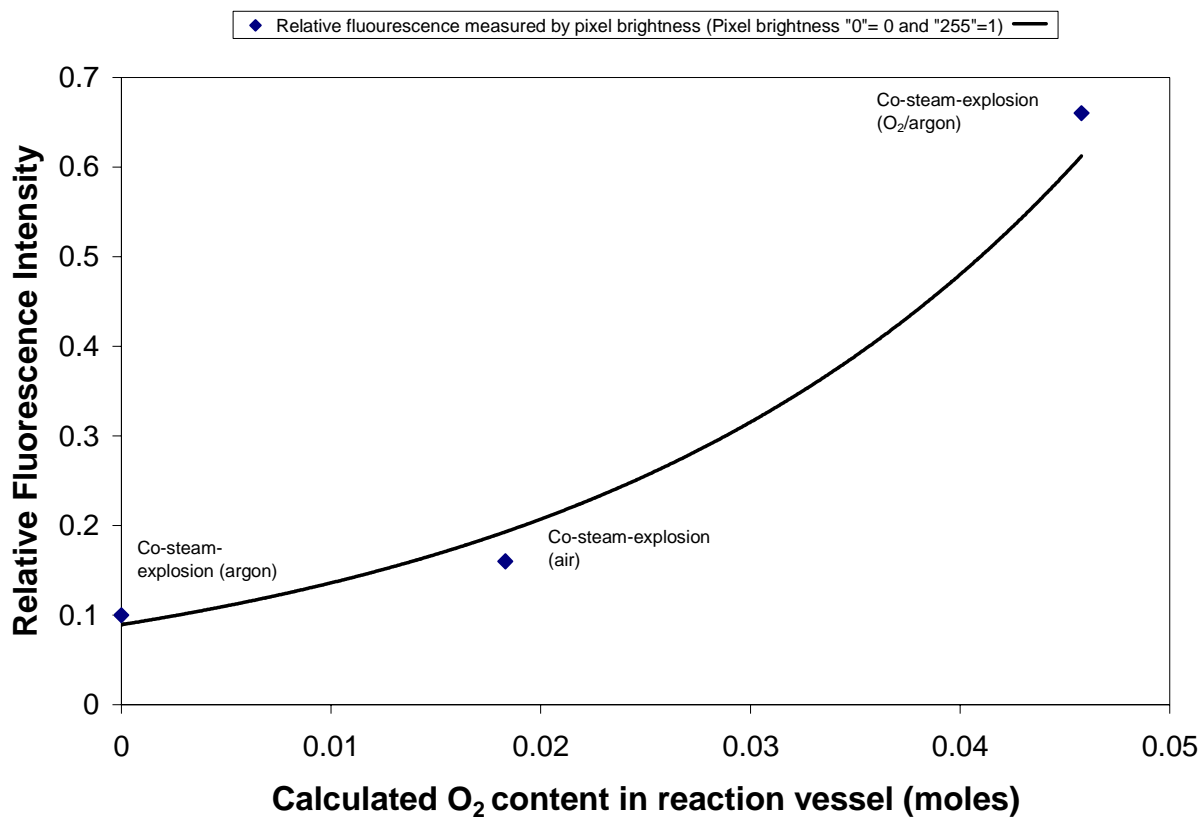


Figure 6.14. Relative fluorescence intensity (for extracted PE) as a function of available oxygen gas.

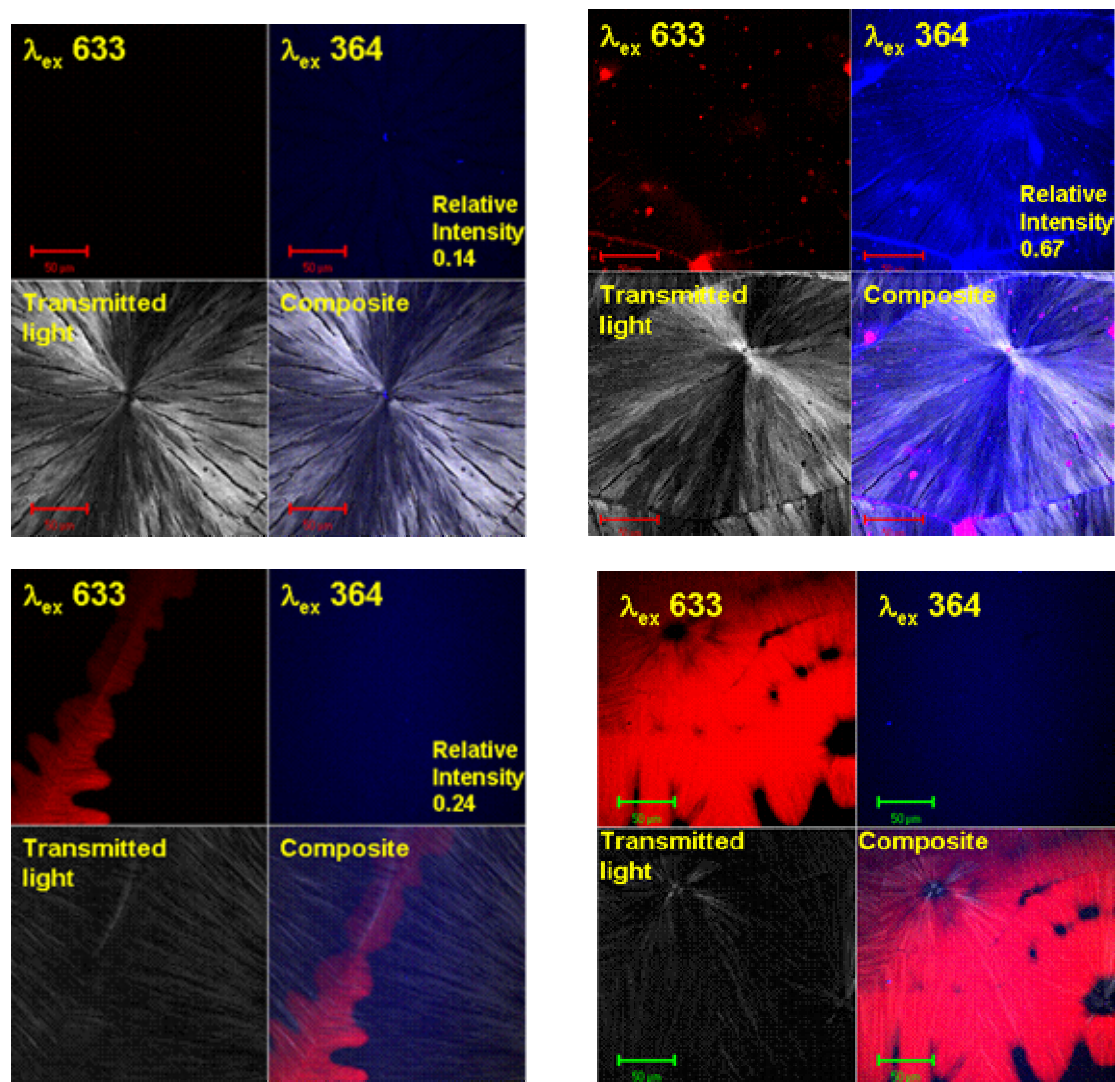


Figure 6.15. Fluorescence from oxidation of extracted iPP films monitored by CLSM. Top left image set: control, extracted neat iPP. Top right image set: extracted iPP from co-steam-exploded wood and iPP (argon). Bottom left image set: extracted iPP from co-steam-exploded wood and iPP (air). Bottom right image set: additional images for extracted iPP from co-steam-exploded wood and iPP (air). Fluorescence excitation wavelengths listed in image. Relative intensity is determined from the average pixel brightness of the image.

GPC

Extracted polypropylene from a dry mixture of steam-exploded wood-neat iPP and the co-steam-exploded wood and iPP (air) were analyzed to determine the influence of steam-explosion on molecular weight (Figure 6.16). Compared to the extracted control sample, extracted polypropylene that underwent co-steam-explosion (air atmosphere) had an increase in the number average molecular weight from 9,502 to 12,457, while the weight average molecular weight increased from 35,843 to 65,645. Generally, the most sensitive fraction to chemical change is the lowest molecular weight fraction. Change in the molecular weight may result from radical coupling of the lower molecular weight polymers forming larger molecular weight polymers (arising from oxidation) or the interaction of lower molecular material directly on fiber surfaces that is not extractable (chemical bonding or irreversible adsorption).

Other investigators concerned with tailoring the molecular weight of polypropylene have shown that controlled degradation by peroxide initiators at low concentrations narrows the molecular weight distribution via chain scission of the largest molecular weight component [31-33]. By doing so the weight average molecular weight decreases, but the number average molecular weight does not change. It is apparent that mechanisms involved in controlled degradation of polypropylene by peroxide initiators at low concentration are different from the mechanisms involved in degradation from co-steam-explosion processing.

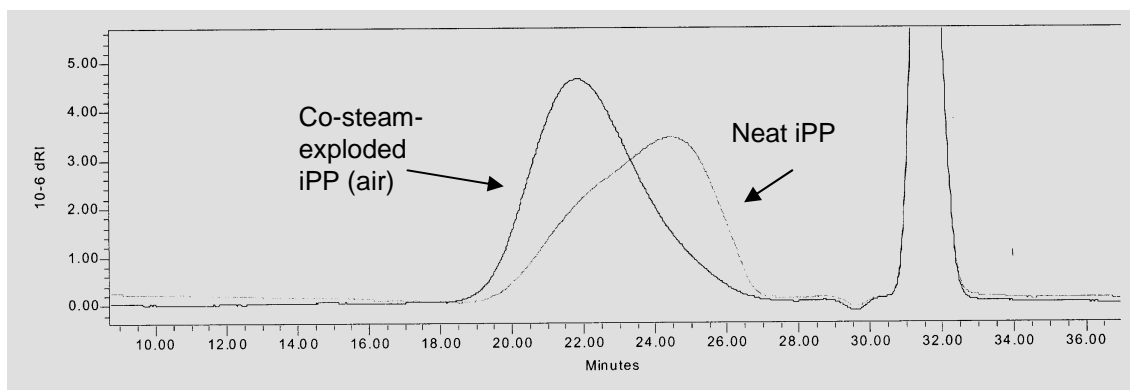


Figure 6.16. GPC molecular weight analysis for neat iPP and iPP extracted from co-steam-exploded wood and iPP (air).

Tetrahydrofuran Soluble Fraction

The above analysis showed that the gaseous atmosphere influences the PO components, while previous microscopy studies demonstrated the distribution of the polypropylene, and therefore, contact of polypropylene with the wood fiber is controlled by the rheology/ molecular weight of the polypropylene [13]. The following analysis examines the polyolefin and lignin for co-steam-exploded wood-iPP as a function of gaseous atmosphere reactivity and molecular weight. Initial investigation of the THF soluble fraction (after water and acetone extraction) from the steam-exploded samples revealed both polyolefin-rich and lignin-rich fractions. The fractions were separated by precipitating the polypropylene in acetone, filtering, and then precipitating the lignin in petroleum ether and subsequently recovered by filtering.

Acetone Precipitate

Infrared Spectroscopy

With the exception of polyethylene contamination seen for the two samples that were steam-exploded in argon atmosphere, FT-IR spectra of iPP extracted with THF and precipitated with acetone have similar absorbance regions for all treatments (Figure 6.17). Contamination is evident in both the methylene stretching ($3000\text{-}2800\text{cm}^{-1}$) and methylene rocking regions (720cm^{-1}) (not shown). Absent from the spectra are signs of oxidation in the carbonyl region. It was expected that the polypropylene portion extracted with THF would have increased absorption for oxygen containing functional groups, however, that is not the case. Most likely the extracted polypropylene is lower in molecular weight compared to the xylene extracted fraction arising from the inherent polydispersity and/or chain scission due to oxidation of the polypropylene. The low molecular weight nature of the sample is confirmed qualitatively by the observation that the THF extracted polypropylene has a wax like texture. No consistent trends for IR absorption based on molecular weight or gaseous reactivity is apparent in this fraction.

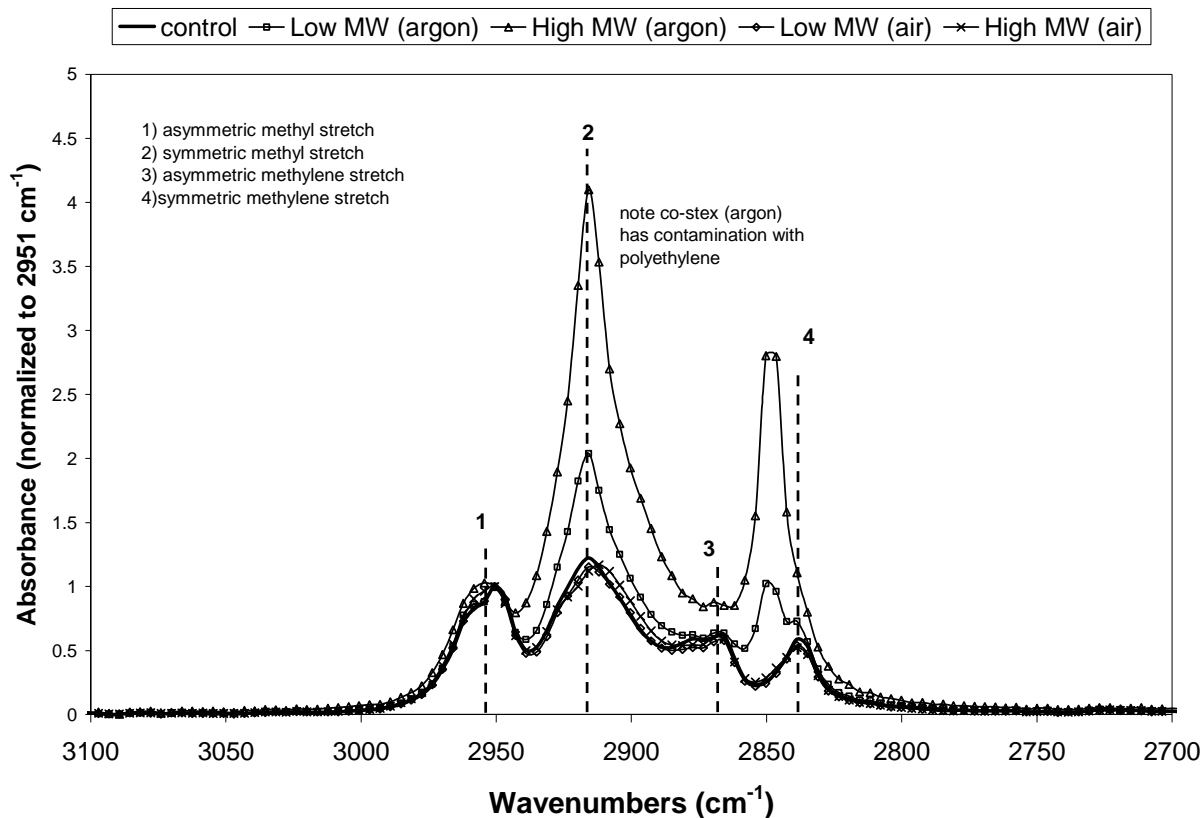


Figure 6.17 FT-IR spectra of THF extracted polypropylene (control is extracted from dry mixed steam-exploded wood and iPP). Note contamination from reaction vessel for co-steam-exploded samples with polyethylene.

Confocal Laser Scanning Microscopy

There is a difference among fluorescent images of the THF extracted polypropylene based upon molecular weight and atmosphere (Figure 6.18). For the low molecular weight polypropylene there is fluorescence for both excitation wavelengths of 364nm and 633nm. The low molecular weight iPP sample steam-exploded in an argon atmosphere has an overlay of the fluorescence generated by both excitation wavelengths. However, the steam-explosion in an air atmosphere has discrete areas of fluorescence for the 633nm wavelength that are opaque in the transmitted light image. This discrete fluorescence may be attributed to lignin-rich material based upon an earlier investigation which showed lignin fluorescing with the 633nm excitation wavelength [13]. This fluorescence data suggests that the low molecular weight iPP from co-steam-explosion in an air atmosphere contains lignin-rich material that is no longer acetone

soluble. The high molecular weight iPP has a reduced fluorescence for excitation with 633 nm while the fluorescence excited with the 364nm is uniform throughout the image. The discrete fluorescence seen in the high molecular weight co-steam-exploded in argon atmosphere may arise from contamination of low molecular weight polyethylene (evident in the FT-IR spectrum).

The degree of dispersion for iPP with wood fiber in co-steam-explosion processing is influenced by the molecular weight [13]. Therefore, the amount of surface area in contact between polypropylene and lignin increases for the evenly dispersed lower molecular weight iPP. Based upon the fluorescent images it is suggested that dispersion and gas reactivity influences the degree of iPP modification. The increased oxygen availability enhances thermo-oxidative breakdown, while dispersion of the material allows significant intimate contact between the polyolefin and lignin. Based on the fluorescent images, the low molecular weight iPP sample that is steam-exploded in an oxygen containing atmosphere has the greatest association of lignin and iPP.

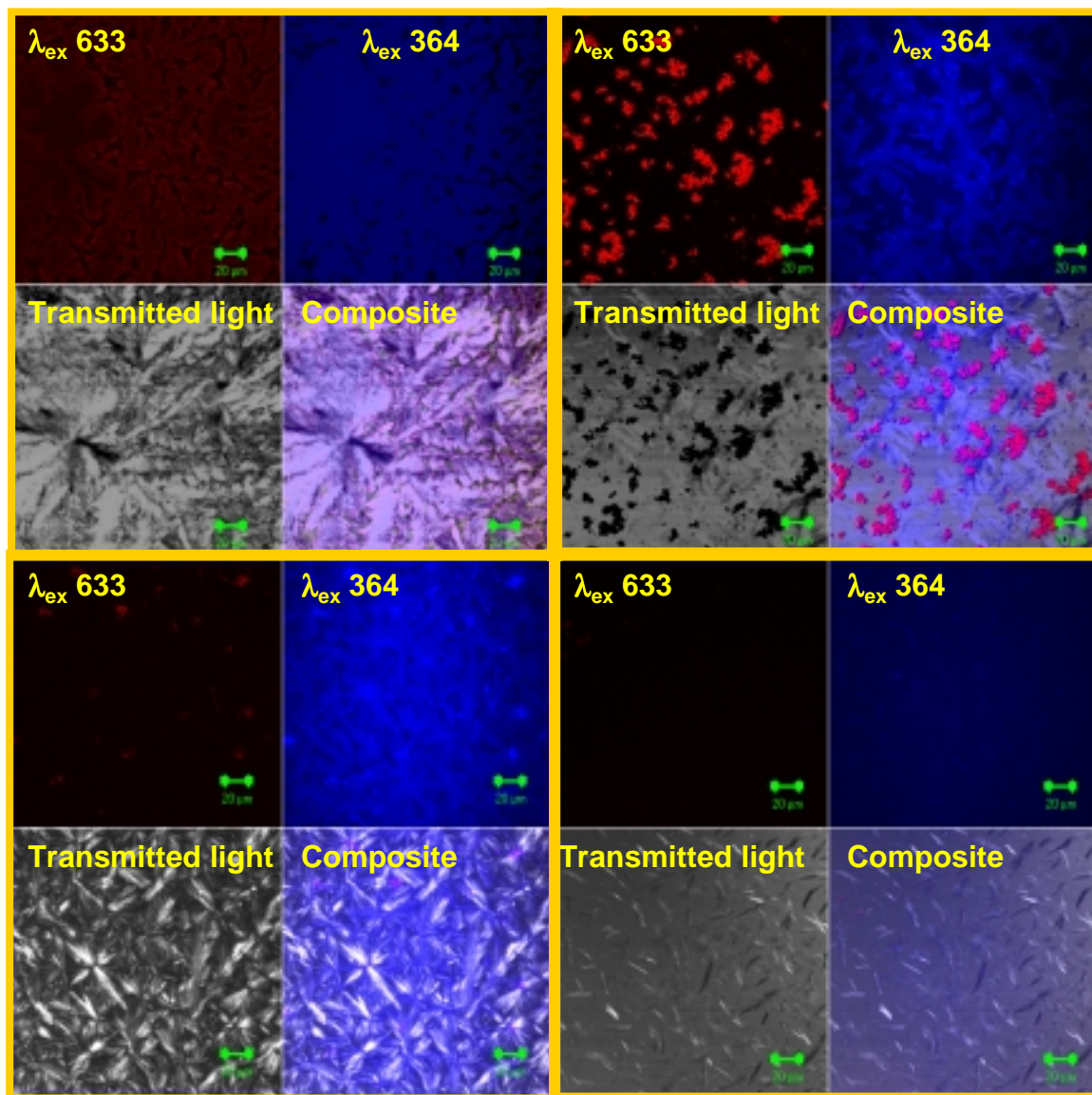


Figure-6.18. Fluorescence from oxidation of THF extracted iPP films monitored by CLSM. Top left image set is **low MW iPP** extracted with THF (co-steam-exploded **argon**). Top right image set is **low MW iPP** extracted with THF (co-steam-exploded **air**). Bottom left image set **high MW iPP** extracted with THF (co-steam-explosion in **argon**). Bottom right image set is **high MW iPP** extracted with THF (co-steam-exploded in **air**). Fluorescence excitation wavelengths listed in image.

Petroleum Ether Precipitated

Infrared Spectroscopy

The lignin extracted with THF from the steam-exploded wood has a similar absorbance spectrum to that of the acetone soluble spectrum (Figure 6.19 and Figure 6.6). The incomplete extraction of lignin by the acetone is most likely the result of the wide array of secondary interactions that occur between the wood and lignin. In other words, THF solvent-wood interaction is different than the acetone solvent-wood interaction.

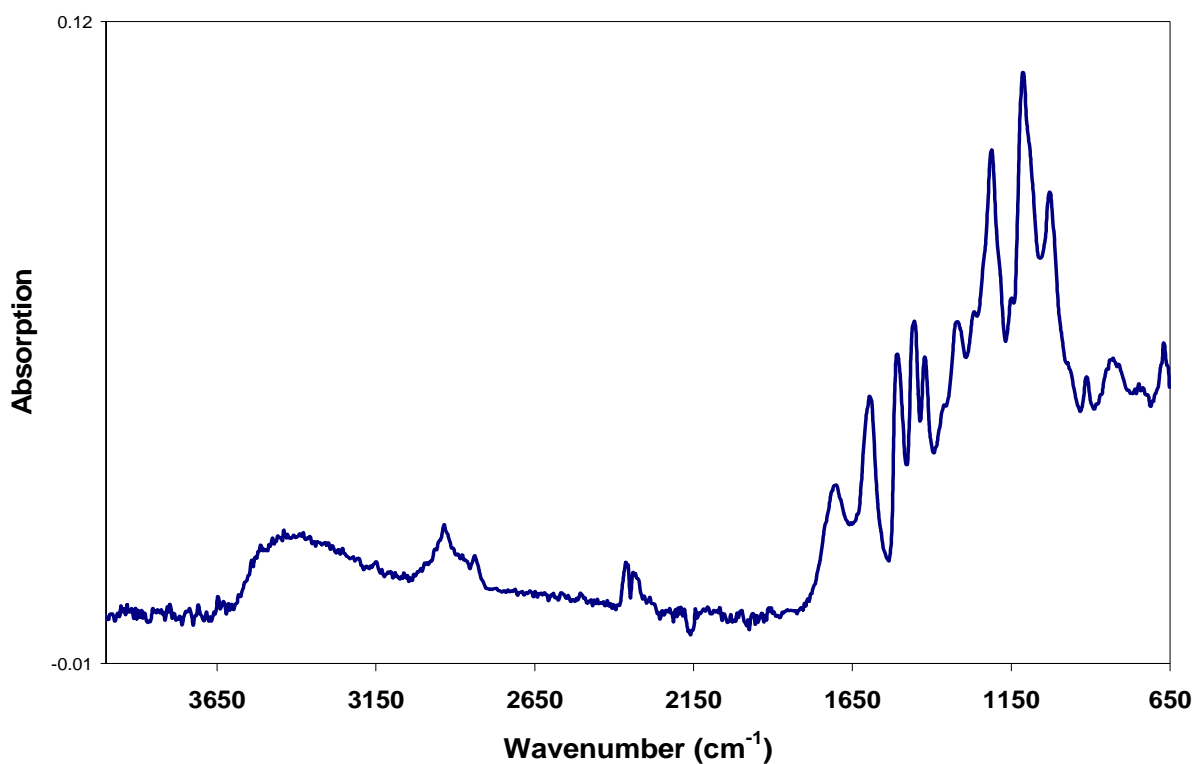


Figure 6.19. FT-IR spectrum of THF extracted lignin precipitated by petroleum ether for steam-exploded wood (after water and acetone extraction).

The co-steam-exploded samples have minor change relative to the control THF extracted sample in the FT-IR spectra (Figure 6.20). The co-steam-exploded wood and iPP shows reduced carbonyl absorption at 1700 cm^{-1} . While the change is subtle, it is reproducible. Degradation of the lignin promotes formation of carbonyl groups. Possibly, this degradation effect is attenuated by a radical scavenging of the iPP. For the lignin extracted with THF, post acetone extraction, it is apparent that the change in chemistry is not influenced by molecular weight of the iPP and gaseous atmosphere reactivity.

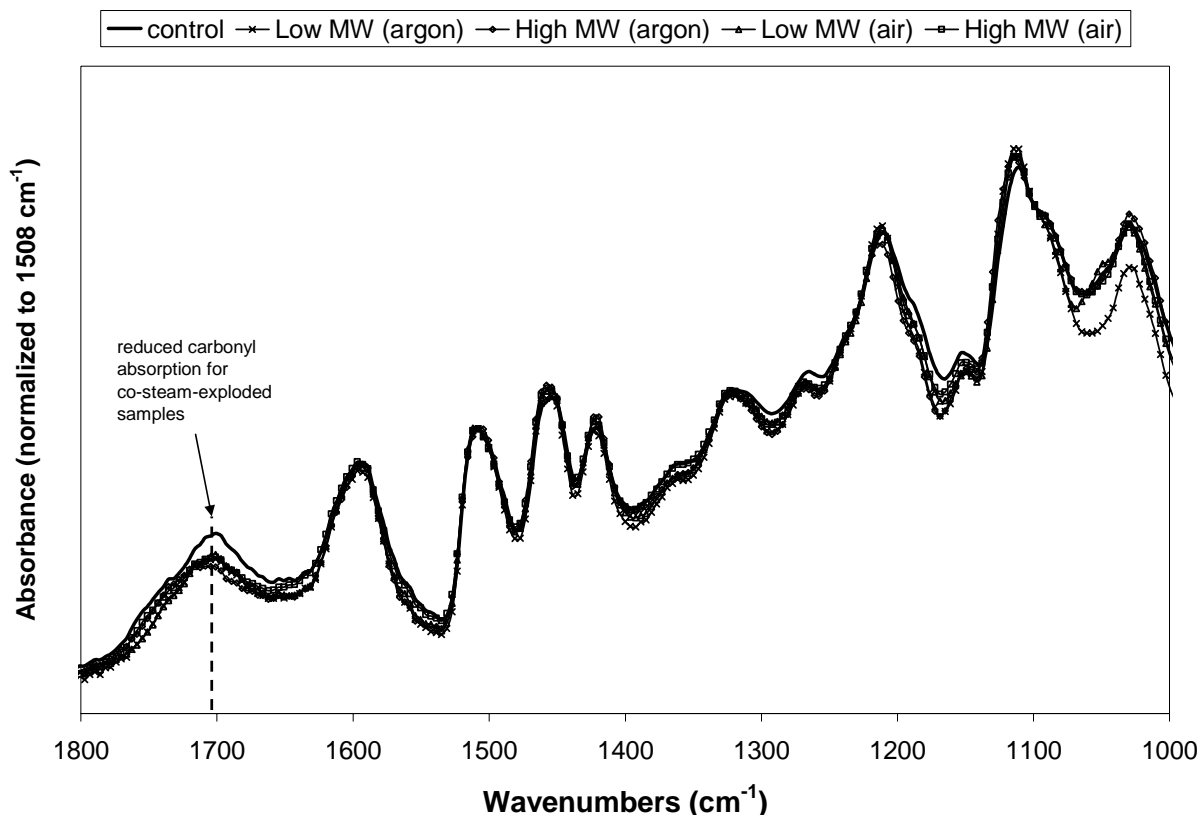


Figure 6.20. FT-IR spectra of THF extracted lignin precipitated by petroleum ether for co-steam-exploded wood and iPP. (Control spectrum is from THF extracted neat iPP that was dry mixed with steam-exploded wood). Note significantly overlap of samples.

Summary of Changes

The above-mentioned analysis of hemicellulose, lignin, and polyolefin from co-steam-exploded wood and polyolefin describes changes in all fractions by co-steam-explosion. Changes in water soluble quantity and chemistry arise as a function of polyolefin type. Water-soluble spectra indicate changes in relative absorbance of lignin for the co-steam-exploded wood and PE. Analysis of the lignin with FT-IR shows enrichment with polyethylene. Modification to the polyolefin includes changes to its molecular weight and fluorescence. Specifically for iPP, the molecular weight increases, the polymer demonstrates fluorescence, and it has changes in its IR spectrum that may be caused by oxygen groups. Likewise, PE also demonstrates fluorescence and it too has a similar trend in the IR spectra relating to oxygen containing groups. Additionally, there is an increase in methyl content for the PE in the most reactive environment (O₂/Ar).

Suggested Pathway

Steam-explosion causes a number of changes in wood such as breakage of the LCC bond, glycosidic bond breakage, increased cellulose crystallinity, homolytic cleavage of the β O₄ linkages, formation of o-quinone-methide structures, formation of sinapyl and coniferyl radicals, and demethylation [19,22]. The conditions during steam-explosion processing also favor recombinations of all reactions. Additionally, thermo-oxidation of polyolefins (increased by moisture) causes the formation of peroxides and chain radicals [34]. Moreover, by-products of polyolefin (PE and iPP) thermo-oxidation are acetic, formic, and glycolic acids.

A hypothetical scheme is given based on the fractionated material analysis (Figure 6.21). Radicals produced from polyolefin oxidation would change the balance of the recombination reactions and influence the ability to fractionate the wood material. Particularly, the reformation of bonds between lignin and hemicellulose would decrease as lignin scavenges the radicals produced by the polyolefin. In turn, the solubility of the hemicellulose component increases as less lignin is attached to the material. Hence, without re-formation of bonds between the lignin and hemicellulose the water-soluble hemicellulose content increases. This hypothesis is documented in two ways: 1) the water extracted for co-steam-exploded wood and PE indicates decreased lignin IR absorbance and 2) acetone soluble spectra of co-steam-exploded wood and PE show enhancement of PE. A possible explanation of why a difference is seen between PE

and iPP is the inherent difference of stability of radicals. Steam-explosion conditions (high heat, pressure, moisture) produce secondary radicals in PE and tertiary radicals in iPP that form a variety of peroxide and carbonyl groups (documented by chemiluminescence). Differences in radical stability may change the transfer of radicals among PO and wood components as well within itself. Chain scission reactions occur to a greater degree for polyethylene relative to polypropylene when oxidation levels are similar [35]. One hypothesis is that iPP may scavenge wood radicals before steam-explosion can separate the lignin and carbohydrates, limiting lignin liberation and flow (Figure 6.21). This claim of limited lignin-carbohydrate fractionation has been presented in a previous study through microscopy analysis [13] and confirmed in another study by solid state NMR [36]. In this case, polypropylene serves as a chain transfer agent with lignin transferring the radical to iPP by the abstraction of hydrogen from the iPP. The radicals produced on the iPP may involve further cross-linking with itself (shown by an increase in iPP's molecular weight) (Figure 6.21). Additionally, lignin's substituted aromatic structure may serve as a radical sink, via resonance stabilization, potentially limiting the modification of holocellulose or additional degradation of the polyolefin. Another path may include radical-radical coupling of the polyolefin directly to lignin (source of polyethylene enrichment of lignin) (Figure 6.21).

In addition, steam-explosion is reported to generate lignin decomposition intermediates such as o-quinone-methide structures. Although it was not determined if these structures are enhanced by co-steam-explosion, they do cause demethylation of the lignin [21]. The availability of the methoxy radicals from the lignin could lead to further oxidation of the polyolefin in an oxygen deficient atmosphere. This outcome would be a synergistic effect that would increase the radical presence in the polyolefin. As mentioned above, a path may include radical to radical coupling- in this case methoxy groups coupled to polyolefin (source of the increased methoxy content for the polyolefin seen in the change of symmetric methylene absorption). In summary, chemical changes arising from co-steam-explosion most likely occur from free radical reactions between polyolefin and wood components.

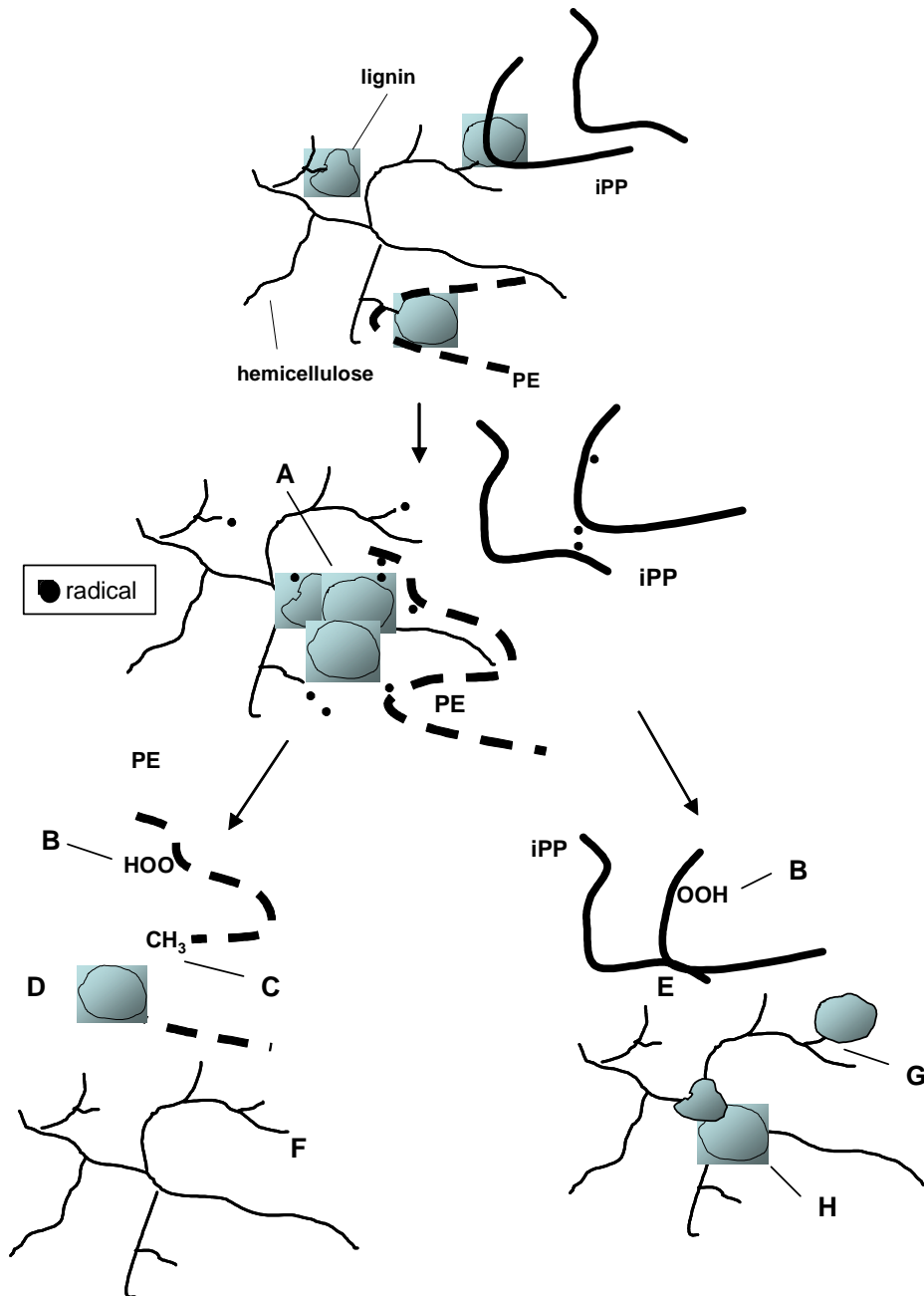


Figure 6.21. Hypothesis of interaction among polyolefin, lignin, and amorphous carbohydrate.

A) Rearrangement of lignin fraction [13], B) Peroxides on PO caused by thermo-oxidation (documented indirectly by chemiluminescence), C) Chain scission with increased methyl groups (FT-IR), D) Polyethylene enriched lignin fraction (FT-IR), E) Crosslinking of iPP (molecular weight increase-GPC data), F) Reduced lignin in water extracted carbohydrate (FT-IR and increase in extractable yield), G) Protection of lignin-carbohydrate complex [13], and H) Recombination of lignin and carbohydrate (similar to steam-exploded wood).

Conclusions

The co-refining of wood chips and polyolefin by steam-explosion is a reactive process that modifies the components of wood as well as the polyolefin. In addition, the amount of oxygen in the reaction vessel prior to the introduction of steam influences the degree of modification of the polyolefin.

Co-processing with wood and PO changed the quantity of the water soluble fraction. There is a difference based on PO type. The co-processing by steam-explosion with wood and iPP had reduced quantity of water extractable material compared to that of co-processed wood and PE that had an enhanced yield of water soluble material. Furthermore, co-steam-explosion of wood and PE caused a reduction in the relative concentration of lignin in the water extracted fraction as demonstrated by FT-IR spectroscopy. However, there was no evidence of polyolefin enrichment of the water-soluble fraction.

Acetone soluble material precipitated in petroleum ether, yielding the lignin fraction, had modification caused by co-steam-explosion of wood and polyethylene. Lignin shows a polyethylene enrichment, which most likely is due to a chemical bond between the two fractions since the lignin solvent was a polyethylene non-solvent. Additional change of the lignin is seen in the examination of the lignin rich THF extract: there was reduced carbonyl absorption in the FT-IR spectra of co-processed wood and polypropylene compared to that of the control.

A number of changes in the polyethylene and polypropylene occur as a result of co-steam-explosion. For polyethylene, fluorescence is increased as a function of vessel atmosphere reactivity, the methyl component increases for co-steam-explosion in the most reactive atmosphere, and there is a possible increase of methoxy component. In the same manner, polypropylene has increased fluorescence for co-steam-exploded samples, a possible enrichment of methoxy component, and an increase in molecular weight.

A hypothesis is given for the interaction of wood components and polyolefin arising from thermo-oxidation of the polyolefin and a number of radical reactions of the wood. Radical coupling and H-transfer most likely cause a synergistic effect during the co-steam-explosion processing of wood and polyolefin leading to modification of polyolefin, lignin, and enhancing or retarding the quantity of water extractable material. Additionally, there is qualitative evidence that suggests, along with atmosphere reactivity, molecular weight of the polyolefin influences the interaction between wood components and polyolefin.

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