

CHAPTER 8

Summary and Conclusion

Steam-explosion processing of wood is a reactive method that changes the hierarchical arrangement, chemistry and morphology of wood's bio-polymer components. Mechanical disruption, hydrolysis, and free radical reactions have been previously shown to contribute to the changes. Because of growing interest in wood-thermoplastic composites, this processing method was investigated as a novel way to modify wood fiber with thermoplastics. Specifically, the processing technique was applied to co-refining wood chips and polyolefin thermoplastics such as polyethylene and isotactic polypropylene. The co-steam-explosion experiments explored variables of polyolefin type, molecular weight, polyolefin loading and gaseous vessel atmosphere reactivity, while keeping the processing time and steam temperature constant.

A thermogravimetric analysis (TGA) method was established to determine polyolefin content in the co-steam-exploded material. A calibration method was created to use with TGA because step method composition analysis requires that the components of the blend have non-overlapping decomposition steps and they do not influence each other's degradation. Blends of steam-exploded wood and low molecular weight polyethylene did not meet either criterion. This was circumvented by calculating the area for the 1st derivative of the peak related to the degradation of polyethylene for a variety of mixtures with known composition. This data was plotted against polyolefin concentration and a double gradient regression was used to derive two calibration curves to calculate the amount of polyethylene contained in the co-steam-exploded material. This method showed little loss of the polyethylene in the co-steam-explosion batch process.

Using a combination of microscopy techniques, the dispersion of the polyolefin among and on wood fiber was shown to be molecular weight dependent. Using three different polypropylenes in the co-steam-explosion process, a window of melt viscosity was revealed where fiber bundles were coated with polypropylene. With melt viscosities above and below, polypropylene would form aggregates and clusters with either micron dimensions or centimeter dimensions, respectively. Furthermore, a model study, where a uniform regenerated cellulose fiber was co-steam-exploded with a low molecular weight fluorescent labeled maleated polyethylene, demonstrated that the regenerated fiber surface had areas that were decorated with patches of polyolefin in the size of hundred's of nanometers. Additionally, with

autofluorescence of the cellulose and lignin, steam-exploded wood fiber was shown to have redistributed lignin on the fiber surface in distinct patches. These patches were diminished and a relative uniform fluorescence was seen for the coated fiber bundles from co-steam-exploded wood and iPP.

Sorption properties were modified for the co-steam-exploded wood and polyolefin fibers. Weight gain at various humidities greater than 40% was reduced as a function of polyolefin loading. Furthermore, the reduction was reduced by 50%, normalized for the amount of wood fiber present, for the co-steam-exploded wood and iPP that contained coated fiber bundles. The kinetics of water sorption was also examined for co-steam-exploded samples. Co-steam-exploded wood and low molecular weight PE had increases in initial rates of sorption. Co-steam-exploded wood and iPP (coated fiber bundles) had either a suppressed initial rate of sorption or a marginal increase in the rate of sorption. The increase in initial sorption rates was shown to correspond with the increase in initial diffusion constants. Three levels of initial diffusion constants were found: dissolving pulp fiber and steam-exploded wood < co-steam-exploded wood and polyolefin in an oxygen deficient gaseous atmosphere < co-steam-explosion in an oxygen containing gaseous atmosphere.

Analysis of fractionated solids from co-steam-exploded material showed a number of changes in the hemicellulose-rich, lignin-rich, and polyolefin material. Water extractable quantity was decreased for the co-steam-exploded wood and iPP compared to that of co-steam-exploded wood and PE. Furthermore, IR subtraction data for the water extracted material from co-steam-exploded wood and PE indicate a decrease in absorbance for lignin related peaks. Co-steam-explosion of wood and iPP did not show this trend. A difference in radical stability of PE and iPP influencing the re-combination of lignin and carbohydrates was suggested for the observed difference. Furthermore, IR data indicated lignin (acetone-extracted) had polyolefin enrichment for the co-steam-exploded wood and polyethylene. Both polyethylene and polypropylene showed oxidation by fluorescence method that is attributed to co-steam-explosion processing.

Chemical and morphological changes *in situ* were realized by solid state NMR. A change in both the acetal and aromatic region of the spectrum was apparent for the co-steam-exploded wood and polypropylene material. An additional shoulder on the methine peak developed in the NMR spectrum for co-steam-exploded wood and iPP after compression

molding the material. This shoulder was not evident in the control samples or the un-pressed sample. Steam-explosion of wood is known to increase the crystallinity of the cellulose; the increase was enhanced by the presence of polypropylene. Furthermore, the lignin and crystalline cellulose have a change in nanoscale relaxations as a result from co-steam-explosion processing with polypropylene. Typically with steam-explosion there is phase-separation of the lignin from the cellulose component, which was demonstrated in this project by confocal laser scanning microscopy. Yet, lignin's $T_{1\rho}$ relaxation parameter is near to that of amorphous cellulose for the co-steam-exploded material. After compression molding the material, the $T_{1\rho}$ relaxation changes to a value that is nearly identical to the control. This effect indicates a meta-stable interaction of cellulose-lignin-polypropylene that changes above the melting temperature of iPP and the softening temperature of lignin.

From these changes it is evident that co-steam-explosion of wood and polyolefin offers a processing technique that gives a unique product, for a specific range of melt viscosity of polyolefin. Furthermore, thermo-oxidation of the polyolefin plays an important role in the modification of the wood fiber. The observed thermo-oxidation influences the cell wall morphology which was examined by solid state NMR and reflected in the initial diffusion coefficients. The effect of thermo-oxidation is suggested to be twofold: 1) free radicals that are produced provide an imbalance to the number of reactions that occur during steam-explosion between lignin and the carbohydrate component and 2) degradation products from thermo-oxidation of polyolefin migrate into the cell wall interacting and reacting with wood polymers. This project demonstrates the viability of co-processing thermoplastics and wood by steam-explosion, for a specific thermoplastic melt viscosity and the importance of free radicals in generating interaction among materials. Future work should look into the modification of lignocelluloses with thermoplastics with additional functionality using co-steam-explosion processing, taking into account the importance of free radical reactions and molecular weight of the thermoplastic.