NOTE

Novel Hollow Core Fibers Prepared from Lignin Polypropylene Blends

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Polymer blending is a convenient method to develop products with desirable properties. The chemical and physical properties of the polymer blends are dependent on monomer type(s), molecular weight, and distribution of the respective polymers.[1] Most polymers are immiscible due to a low entropy of mixing.[1–3] Only through specific intermolecular interactions can favorable polymer blending occur and composite materials with desirable properties be produced. Nonetheless, a large number of technologically interesting polymers are multiphase inhomogeneous materials.[4] Properties such as prevention and control of gas and liquid permeation, gas and liquid adsorption/desorption and transmission, and reflection of light are dependent on phase behavior, and more specifically on the size of the domains within the material.

Lignin, second only to cellulose in natural abundance, is an amorphous natural polymer existing in the cell wall of plants.[5] Its utilization in solid material systems is constrained by the extensive crosslinking, strong intramolecular interactions, and high molecular weight of most lignins, which upon heating decompose rather than soften and flow. However, through polymer blending[6–13] or lignin derivatization[13–19] these interactions are disrupted, thus altering the lignin's viscoelastic properties and allowing for flow.

Recently, we have developed lignin fibers for carbon fiber applications through thermal spinning of lignin-synthetic polymer blends.[20] Through careful control of processing conditions, miscible continuous fibers are produced.[21] However, fibers with core-shell morphology can be formed through manipulation of processing conditions and/or blend composition. The premise behind this method for the production of porous hollow-core

lignin fibers is based on the differences in thermal stabilities of polymers (Scheme 1).[22] This method uses selected polymers with different thermal stabilities, i.e., one tends to crosslink at high temperatures while the other one melts and flows from within the fiber. If the affinities of the two polymers are weak enough, they will form an immiscible two phase material. Thermal treatment will produce pores because of the melting or pyrolysis of the low melting polymer. At high levels of the low melting polymer, hollow fibers may be formed. Controlling the structure of the polymer blends will provide a way to obtain fibers with tailored porous hollow core morphology.

In this study we have selected a commercial technical lignin and polypropylene as the thermally stable polymer and thermally unstable one, respectively. Here we report a preliminary study on the porous hollow-core fibers produced from this method.
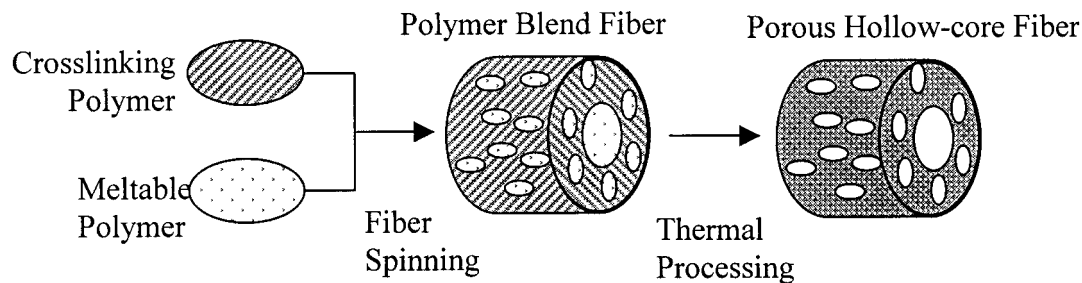
Hardwood Kraft lignin, HWKL (Indulin® AT—Westvaco Corp.) was desalted and thermally processed prior to fiber blending using a previously published meth-
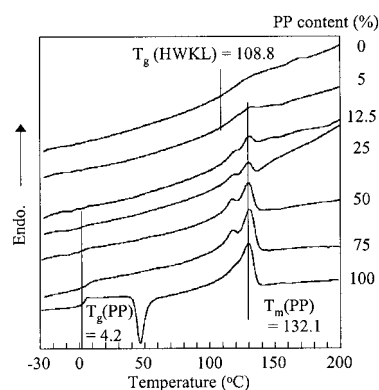
Figure 1 Differential scanning calorimetry profiles of lignin-PP fibers of varying lignin/PP ratios.

Scheme 1   Production of porous hollow-core fibers from the thermal treatment of immiscible polymer blended fibers containing a meltable polymer and a thermally stable polymer.

od,[20] and mechanically blended with polypropylene (PP, syndiotactic, $\bar{M}_w$ ~127,000, Aldrich). The blend ratios were set at 87.5/12.5, 75/25, 50/50 (HWKL/PP) by weight. Control fibers were made with no PP and no lignin. The samples were then extruded in an Atlas mixer/extruder with a 1/32-inch spinneret to produce fine fibers. The optimal temperatures for fiber production were obtained by slowly increasing the temperature until fiber formation occurred. Fiber spinning was then performed isothermally at that temperature. The spinning temperature is closely related to the molten viscosity of the sample; a low spinning temperature is indicative of a low molten viscosity. The spinning temperature was 220°C for the HWKL and did not change with increasing PP content.

Phase immiscibility in the lignin-PP blend is shown in Figure 1, in which a melting point (T_m) and glass transition point (T_g) of the PP phase and a T_g of the lignin phase are distinctly observed at all ratios of lignin/PP. Further, the T_g of the lignin and PP phases appear independent of the lignin/PP ratio, further indicating negligible mixing of the two polymers.

The spun fibers were heated to 250°C to remove the polypropylene and induce crosslinking of the lignin phase. Upon heating, the PP flowed from the fiber and was visually observed to pool outside of the fiber. Fiber stability was dependent on heating rate and PP blend content. Increasing the heating rate above 1.5°C min^{-1} resulted in the fibers in contact with one another fusing together. As the temperature increased at a heating rate below 1.5°C min^{-1} the T_g of the lignin increases faster than the temperature, maintaining the material in the glassy state ($T_g > T$): nontacky. At heating rates above 1.5°C min^{-1}, the crosslinking reactions are not able to maintain $T_g > T$, and the material devitrifies entering the liquid rubbery state, tacky, and thus fuse
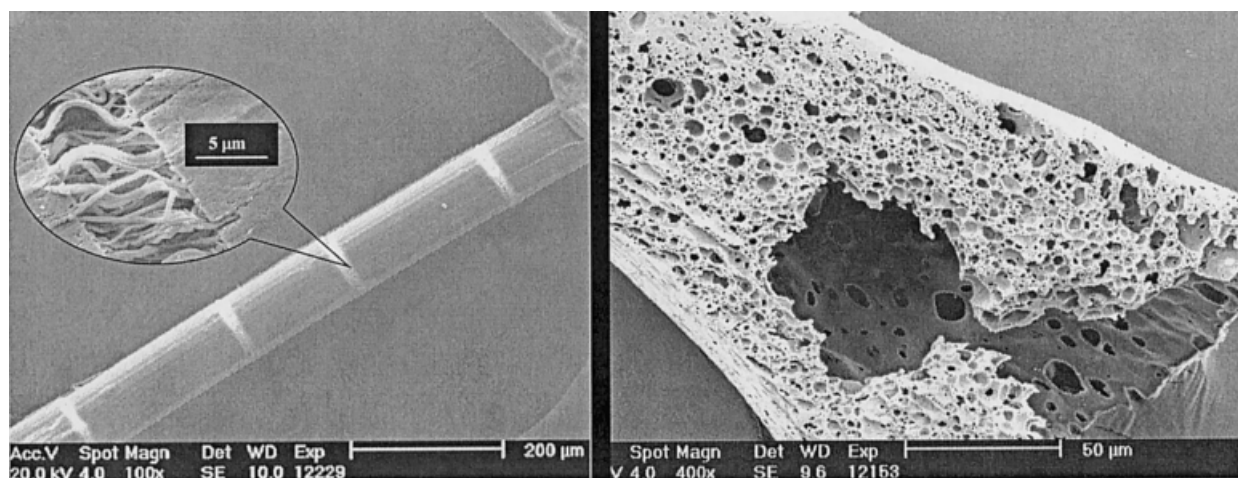
Figure 2   Scanning electron micrographs of HWKL/PP (75/25) fibers. The fiber to the left is prior to thermal treatment. It has been stretched to produce fractures along the fiber. The inset shows the "stringy" polypropylene phase dispersed throughout the lignin phase at a point of fracture. The fiber to the right is after thermal treatment. It has been cut at a 30° angle with respect to the fiber axis to show the extent of the porous structure and the hollow-core nature of the fiber.

together. Gillham and coworkers have described such phenomena in continuous heating transformation (CHT) diagrams.[23] Thus, the thermoplastic character of the lignin is changed to thermosetting, enabling the lignin fibers to maintain fiber form while the PP is removed. Figure 2 shows the HWKL/PP (75/25) fibers before (green fibers) and after (crosslinked fibers) thermal treatment. Stretching of the green fibers (magnified inset) reveals the polypropylene phase as distinct "strings" dispersed throughout the lignin fiber. In the corresponding thermally treated fibers the removal of the polypropylene phase(s) produces the observed porous microstructure.

In this article, we described the production of porous hollow fibers made from a wood-based biopolymer and a recyclable petrochemical polymer. It is expected that these fibers relative to solid lignin fibers will have high specific surface area and a high flexural strength/mass ratio due to the lignin shell/hollow core morphology. We are now studying the effect of the mixing ratio, molecular weight and temperature on the dispersion of PP in the lignin matrix, and the relation of the initial dispersion and the pore size distribution in the final product fibers. Production of activated porous carbon fibers is also a current subject and research is underway.

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