Bark Derived Materials For High Performance Polypropylene Composites

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Summary

Millions of tons of bark are generated by the forest products industry as waste each year in Canada. Most of them are disposed by burning, and limited amount are used for low grade applications. In this study, we have demonstrated the use of various high lignin containing bark fractions as filler/reinforcements in developing high performance polypropylene (PP) composites. Bark extractives and micron sized lignocellulose fibrils were produced from western red cedar (*Thuja plicata*) bark fibers. Both these fractions were spray dried and melt blended with PP followed by hot pressing to make composites. The use of spray dried high lignin containing micron sized fibrils in polypropylene matrix increased both the tensile strength and modulus compared to neat PP. Also, the use of high lignin containing extractives and fibrils imparted high UV stability for the composites.

1 Introduction

The increasing environmental awareness and legislated requirements have prompted a lot of industrial sectors such as building, aerospace and automotive industry to consider natural fibers as a substitute for conventional synthetic fibers in reinforcing various polymer composites. In addition to renewability and biodegradability, natural fibers have various advantages such as low cost, low density, high specific strength, nonabrasiveness, undergoes lesser damage while processing, high flexibility, and low toxicity levels compared to synthetic fibers.[1,2] The natural fiber sources used for making composites can be mainly classified as those derived from wood and those from fiber crops obtained from bast, seed, leaf, grass and fruits.[3] In addition to these sources, agricultural waste generated during processing of crops, industry generated wood waste, and various municipal solid waste containing wood and paper can also serve as a potential source for natural fibers.[3–5] The effective extraction and utilization of these fibers from waste will ensure a sustainable supply of natural fibers and also help to solve environmental concerns such as waste disposal management.

Huge amounts of bark are created as waste every year by the forest product industry in Canada as a by-product of wood processing.[6] Bark includes the peripheral layers of stems, roots of woody trees and shrubs. Majority of the bark as disposed of by burning, while some are used for low grade utilisation such as fuel, charcoal, mulching and soil amendment. Bark of woody plants contains 2-25 wt% of extractives, 40-55 wt% of lignin and 30-48 wt% of polysaccharides.[7]

Over the past few decades, several studies have been centered around creating different resins and foams from liquified bark or phenolic compounds derived from bark.[8–10] However, very few studies have focussed on utilizing bark based or different bark fractions as fillers or reinforcements in different polymers for developing high performance natural fiber-based composites. Some of the previous studies used bark as a filler in polyolefin composites.[11–13] However, compared to wood-based composites, bark reinforcement showed negative effect on mechanical properties mainly due to high amount of extractives.[11] Recently, our group have been successful in isolating cellulose micro and nano sized fibrils with approximately 20 - 23 % (w/w) of lignin after careful extraction of all extractives from bark of coniferous softwoods.[14,15] These fibrils doubled the mechanical properties when used as reinforcement in epoxy composites. The high amount of lignin on the cellulose fibrils increased the compatibility between the hydrophilic cellulose and hydrophobic epoxy.[16] Compared to other parts of plants, bark contains high amount of extractives and lignin.[7] These extractives are rich in polyphenolic compounds which are good absorbers of solar UV radiation. Different studies have shown the positive effect of extractives in slowing down the wood degradation by UV radiation.[17,18] Lignin also contains high amount of UV absorbing functional groups such as phenols, ketones and chromophores. The presence of lignin has shown excellent UV shielding efficacy in various composites.[19,20]

In our study, western red cedar (*Thuja plicata*) bark fibers will be used as the raw material to obtain high lignin containing cellulose fibrils and extractives. The air-dried bark fibers will be subjected to mild alkaline treatment and the resulting extract will be filtered through appropriate filter paper to obtain the extractives (alkaline filtrates). The solid fibers left after the alkaline filtration will be fibrillated using micro grinding to obtain the high lignin containing cellulose fibrils. Both these fractions will be incorporated into polypropylene (PP) to make composites films. Our major objective is to compare the effects of these bark fractions on mechanical, and UV stability of PP composites.

2 Materials and methods

2.1 Materials, bark extraction and fibrillation

Western Red Cedar (Thuja plicata) bark was provided by Terminal Forest Products. The PP pellets (3927WZ, Refining INC., TX, USA) with a melt flow index of 60 g/10 min was obtained. All other chemicals were purchased from Caledon labs (Georgetown, ON, Canada). The air-dried bark fibers were subjected mild alkaline treatment using 1% NaOH solution at a temperature of 90 °C for 120 min with a liquor to bark ratio of 10:1. The resulting extract was filtered through appropriate filter paper to obtain the extractives (alkaline filtrates). The extractives and fibers were analysed to determine the amount of holocellulose, cellulose, klason lignin, and ash contents.[21,22] The solid fibers left after the alkaline filtration were extensively washed and fibrillated using Super-MassColloider (MKZA10-15J, Masuku Sangyo Co., Ltd, Japan) at 1500 rpm to obtain the high lignin containing fibrils. Both these fractions were spray dried using a laboratory spray drier (ADL311, Yamato Scientific Co., Japan).

2.2 Production of composites, mechanical testing and UV irradiation

PP pellets and spray dried fractions (fibrils, extractives) were melt blended using a Brabender mixer (C.W. Brabender Instrument Inc., USA) at temperature of 170 °C, and a speed of 80 rpm. The mixture contained 5 wt % each bark fractions to the total weight of PP. The mixtures were later hot pressed to composite films using a Carver Laboratory Press (Carver Inc., Wabash, IN) at 170 °C for 5 min at 0.6 MPa. The films were tested according to ASTMD 638-Type V specifications, performed using an Instron machine (Model 3367) equipped with a 2 kN load cell. Neat PP films were also compression molded the same condition and tested the same way.

PP and composite films were exposed to UV irradiation in a chamber using eight UV light lamps at 340 nm with a UV irradiance of 0.89 W/m^2 for a duration of 120 h at ambient temperature.

2.3 Characterization

The morphologies of various bark fractions, cross sectional surfaces of neat PP and composites, and the surface of UV irradiated samples were examined by a scanning electron microscope (JEOL 6610LV, Seal Laboratories, El Segundo, CA, USA) operated at 15 kV. Absorbance spectra of the neat PP and composite films in the visible region (200–500 nm) were obtained with a UV–vis spectrophotometer (Lambda 2, PerkinElmer, Waltham, MA, USA).

3 Results and Discussion

The alkaline treatment resulted in high extractive yield of around 32 wt% of dry bark weight. Table 1 shows the chemical composition of extractives and the fibers after extraction. The diameter of fibers after the alkaline extraction was found to be betweeen 25 and 40 µm (Figure 1a). Aqueous suspension of fibers were succesfully fibrillated to smaller sized fibrils (< 1µm) by microgrinding (Figure 1b). However, polyolefins like polypropylene are highy hydrophobic and a wet mixing or mixing of PP with moisture containing lignocellulose fibers can result in mutually incompatibility and poor composites. Therefore, the fibrils obtained after microgrinding were spray dried before mixing with PP. In comparison to other common drying techiques such as freeze drying or super critical drying, spray drying offers a lot of advantages such as shorter drying times, low labour and maintenance costs. Figure 1c, d shows the SEM images of spray dried fibrils and the extractives. After spray drying, nearly three-fourth of the high lignin containing fibrils were having diameter less than 1.5 µm. A small portion of fibrils ranged above this size. The average diameter size of fibrils obtained after spray drying in our study are way lower than some of the previous studies using fibrillated lignocellulose fibers with very low lignin content or bleached fibers. The high amount of lignin on the surface of fibrils resulted in less aggregation of fibrils during drying. In addition to hydroxyl groups, lignin also contains high amount of non-polar hydrocarbon and benzene groups which can alleviate the aggregation of fibrils while drying. In comparison to fibrils, the extractives after spray drying appeared as spherical particles, with the diameter ranging from 2 to 10 µm.

Table 1. Chemical composition of spray dried alkali extracted fibers and extractives

Samples	Klason lignin (%)	α-cellulose (%)	Hemicellulose (%)	Ash content (%)
Alkali extracted fibers	25.59 ± 0.30	58.12 ± 0.41	13.34 ± 0.24	2.95 ± 0.28
Extractives	61.87 ± 0.92	4.33 ± 0.72	32.57 ± 0.52	1.23 ± 0.17

Figure 1. SEM images of (a) alkaline extracted fiber, (b) high lignin fibrils, (c) spray dried high lignin fibrils (d) spray dried extractives
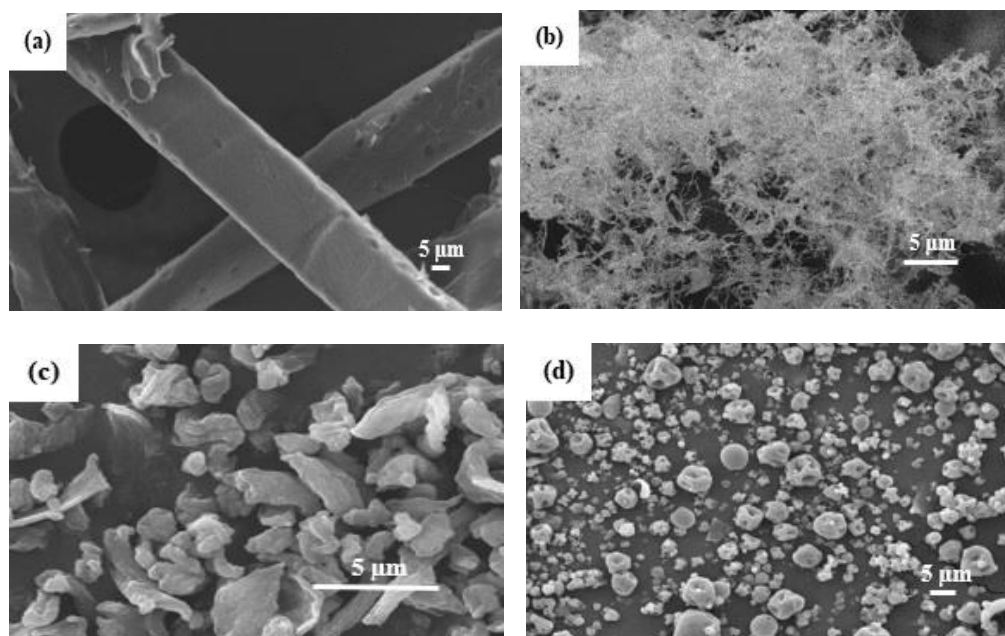
The spray dried bark fractions were melt blended with polypropylene and were successfully hot pressed to various composite films. The average mechanical properties of the composites are shown in Table 2. For the composites using spray dried fibrils, there is clear increase in mechanical properties compared to neat PP. Previous studies based on cellulose reinforced PP composites showed poorer tensile properties, mainly strength than neat PP, mainly due to poor interfacial bonding between non-polar PP and polar cellulose.[23,24] The fibrils, we used in this study is comprised of high amount of lignin (25.59 wt%). The presence of high amounts of lignin on cellulose can show affinity towards hydrophobic PP molecules and can create an effective interphase around the filler particles. Also, lignin plasticisation can occur at high temperature during blending or hot-pressing and form effective lignin-PP bonds in the composite.[16] However, the addition of extractives showed a decrease in tensile strength. This could be due to the low cellulose content within the fraction and the low aspect ratio of spherical extractive particles. Figure 2 shows the fracture surfaces of neat PP and composites. The composites did not show much voids or fiber/particle pullouts, suggesting its good dispersion and compatibility with PP.

Table 2. Tensile properties of neat PP, and composites

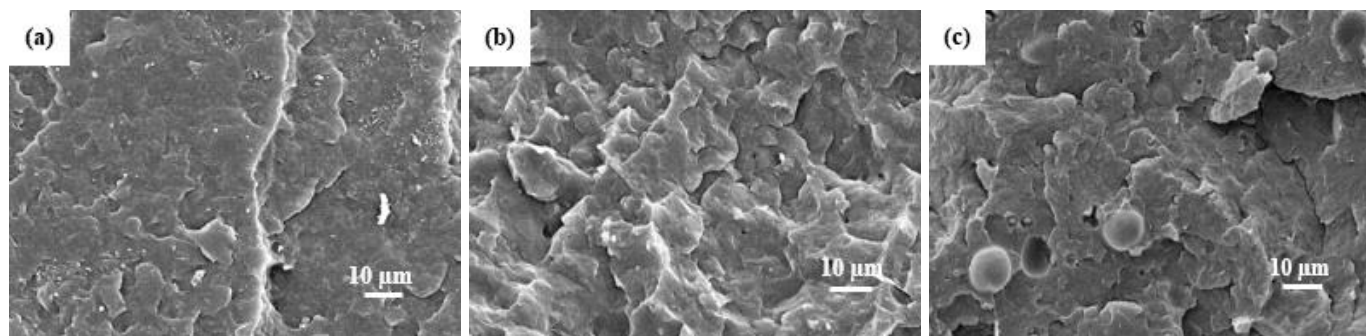| Samples	Tensile strength (MPa)	Tensile modulus (GPa)
PP	30.61±1.45	1.47±0.11
High lignin fibrils/PP	38.34±1.40	2.08±0.24
Extractives/PP	23.94±2.14	2.04±0.11

Figure 2. SEM images of cross-sectional fracture surface of (a) neat PP, (b) high lignin fibril/PP composite, (c) extractive/PP composite

Figure 3 shows the surface morphologies of neat PP, and composites after 120 h of UV irradiation. It appears that some cracks started appearing on the surface of PP. Compared to PP, the composites with bark fractions showed more compact surface layer with no cracks. Figure 4 shows the UV absorbance for neat PP and composites. PP showed the lowest absorption and the addition of bark fractions enhanced the absorption and almost showed a complete absorption in the UV light region (200-400 nm) (Figure 4). The bark fractions in the composite with high amount of lignin are strong absorbers of UV light, thus slowing down the photodegradation of PP.[19,20] This accounts for the limited cracks on the surface of composites.
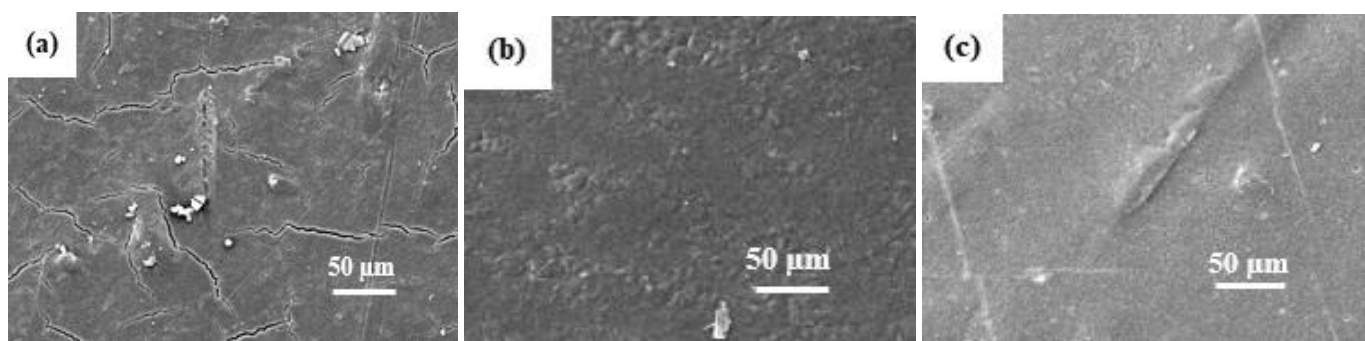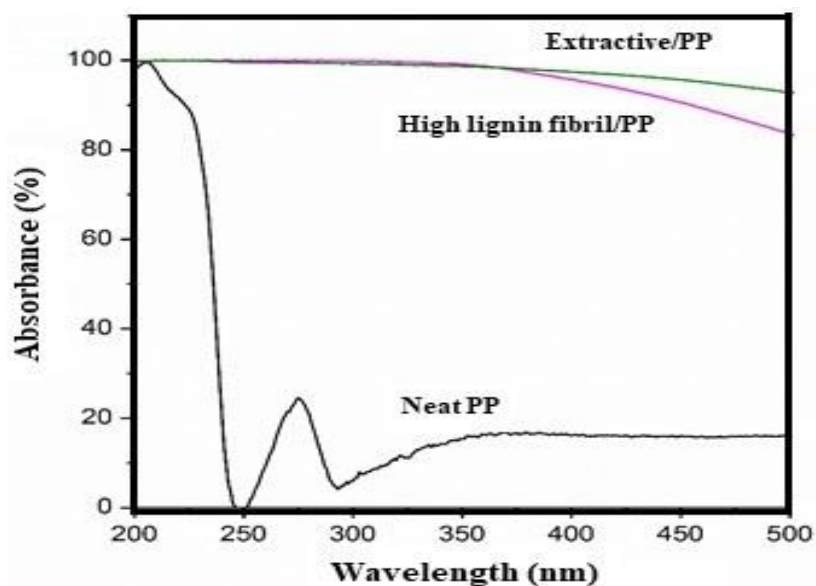

Figure 3. SEM images of the surface of (a) neat PP, (b) high lignin fibril/PP composite, (c) extractive/PP composite after UV irradiation for 120 h

Figure 4. UV-Vis spectra of PP and composites

4 Conclusions

High lignin containing extractives and cellulose fibrils were successfully produced from bark. The incorporation of these fractions in PP resulted in composites with better physical properties than neat PP. While most of the previous studies based on cellulose fibril reinforced PP composites showed poor mechanical properties due to the mutual incompatibility between the hydrophilic cellulose and hydrophobic PP, the use of high lignin containing cellulose fibrils derived from bark in PP matrix significantly enhanced the mechanical properties compared to neat PP. The presence of non-polar groups on lignin can show better affinity towards hydrophobic PP molecules, creating an effective interphase around the filler particles. The addition of extractives showed a decrease in tensile strength mainly be due to the low cellulose content within the fraction and the low aspect ratio of spray dried spherical extractive particles. However, the use of both fractions enhanced the UV stability of composites compared to neat PP films. Lignin which are responsible for huge amount of UV absorption helped in slowing down the PP degradation in composites.

5 Acknowledgments

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