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Development and morphological characterization of wood pulp reinforced biocomposite fibers

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Abstract Biocomposite fiber has been developed from wood pulp and polypropylene (PP) by an extrusion process and the generated biocomposite fibers were characterized to understand the nature of interaction between wood pulp reinforcement and PP matrix. The use of maleated polypropylene (MAPP) as a compatibilizer was investigated in relation to the fiber microstructure. Fiber length analysis showed that most of the fiber lengths lie within the range of 0.2–1.0 mm. Changes in absorption peaks were observed in Fourier transform infrared spectroscopy of biocomposite fibers as compared to the virgin wood pulp, which indicated possible chemical linkages between the fiber and polymer matrix. SEM study was carried out to observe fiber–matrix adhesion at the interface within the composite and MAPP treatment was found to be effective in increasing reinforcing fibers–matrix compatibility. X-ray computed tomography was conducted to understand the internal architecture of the biocomposite fiber and the results showed that with incorporation of additional wood pulp content, the fiber becomes more aligned along length axis possibly due to compression and die geometry of the extruder.

Introduction

Growing awareness for an eco-friendly environment has revived the interest to develop composite fibers from bio-based products. Lately, natural fibers have drawn much attention of scientists as they are biodegradable, renewable, inexpensive and readily available from natural resources. Besides, these fibers have relatively light weight, high strength, and stiffness. Several studies have been conducted to generate reinforced composites based on the potential of cellulose-based fibers [1–12]. However, it is important to understand that while fully renewable bio-based materials are more eco-friendly, such materials may lack some performance attributes designed for specific industrial applications. One alternative solution is to use polymers and materials derived from mixed renewable and fossil fuel sources, which not only alleviate the fossil fuel dependency but also have an added advantage of delivering the desired performance from a more sustainable stock material. However, with such composites, there are some associated problems including poor wettability, high moisture absorption, and less dispersion of natural fibers within the polymeric matrices. The fiber–matrix adhesion is a vital problem among all disadvantages. The hyprophilic nature of fibers unfavorably affects adhesion to a hydrophobic matrix; eventually resulting into poor mechanical properties. A good interfacial adhesion between fiber and matrix is therefore required to enhance the mechanical performances of a composite. These properties may be achieved by modifying the natural fiber surface; graft copolymerization of polymers onto the fiber surface, physical treatments (cold plasma treatment, corona treatment) etc. [11–13]. Many researchers have reported that coupling agent such silanes, maleic anhydride, titanates, zirconates, triazine compounds can also increase the fiber–matrix adhesion [13]. There are several methods available for fiber manufacturing of which melt spinning, solution spinning, and electro-spinning are the most commonly employed methods. Extrusion is a modified version of melt spinning in which polymer chips are fed through the hopper and the

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extrudate is obtained after passing through different zones of the extruder. It has the advantages of being a simple process, and technically elegant method and solidification of the melt thread involves only heat transfer. Another potential merit of extrusion approach is that no solvents are required to produce polymer solution.

However, the relevance of all these concepts within the context of development of continuous biocomposite fiber from wood pulp and a suitable polymer has not been studied to date. Related experimental data are therefore difficult to find, and characterization results are virtually non-existent. Therefore, development of a novel method to produce wood pulp–polypropylene (PP) biocomposite fibers in an extrusion process seems to be a promising technique, which provides a simple and low processing route. In this study, PP was used as matrix because it is inexpensive, recyclable and has high thermal stability. Wood pulp was used as a reinforcing fiber. MAPP was used as a compatibilizer with PP to enhance the interfacial adhesion between fiber and matrix. Scanning electron microscopy (SEM) studies were performed to investigate the fiber–matrix adhesion at the interface. The internal structures of biocomposite fibers were also studied by X-ray computed tomography. Fourier transform infrared spectroscopy (FTIR) was used to investigate the nature of functional group in the composite fiber, which in turn suggested the compatibility between reinforcement and matrix.

Experimental

Materials

Matrix

Polypropylene resin (PP3622) was supplied by Arkema, Canada. The melt flow index (MFI) of supplied PP was 12 g/10 min.

Reinforcements

Bleached kraft wood pulp was collected from the Erving Paper Inc., New Brunswick, Canada.

Coupling agent

Maleic anhydride (in the form of maleated polypropylene, MAPP) was supplied by Atofina, Canada.

Fabrication of biocomposite fibers

A twin screw extruder with a screw nominal diameter of 25 mm, screw center distance 21.2 mm, and L/D of 40 was used to produce the biocomposite fibers. Wood pulp was initially crushed by grinder. The crushed wood pulp was then kept at ambient temperature for 24 h. Biocomposite fibers were manufactured by two steps.

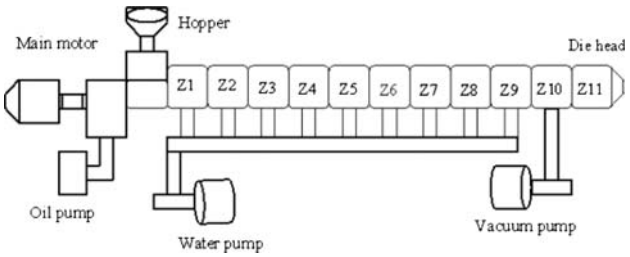

Fig. 1 A schematic diagram of twin screw extruder

First, wood pulp and polymer were mixed together manually and placed in the extruder main feeder (Hopper). The compounded materials were passed through the different zones of the extruder and finally extruded through the spinneret holes (diameter of hole $\sim$6 mm). The extrudates coming out of the extruder were cooled down by using cold water for a better dimensional stability and wound up manually. Finally, the biocomposite material was pelletized by a pelletizer. A schematic representation of twin screw extruder was shown in Fig. 1. The temperature profile of the extruder in the respective zones is shown in Table 1.

In the second step, the pelletized material was fed into twin screw extruder and the biocomposite fibers were generated by using same processing parameters of first step except the spinneret hole. In this case, the diameter of spinneret hole utilized was 1.5 mm instead of 6 mm to reduce the end diameter of biocomposite fibers.

Fiber length determination

The mean length of short fiber (wood pulp) was determined by the fiber quality analyzer (FQA). FQA was used to analyze the medium density fiber length. The FQA has a fully integrated sensor unit containing the optics, control, and measurement electronics. It suspends the fibers in water, uptakes the fibers into the machine itself, and analyzes them using the imaging sensor. The FQA reports average length with the accuracy to 70 μm. Small amount of fibers were well separated and stirred into approximately 500 ml of water in a beaker. The beaker was then placed under the stirring device, which allows the fibers to be fully suspended during test, and the suction tube, which uptakes the fibers into the machine for analysis. In this technique, 10,000 short fibers were counted to determine an average fiber length of wood pulp.

Table 1 Processing parameters for extrusion

Processing settings	
Material	PP/wood pulp
Motor rpm	40
Feeder rpm	13
Vacuum vent	Yes
Temperature profile (°C)	
Zone 1 (PP, wood pulp)	180
Zone 2	180
Zone 3	180
Zone 4	180
Zone 5	180
Zone 6	180
Zone 7	180
Zone 8	180
Zone 9	180
Zone 10	185
Zone 11	185

Fourier transform infrared spectroscopy (FTIR)

Bruker FT-IR model TENSOR 27 using 32 scans in ATR mode was used to investigate the nature of adhesion between fiber and matrix. Both wood pulp and biocomposite fibers were used to identify the functional groups and also corresponding changes that appeared in biocomposite fibers with and without coupling agent.

Scanning electron microscopy (SEM)

Scanning electron microscopy was used to determine the topography of the composite fibers and also to investigate the effect of MA at the fiber–matrix interface. The samples were broken down in liquid nitrogen to observe fractured surface of the biocomposite fibers. In order to achieve the required electrical conductivity, the samples were sputtered with Au/Pd for 3–4 min in SC7620 Mini Sputter Coater machine. Fractured surfaces of the specimens were studied with a JEOL JSM-840 SEM with an acceleration voltage of 12 kV.

X-ray computed tomography

The samples were examined using the high-resolution micro-CT system SkyScan 1172 (SkyScan, Belgium). The X-ray source was an air-cooled, sealed microfocus X-ray tube with a focal spot size <8 μm. The X-ray tube was operated at 40 kV and 150 μA (no filter). The X-ray CCD (charge-coupled device) camera is based on a 2000 × 1048 12-bit cooled CCD sensor with fiber optic coupling to the X-ray scintillator. The system was controlled by a PC workstation. Scanning of the specimens was done with 180° rotation around the vertical axis and a single rotation step of 0.4. The cross-sectional pixel size was 4.01 μm.

After a half circle (180°) was completed, the entire set of radiographs was synthesized by computer software. The raw dataset was reconstructed with the software NRecon. An automatic filter changer for beam-hardening compensation during reconstruction was used at a level of 35%. The reconstructed 2D images were saved as a stack of uncompressed 16-bit TIFF files. These TIFF files were then used to create a three-dimensional (3D) image of microstructure with the software Image-Pro Plus 6.1.

Results and discussion

Fiber length analysis

During the extrusion process, the shear stress applied by the screw will break the fibers. The resultant fiber lengths will affect the ultimate mechanical properties and in addition to the influence of fiber damage and breakage during processing, the final fiber lengths are determined also by the initial fiber length in the feedstock. It is therefore important to analyse the initial fiber length distribution. The fiber length distribution is presented by a histogram curve in Fig. 2. The arithmetic, length weighted, and weight weighted values of the fiber length were found to be 0.43, 0.98, and 1.52 mm, respectively. Most of the fiber lengths lie within the range of 0.2–1.0 mm since crushed wood pulp was used in this study. 10,000 single fibers were taken into consideration to obtain these average fiber lengths.

FTIR investigation

The nature of interaction between fiber and matrix was explored using FTIR. The C–H stretching vibrations were observed at about 2,800–3,000 cm^{-1} in pure wood pulp, and all composite fibers, which are shown in Fig. 3

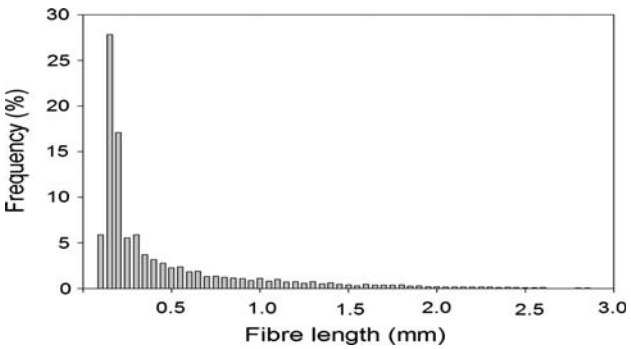

Fig. 2 Length histogram of crushed wood pulp

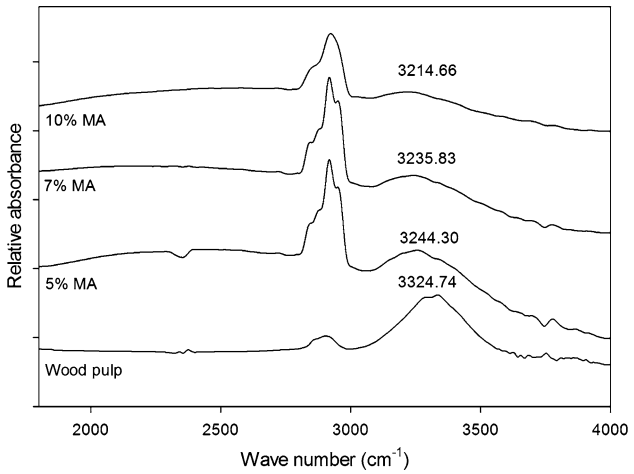

Fig. 3 FTIR spectra of 100% wood pulp and 30% wood pulp–PP biocomposite fiber with variation of MA percentage

[14–16]. FTIR spectra of composite fibers were significantly more intense, compared to a spectrum of pure wood pulp. It is assumed that PP and MA would react with pure wood pulp, and eventually the intensity of C–H stretching of pure wood pulp might be affected in the composite system**.** The mechanical properties of wood pulp–PP biocomposite fibers depend upon how strongly the fiber and matrix are linked by chemical bonds. The infrared (IR) absorption peak of free –OH groups of wood fiber was observed in Fig. 3 at 3,324 cm^{-1}. As shown in Fig. 3, the hydroxyl absorption peak in all biocomposite fibers has shifted to lower wave numbers (3,214–3,324 cm^{-1}). MAPP may potentially be grafted to the wood fiber surfaces by hydrogen bonds or ester linkage. The hydroxyl absorption peak will move to lower wave number when hydrogen bonds are generated due to reaction of MAPP with wood fiber. If ester linkages are established between MAPP and the hydroxyl groups, an indication of new ester group stretch would be viewed at about 1,740 cm^{-1}, which was not observed from the FTIR spectra. The shift of hydroxyl absorption was, however, noticed for all biocomposite fibers. The higher the spectral shift, the more hydrogen bonds created. The greater spectral shift corresponds to a greater extent of MA. These results are in good agreement with the studies of Luo et al. [17]. A considerable changes in IR absorption peak of free –OH groups of wood pulp–PP biocomposite fibers was also observed as compared to the cellulose fiber (wood pulp). A significant spectral movement is detected in wood pulp–PP biocomposite fibers owing to use of various percentage of MA. Mechanical properties of biocomposite fibers can therefore be controlled with varying content of MA, which in turn would influence the interfacial bonding between wood fiber and MAPP due to the generation of hydrogen bonds.

Analysis of microstructure by SEM

Scanning electron microscopy was used to investigate the fracture surface of neat PP and wood pulp–PP biocomposite fibers with and without MA. SEM observations indicate substantial differences across the surfaces among neat PP, wood pulp-PP biocomposite fiber with and without MA. The fracture surface of pure PP appears smoother than any other samples of biocomposite fibers because of the homogeneous system. Figure 4a–f shows the fracture surfaces of the pure PP and biocomposite fibers with increasing fiber content. The fibers tend to agglomerate when MA was not used as a coupling agent, which is presented clearly in Fig. 4c–e. It can also be observed that the wood fibers are dispersed within the matrix. Fiber distribution seems to be more uniform in the PP matrix with MA. Figure 4f represents fracture surface of wood pulp–PP biocomposite fibers with MA (30%F/65%PP/5%MA). As compared to Fig. 4c, the reinforcing fibers appeared to be impregnated due to the presence of MA with PP, which should have increased the reinforcing fibers–matrix compatibility. Overall, this would affect the mechanical and thermal performance of the substrate where the fibers will potentially be used.

X-ray computed tomography studies

The fiber orientation plays a crucial role in obtaining the behavior of short-fiber composites. Although, majority of the processing method involving short-fiber reinforced composites produces random fiber orientation, fabrication kinetics can lead to semi orientation, which may increase the anisotropic properties. Fabrication method can alter the degree of fiber orientation in composite system slightly. During extrusion process, progressive and continuous changes in fiber orientation take place in composite system. Several other factors are also responsible for changes in the orientation of fibers including the flow behavior of polymer matrix, the size and amount of fibers, the processing parameters, and die geometry. Mechanical properties changes due to directional differences, which is correlated with the orientation of fibers. Knowledge of fiber orientation of is, therefore, important in composite part because it controls the mechanical properties of the finished product. The composite is stronger and stiffer in the direction in which most short fibers are oriented. The mechanical performance of composite will be poor in the direction of less oriented. An understanding of fiber orientation, nature of distribution is therefore important in terms to processing and mechanical performance of biocomposite fibers.

Fiber–matrix networking microstructures were investigated by X-ray computed tomography. Figure 5a–c reveals the internal architecture of biocomposite fibers. With

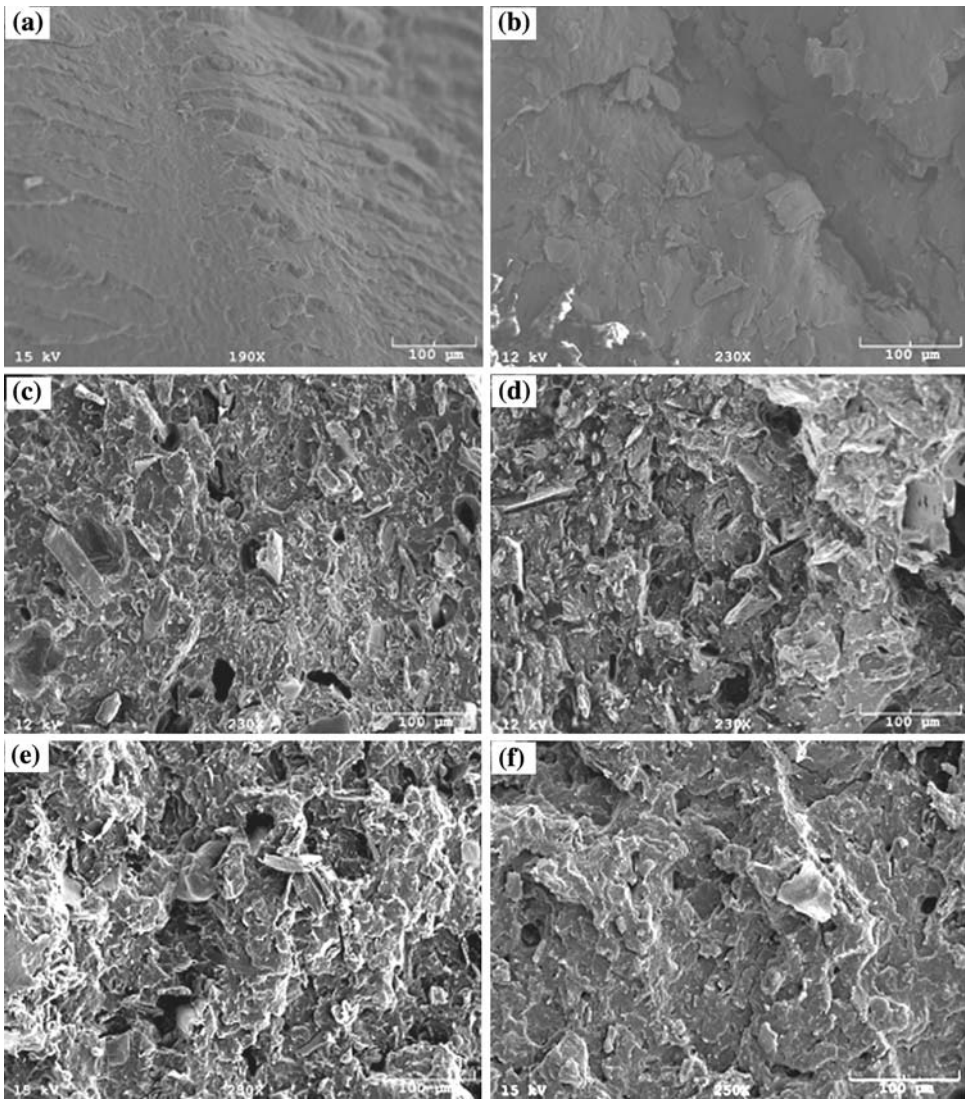

Fig. 4 Fractured surface of pure PP and short fiber/PP–composite fibers (×250): **a** pure PP (×190), **b** 10%F/90%PP (×230), **c** 30%F/70%PP (×230), **d** 50%F/50%PP (×230), **e** 70%F/30%PP (×230), and **f** 30F/65%PP/5% MA (×250)

increasing fiber content, the reinforcing fibers became more prominent, leaving less void spaces. The reinforcing fibers were found to be aligned along the length axis in biocomposites fibers possibly due to compression and geometry of the die of extruder. It is expected that the desired orientation and in turn the mechanical properties of biocomposite fibers can be achieved by carefully optimizing the fiber content, die geometry, and processing parameters.

Conclusions

In this study, biocomposite fibers have been generated from wood pulp and PP using a twin screw extruder. The developed fiber has been characterized using several techniques. Analysis of fiber length provided the data for average fiber length and the fiber length distribution within the wood pulp reinforcement. Results show that most of the fiber lengths lie within the range of 0.2–1.0 mm. FTIR spectroscopy analysis indicated considerable changes in absorption of wood pulp–PP biocomposite fibers as compared to the virgin wood pulp, which in turn relates to a possible chemical linkages between the fiber and polymer matrix. SEM study also indicated fiber–matrix interaction within the composite, which was found to be enhanced on treatment with MA and as a result increased reinforcement–matrix compatibility. X-ray computed tomography has been applied as a useful tool for the non-destructive investigation of the wood fiber orientation in a composite system. X-ray computed tomography studies were conducted to understand the internal microstructure of the biocomposite and it has been clearly shown that with increasing fiber content, the reinforcing wood fibers become more aligned along length axis possibly due to compression and die geometry of the extruder.

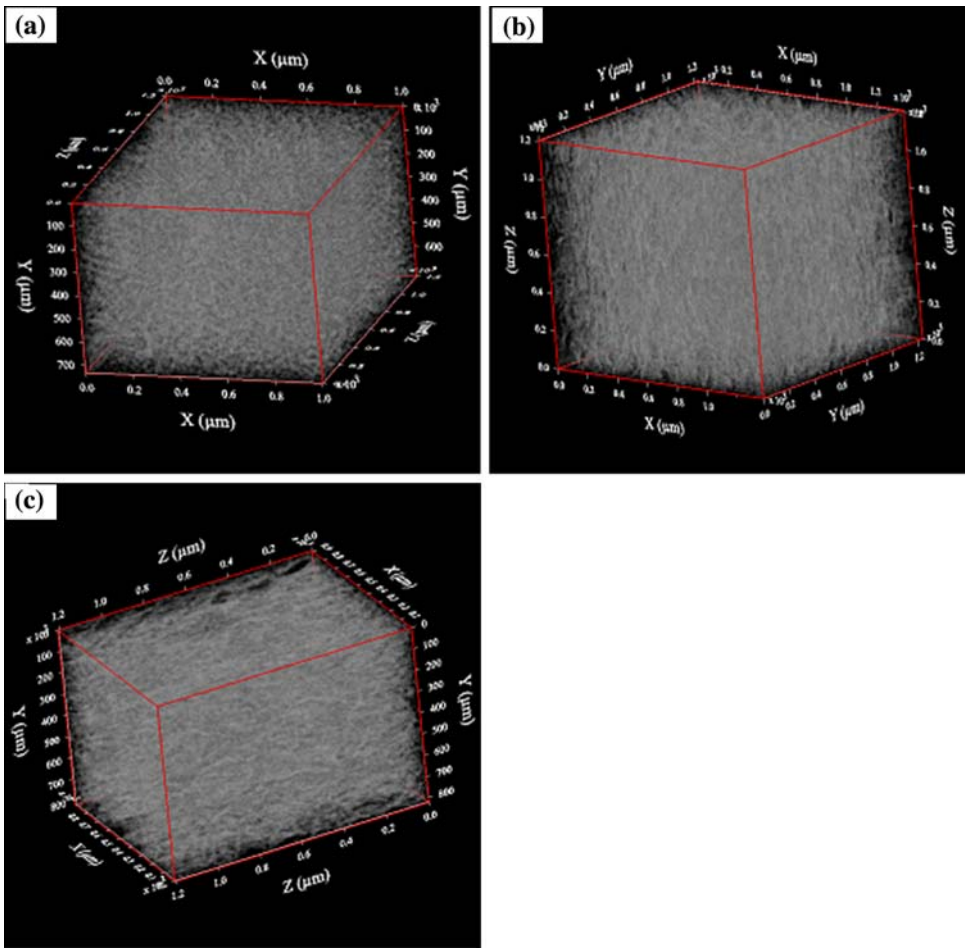

Fig. 5 3D image of **a** Pure PP, **b** 50 wt% fiber and 50 wt% PP, and **c** 70 wt% fiber and 30wt% polymer

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