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Thermal properties and spectral characterization of wood pulp reinforced bio-composite fibers

A. Awal · S. B. Ghosh · M. Sain

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Abstract Bio-composite fibers were developed from wood pulp and polypropylene (PP) by an extrusion process. The thermo-physical and mechanical properties of wood pulp-PP composite fibers, neat PP and wood pulp were studied using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The thermal stability of bio-composite fibers was found to be significantly higher than pure wood pulp. An understanding into the melting behaviour of the composite system was obtained which would assist in selecting a suitable temperature profile for the extruder during processing. The visco-elastic properties of bio-composite fibers were also revealed from the study. The generated bio-composite fibers were also characterized using Fourier transform infrared spectroscopy (FTIR) to understand the nature of chemical 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. Changes in absorption peaks were observed in FTIR spectra of bio-composite fibers as compared to the pure wood pulp which indicated possible chemical linkages between the fiber and polymer matrix.

Keywords Wood pulp · Polypropylene · Bio-composite fiber · Extrusion · Thermal properties

A. Awal (✉) · S. B. Ghosh · M. Sain
Center for Biocomposites and Biomaterials Processing,
Faculty of Forestry, University of Toronto, 33 Willcocks St,
Toronto, ON M5S 3B3, Canada
e-mail: a.awal@utoronto.ca

Introduction

Growing awareness for an eco-friendly environment has revived the interest to develop composite fibers from bio-based products. Considerable interest has been generated to use natural fibers with thermoplastic polymers 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 [1–22]. However, it is important to understand that while fully renewable bio-based materials are more environment-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 reduce 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 essential 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, 12, 23]. Many researchers have reported that coupling agents such as silanes, maleic anhydride, titanates, zirconates, triazine compounds can also increase the fiber-matrix adhesion [23]. 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 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 difficult to find and characterization results are virtually non-existent. Therefore, development of a novel method to produce wood pulp- polypropylene bio-composite fibers in an extrusion process seems to be a promising technique which provides a simple and low processing route. In this study, polypropylene (PP) was used as matrix because it is inexpensive, recyclable and has high thermal stability [24, 25]. Wood pulp was used as reinforcing fiber. Maleated polypropylene was used as a compatibilizer with PP to enhance the interfacial adhesion between fiber and matrix. 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. The thermo-physical and mechanical properties of wood pulp-PP composite fibers, neat PP and wood pulp were studied using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA).

Experimental

Materials

Matrix

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

Reinforcement

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

Coupling agent

Maleated polypropylene (M_w of 900 and containing 1.06% of anhydride groups) was supplied by Atofina, Canada.

Methods

Fabrication of bio-composite fibers

A twin screw extruder with a screw nominal diameter of 25 mm, screw centre distance 21.2 mm and L/D of 40 was used to produce the bio-composite fibers. Wood pulp was initially crushed by grinder. The crushed wood pulp was then kept at ambient temperature for 24 h. Manufacturing of bio-composite fibers were carried out in two steps.

Firstly, 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 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 bio-composite material was pelletized by a pelletizer. A schematic diagram 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 bio-composite 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.

Thermogravimetric analysis

Thermogravimetric analysis was performed using TA instrument Q500 with a heating rate of 10 °C/min. The samples were heated from 40 to 600 °C to determine the complete thermal degradation of wood pulp-PP composite fibers, neat PP and wood fiber. All tests were carried out in nitrogen atmosphere using a flowing rate of 60 mL/min.

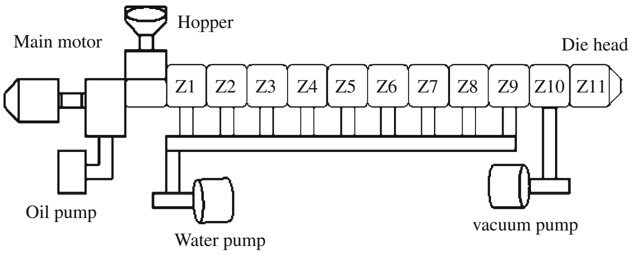

Fig. 1 Schematic diagram of twin screw extruder

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	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

Differential scanning calorimetry

The melting temperature and crystallization behaviour of the biocomposite fibers and polymer were investigated using a TA instrument Q1000 differential scanning calorimeter (DSC) attached with a cooling system under a nitrogen atmosphere. DSC instrument were run from 40 to 250 °C with a heating rate of 10 °C /min. The sample weight was about 5 mg. The specimens were sealed in aluminum pans by pressing and the prepared samples were placed in the furnace of DSC with an empty reference pan. The heat flow rate as function of temperature was recorded automatically. Melting temperature was identified on the peak point of the DSC curves. The melting of polymer within a composite system would assist to select a suitable temperature profile for the extruder when the fiber and matrix were compounded to produce biocomposite fibers.

Dynamic mechanical analysis

The storage modulus, loss modulus and tan delta of wood pulp-PP composite fibers were determined using a TA Q800 Dynamic Mechanical Analyzer (TA Instruments, New Castle, DE, USA). DMA were run in the three point bending mode and the length and diameter of the specimens were 35 mm and 1.35 mm, respectively. The samples were heated from 40 to 170 °C with a heating rate of 1.5 °C/min, strain amplitude of 30 μm and using a frequency of 1 Hz.

Fourier transform infrared spectroscopy (FTIR)

Bruker FTIR model TENSOR 27 using 32 scans in ATR (Attenuated total reflection) mode was used to investigate the nature of adhesion between fiber and matrix. Both wood pulp and bio-composite fibers were used to identify the functional groups and also corresponding changes that appeared in bio-composite fibers with and without coupling agent.

Results and discussion

Thermogravimetric analysis

The degradation of wood fiber and polymer is a very important issue to produce bio-composite fibers. The thermal degradation of fibers leads to poor mechanical performance, deterioration of color, odor, darkening of the product etc. On the other hand, changes in surface chemistry can also lead to inferior mechanical properties which are responsible for adhesion between fiber and polymer at the interface. It has to be noted that high melt processing temperature is one of the major concerns during extrusion in developing bio-composite. A massive decomposition of wood pulps due to high melt processing temperature during extrusion would lead to poor mechanical performances of the composite fibers. A lot of physical and chemical changes can occur due to thermal treatment of fibers and polymers during processing in an extruder. TGA applies heat to force reactions and physical changes in the specimens to detect mass loss. The quantitative measurement of mass alteration in specimens is given through transition and thermal degradation by TG instrument. The change in mass was achieved by dehydration, decomposition, and oxidation of specimen with respect to temperature and time. This characteristic thermogravimetric curve is also related to the molecular structure of the specimen. The thermal stability of wood pulp, PP and wood pulp-PP composite fibers was studied by thermogravimetric analysis. Figures 2, 3 and 4 show the loss of wt% with increasing temperature of wood pulp, PP and wood pulp-PP composite fibers. The thermal degradation of wood pulp is shown in Fig. 2. The wood fiber starts degrading at approximately 230 °C. The TG curve shows first mass loss step between room temperature and 230 °C and second mass loss step between 230 and 390 °C. A mass loss of 5.966% was measured between room temperature and 230 °C. The second mass loss step (decomposition step) occurred between 230 and 390 °C and the mass loss was found to be about 76.361%. The thermal degradation of the thermoplastic polymer (PP) started at about 370 °C and completed at around 483 °C which is presented in Fig. 3. In this case, the TG curve exhibits first

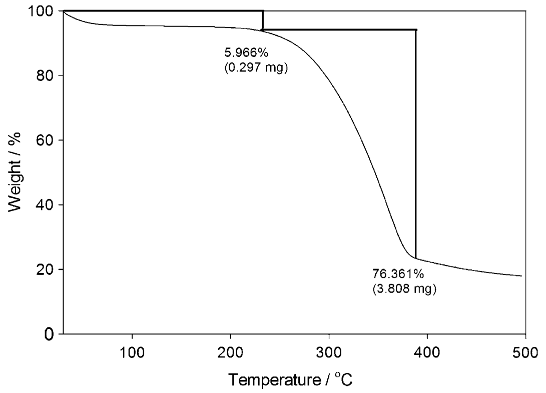

Fig. 2 The TG curve of pure wood pulp

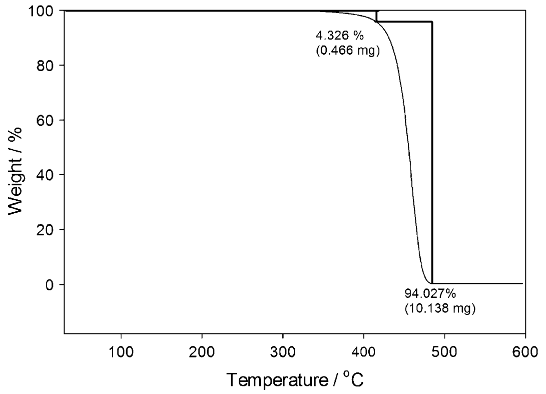

Fig. 3 The TG curve of neat PP

mass loss step between room temperature and 415 °C and second mass loss step between 415 and 483 °C. The mass loss that was measured was around 4.326% between room temperature and 415 °C. The second mass loss step (decomposition step) occurred between 415 and 483 °C and mass loss was found about 94.027%. The decomposition temperature can vary depending on the experimental conditions of a material. As shown in Fig. 4, thermal degradation of wood pulp-PP bio-composite fiber occured at different stages. The degradation initiated at approximately 266 °C (for fibers) followed by degradation at 379 °C (for PP). TGA curves of composite fibers showed that thermal degradation of composite fibers is a combined phenomenon of thermal degradation of wood pulp and PP. Thermal degradation of composite fibers onset at around 266 °C and completed at 493 °C, whereas onset point for wood pulp was 230 °C and degradation completed at round 390 °C. The TG curve also shows mass loss of 2.542% at 273 °C and 95.566% mass loss was observed at 439 °C during decomposition. A clear indication therefore is that, in the composite system, when wood pulp was incorporated in the matrix (PP), thermal degradation was delayed as compared to pure wood pulp without matrix. The explanation lies in the fact that within the bio-composite fiber, wood pulp was impregnated and covered by PP and the decomposition temperature of PP is considerably higher than wood pulp.

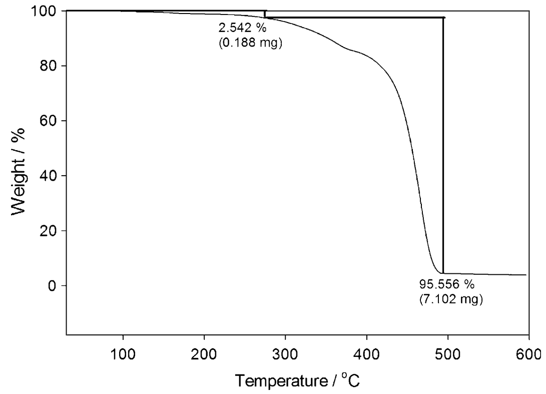

Fig. 4 The TG curve of bio-composite fibers (30% wood pulp/70% PP)

Differential scanning calorimetry

Differential scanning calorimetry is the widely used technique to determine the thermal behaviour of a material.

It determines the temperature and heat flows involving phase transition in polymer as a function of temperature. A number of crucial information regarding chemical and physical changes can be obtained by DSC studies including endothermic, exothermic effects, glass transitions and heat capacity changes [26]. The main function of DSC is to determine the differential heat flow between a reference material and sample. The melting behaviour of a material should be studied by DSC. It can also detect the thermal response of a specimen with changing temperatures or isothermally. The equal temperature profile is used for both a reference pan and a material, and the variation in heat flow is measured for every pan. When the heat is absorbed from a material, the transitions exhibit as endothermic peaks. If the heat is exited from material, the exothermic peaks appear during the transitions period [27]. An example of endothermic event is shown in Fig. 5. The endothermic or exothermic event depends on less or more heat flowing rate through the sample. For instance, a sample needs more heat to keep the temperature constant as like a reference sample. In that case, the heat is absorbed by the sample and the phase transitions will be endothermic. Similarly, the sample needs less heat to increase the temperature during the exothermic event such as crystallization. By measuring the temperature differences between the sample and reference material DSC calculates the amount of heat is released or absorbed when such thermal transitions are occurred [28–32]. DSC experiment is conducted using mainly two methods such as heat-flux DSC and power-compensation DSC. The main advantages of heat-flux DSC are ease of handling, straightforward

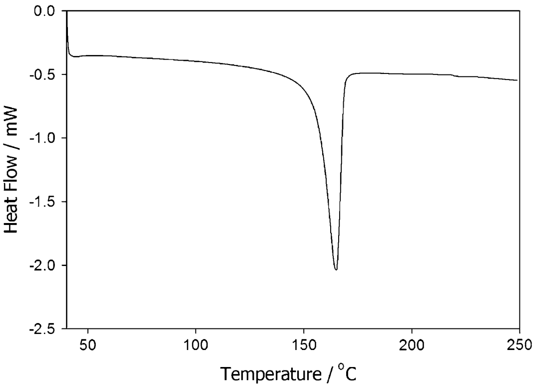

Fig. 5 DSC curve of neat PP

measurement and its relative robustness. DSC experiments carried out in this study followed the heat flux method.

The DSC thermographs (Figs. 5 and 6) revealed the thermal behaviour of PP in the wood pulp-PP bio-composite fibers. The melting temperature of PP was measured at 165 °C which is presented in Fig. 5 and almost similar melting phenomenon was observed in wood pulp –PP bio-composite fibers. Dual endothermic peaks appeared in bio-composite fibers as shown in Fig. 6. A weak endothermic peak was exhibited at 128 °C. The reason may be associated with impure polymeric materials or imperfections of wood pulp. Different degree of perfections might escalate the dual melting behaviour due to changing level of imperfections in the PP backbone and varying degrees of tacticity [33]. However, the incorporation of wood pulp in bio-composite fibers was found to alter the melting behaviour of the system to a minor extent. The melting temperature of PP was shifted to 167 °C in bio-composite fibers as shown in Fig. 6 as compared to melting temperature of pure PP which was found to be 165 °C.

Dynamic mechanical properties

DMA is an important instrument to investigate the visco-elastic behavior of plastic and polymer composite materials. The dynamic storage modulus, loss modulus and tan delta of wood pulp-PP bio-composite fibers (30% wood pulp/70% PP) are shown in Fig. 7. The storage modulus and loss modulus of composite fibers demonstrate nearly similar patterns and it can be classified into two different zones. The first zone is designated as glassy-rubbery transition in the temperature range of 40 to 65 °C and the second zone is the rubbery zone in the temperature range of 65 to 180 °C. Two transitions were observed in the spectra of storage modulus and loss modulus. As the temperature of the bio-composite fiber crosses glassy-rubbery state, the specimen starts becoming soft and both moduli start to reduce [34]. On the tan delta curves, there is a clear transition peak at around 70 °C (α relaxation shoulder) which can be attributed to the lamellar slip and changes in the crystalline state [35].

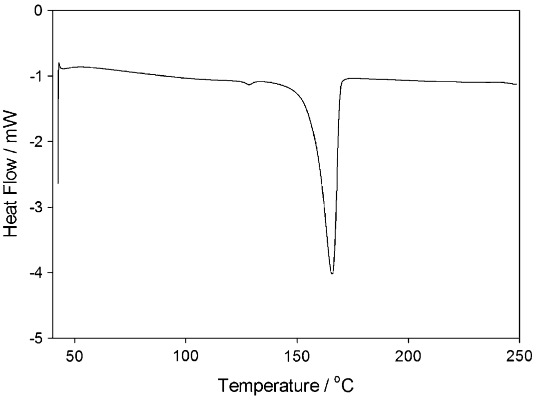

Fig. 6 DSC curve of bio-composite fibers (30% wood pulp/70% PP)

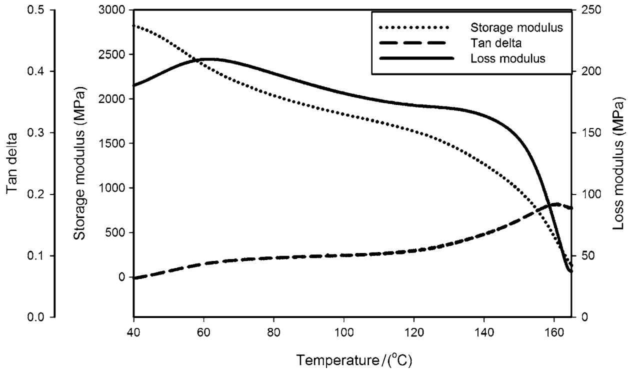

Fig. 7 Storage modulus, tan delta and loss modulus curves of bio-composite fibers

FTIR investigation

The nature of interaction between fiber and matrix was explored using FTIR spectroscopy. The C–H stretching vibrations were observed at about 2,800–3,000 cm^{-1} in pure wood pulp and all bio-composite fibers as shown in Fig. 8 [36, 37]. FTIR spectra of bio-composite fibers are

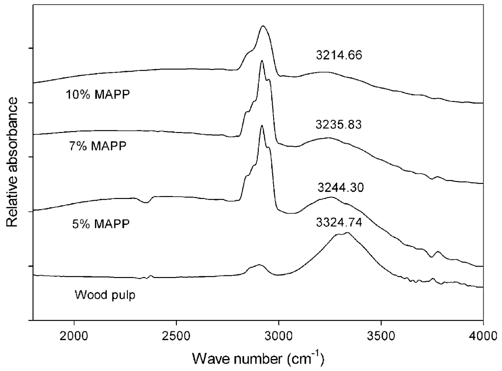

Fig. 8 FTIR spectra of 100% wood pulp and 30% wood pulp-PP bio-composite fiber with variation of MAPP percentage

significantly more intensive compared to spectrum of pure wood pulp. It is assumed that PP and MAPP would react with pure wood pulp thereby eventually affecting the peak intensity of C-H stretching in the bio-composite fibers. The mechanical properties of wood pulp-PP bio-composite fibers depend upon how strongly the fiber and matrix are linked by chemical bonds. The infra-red (IR) absorption peak of free –OH groups of wood fiber was observed (Fig. 8) at 3,324 cm^{-1}. As shown in Fig. 8, the hydroxyl absorption peak in all bio-composite fibers shifted to lower wave numbers (3,214 cm^{-1} from 3,324 cm^{-1}). The spectral shifting from higher to lower wave number confirms that hydrogen bonds were generated as ester linkage between fiber surfaces and matrix. These results agree well with the studies by Luo et al. [38]. However, no significant trend in spectral movement was detected in wood pulp-PP bio-composite fibers owing to use of various percentage of maleated polypropylene.

Conclusions

Thermal degradation behavior of wood pulp-PP bio-composite fibers has been analyzed by TGA. The degradation process was found to be one step degradation process. DSC studies helped in understanding the melting behaviour of the composite fiber which would help to choose an optimal temperature profile to process wood pulp and PP polymer in an extruder. Also, DSC results indicated the different stages of the melting and crystallization process of bio-composite fibers and the role of wood pulp reinforcements in crystallization. DMA studies provided visco-elastic properties of bio-composite fibers measuring the technical value of storage modulus, loss modulus and tan delta. Multiple transition zones were identified and a glassy-rubbery transition was observed in the temperature range of 40 to 65 °C. A second rubbery zone was detected in the temperature range of 65 to 180 °C. FTIR analysis indicated changes in absorption spectrum of wood pulp-PP bio-composite fibers as compared to the pure wood pulp which in turn relates to possible chemical linkages between the wood pulp and polypropylene matrix.

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