



Reactive processing preparation of sustainable composites from canola meal reinforced by chemical modification

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ABSTRACT

Canola meal (CM), a by-product of canola oil extraction, was modified by poly (styrene-co-glycidyl methacrylate) (PSG) and could potentially be used as a sustainable natural composite. Infrared analysis indicated that PSG could efficiently react with the proteins in CM and become covalently bonded. DSC results revealed that the modified CM composites showed new glass transition temperatures (T_g) decreasing with the introduction of PSG, which were attributed to the disruption of intermolecular association. Torque curves and melt flow index tests showed the flow property of the modified CM composites increased due to interference by PSG of the hydrogen and disulfide bonding among the protein species. DMA results showed greater amorphous character for the modified CM composites and new glassy plateaus with increased storage moduli, indicating a change in molecular structure and enhancement in mechanical property and usability below T_g . Furthermore, the thermostability, the tensile strength, and the elastic moduli of the modified CM composites increased because of the formation of cross-linked proteins in the CM composites, which will potentially increase the application value in some fields, such as single-use agricultural planting containers replacing high-impact polystyrene (HIPS) containers, and food or coffee trays.

1. Introduction

With the ever-growing environmental pressures caused by the widespread consumption of petroleum based polymers, there has been increased interest in biodegradable polymer products based on agricultural materials [1–3], and new approaches based on blending degradable natural materials with other biodegradable polymers such as poly(trimethylene terephthalate) (PTT) [4], poly(butylene adipate-co-terephthalate) (PBAT) [5], poly(butylene succinate) (PBS) [6], polyhydroxybutyrate (PHB) [7], and poly(lactic acid) (PLA) [8,9] have been used to prepare biodegradable composites. The development of biodegradable composites based on natural fillers in combination with synthetic biodegradable polymers is a preferred alternative to reduce the utilization of petroleum-based polymers [10]. However, the presence of these hydrophilic fillers will commonly reduce the mechanical properties of a composite because of their incompatibility with the polymer matrix and retention of water. Furthermore, the production costs with biodegradable composites are still unacceptably high for most disposable applications, such as food or coffee trays, containers, and

flower pots. Currently, some wholly naturally biodegradable bio-based polymers are commercially available, such as starch-based polymers, cellulose ester-based polymers, and protein-based polymers. However, even the use of these polymers translates into high production costs and limits the mechanical properties of final products [11].

Canola (*Brassica napus* L.) is an increasingly important oilseed crop worldwide. Canola seeds have an oil content of 44% [12]. After the oil is extracted, the canola meal contains 36% crude protein. Of this, cruciferin (12S globulin) and napin (2S albumin) are the two main storage canola proteins, which account for 60% and 20%, respectively of the total canola crude protein [13]. Although canola protein possesses a well-balanced amino acid composition, the meal is not used in human food applications or animal feed because of the presence of glucosinolates (interfere with thyroid function which inhibits growth), erucic acid (a potential toxin affecting the heart), phytates (species that strongly bind polyvalent metal ions such as zinc and iron, and make them unavailable for metabolism), and phenolics (bitter flavored species) [14]. Nevertheless, due to its high storage protein content and low cost, canola meal (CM) is ideal for high-value non-food applications

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such as adhesives, plastics, and biocomposites, which will in turn have the potential to enhance the economics of the canola industry [15]. Additionally, the development of wholly naturally biodegradable CM composites with acceptable mechanical properties could efficiently decrease societal dependency on petroleum-based polymers and reduce the production cost of the composite. However, literature on developing commercially viable industrial products from CM has not been found to date.

Recently, researchers have started to develop corn gluten meal (CGM)/polymer composites. Plasticized CGM has been blended with polymers like PBS [10], poly(hydroxybutyrate-cohydroxyvalerate) (PHB-V) [16], poly(ϵ -caprolactone) (PCL) [17], PBS [18], PBAT [19], and polyethylene [20] to produce CGM-based composites. CGM/wood fiber composites with 10–50% wood fibers, plasticized by glycerol, water and ethanol, were extruded to develop low-cost biodegradable composites [21]. Similarly, camelina meal was used to prepare biodegradable composites by blending with recycled newspaper [22] and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3,4)HB) or PBS [7]. The only studies known to involve canola biomass as a bioplastic focused on the wet-casting technique [23–26], and then only with more costly protein isolates rather than CM. Because of the availability and low cost of CM, there is a strong motivation to use suitably modified CM for the manufacture of biodegradable plastics. One of the objectives in this research is to use CM as the matrix to produce low-cost biodegradable composites that are anticipated to replace some wood fiber disposable products, such as egg cartons, organic waste containers, flower pots, and food or coffee trays to conserve limited forestry resources. Like other agricultural byproducts, CM consists of crude fibers and canola proteins and thus is difficult to be plasticized and possesses poor mechanical property. In this research, CM composites plasticized with glycerol and water were prepared via reactive extrusion for the first time. Meanwhile, to further increase the mechanical property of CM composite, an epoxy copolymer, poly(styrene-co-glycidyl methacrylate) (PSG) was prepared as a chain extender to reinforce the composite. The properties of the modified CM composites were investigated and the effects of the polymeric chain extender on the properties of the modified CM composites were also studied.

2. Materials and methods

2.1. Materials

Glycerol, xylene, styrene, glycidyl methacrylate (GMA), and benzoyl peroxide (BPO) were all purchased from Sigma Aldrich and used as received. Conventional dark-seeded (*Brassica napus*) defatted canola meal was provided by Bunge Canada (Altona, Manitoba). The raw CM was tested for composition which showed 36.5% protein, 11.7% crude fibre, 9.8% moisture, and 7.3% ash, in the labs of the Department of Food Science at the University of Manitoba, Canada. The meal was ground into powder using a mill (A10 analytical mill, Ika Works, Wilmington, NC) to pass through a 250 μ m sieve for use.

2.2. Synthesis of PSG copolymer

Initiator, BPO (0.25 g, 1.0 mmol) was dissolved in a mixture of GMA (2 g, 14.1 mmol) and styrene (28 g, 269.2 mmol) monomers. Xylene solvent (250 mL) was added to a three-necked round-bottomed flask with a magnetic stir bar and heated to 90 °C. The mixture, including monomers and initiator, was added drop-wise into xylene solvent during a 1 h period, with stirring. The reaction proceeded at 90 °C for 4 h to obtain the copolymer, PSG (29.1 g, 91%).

2.3. Preparation of CM composites

Raw CM (100 g) was mixed with 40 g of glycerol and 10 g of distilled water by a food mixer, and the mixture was conditioned at least

24 h at room temperature for the next step. The mixture of raw CM/glycerol/water was processed in a Haake Rheomix 600p mixer at 135 °C and 80 rpm for 5 min. The transient torque curve was recorded by the software during processing. The resulting mixture was compression molded into a film at 135 °C for 5 min to obtain the unmodified CM composite. To prepare the modified CM composites, 1 wt%, 2 wt%, 5 wt%, or 10 wt% of PSG based on the total weight was mixed with the mixture of raw CM/glycerol/water before the processing and the same processing procedure was followed as used with the unmodified CM composite. The transient torque curves were also recorded by the software during the reaction. Compression molded films of the modified composite samples with 1 wt%, 2 wt%, 5 wt%, or 10 wt% PSG were denoted as CM-PSG1, CM-PSG2, CM-PSG5, and CM-PSG10, respectively. All of the samples were stored at 5 °C until further testing.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

Each of the unmodified and modified CM composites were ground into powders and cleaned by soxhlet extraction with refluxed xylene for 24 h to remove unreacted PSG before infrared analysis. The cleaned samples were dried in a vacuum oven for 24 h. Infrared spectra of the purified unmodified and modified CM composites were recorded between 4000 and 500 cm^{-1} with a Digilab FTS 7000 spectrometer (Digilab USA; Randolph, MA) equipped with a thermoelectrically cooled deuterated tri-glycine sulphate (DTGS) detector using an attenuated total reflectance accessory at a resolution of 4 cm^{-1} by 64 scans. A half-band width of 15 cm^{-1} and a resolution enhancement factor of 1.5 with Bessel apodization were employed. Spectra were subjected to ATR correction (Algorithm 1, correction 1.000), deconvolution (k factor 1.9, half width 24, Bessel apodization), and a multipoint linear baseline correction using Win-IR Pro software.

2.5. Differential Scanning Calorimetry (DSC)

DSC analysis was performed using a differential scanning calorimeter (Q20 DSC, TA Instruments, New Castle, DE, USA) equipped with a refrigerated cooling system. A high-volume pan was loaded with a film sample and then hermetically sealed. The scanned temperature range was from 20 to 150 °C at a heating rate of 10 °C/min with a nitrogen purge. The instrument was calibrated with indium and an empty pan was used as a reference.

2.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of the CM composite samples were measured using a dynamic mechanical analyzer (DMA) Q800 (TA Instruments, New Castle DE, USA) operated in a multi-frequency strain mode. The specimens were cut into a nominal dimension of 55 mm \times 12 mm \times 3 mm and were conditioned in a laboratory atmosphere (22 °C and 55% relative humidity) for 48 h prior to testing. Each specimen was mounted on the dual cantilever beam clamp, and an amplitude of 15 μ m was applied to the specimen at a frequency of 1 Hz. The storage modulus, loss modulus, and tan delta were recorded as the samples were heated from ambient temperature to 150 °C at a heating rate of 5 °C/min. Each sample had two replicates.

2.7. Mechanical property

Mechanical properties were measured using a Com-Ten testing system (model 701SN) with a 0.5 kN load cell according to the Standard Test Method for Tensile Properties of Plastics (ASTM D638). Type-IV tensile specimens were prepared by die cutting and were conditioned in a laboratory atmosphere (22 °C and 55% relative humidity) for 48 h prior to tensile testing. A crosshead speed of 10 mm/min was used. The tensile testing was conducted at ambient conditions (23.8 °C, 50% RH). The stress, strain, tensile strength, elongation at break, and elastic

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