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Extraction, Characterization of Components, and Potential Thermoplastic Applications of Camelina Meal Grafted with Vinyl Monomers

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ABSTRACT: Camelina meal contains oil, proteins, and carbohydrates that can be used to develop value-added bioproducts. In addition to containing valuable polymers, coproducts generated during the production of biofuels are inexpensive and renewable. Camelina is a preferred oilseed crop for biodiesel production because camelina is easier to grow and provides better yields. In this research, the components in camelina meal were extracted and studied for their composition, structure, and properties. The potential of using the camelina meal to develop thermoplastics was also studied by grafting various vinyl monomers. Oil (19%) extracted from camelina meal could be useful for food and fuel applications, and proteins and cellulose in camelina meal could be useful in the development of films, fibers, and thermoplastics. Thermoplastic films developed from grafted camelina meal had excellent wet tensile properties, unlike thermoplastics developed from other biopolymers. Camelina meal grafted with butylmethacrylate (BMA) had high dry and wet tensile strengths of 53.7 and 17.3 MPa, respectively.

KEYWORDS: *camelina, biodiesel, coproducts, biothermoplastics, grafting*

INTRODUCTION

The quest to replace petroleum-based fuels and achieve energy independence is being aggressively pursued in the United States. New energy sources are being constantly explored to develop indigenous, renewable, and sustainable sources for energy. Biofuels from food crops and biomass and wind, solar, and tidal power are being harnessed as clean energy alternatives to gasoline. Food crops such as corn, soybeans, wheat, and canola are some of the sources being explored for biofuel production. Whereas ethanol is predominantly produced from corn, soybeans and canola have so far been the main sources for biodiesel production. However, algae, jathropa, and other sources are being studied as potential sources for biodiesel.

Camelina is projected to be one of the most promising oilseed crops for biodiesel production. Camelina is relatively easy to grow, requiring minimal resources, has a high yield of seeds, and is projected to be more profitable than canola or rapeseed oil.[1] It has been estimated that camelina yields a net return of $169 per acre compared to $52 for canola.[2] However, producing biodiesel from oilseeds generates up to 70% of the seed as one of the major coproducts. Studies have suggested that new markets have to be developed for the coproducts of biofuel production to make the biofuels economically competitive with and sustainable as compared to fossil fuels.[3] The meals are generally composed of proteins, carbohydrates, and oil and mostly used as animal feed. However, the amount of meal that can be used to feed animals is restricted, leading to excess availability of the meal on the market.[4] Meals from oilseeds currently sell for $150−250 per ton, much lower than synthetic polymers such as polyethylene and polypropylene that sell at $1750−2000 per ton. In addition to being inexpensive, oil meals are derived from renewable resources and are biodegradable.

The large availability and low cost make oilseed meals attractive raw materials, especially the proteins and carbohydrates, for various applications.[5] Efforts have been made to utilize the coproducts for various applications. It has been demonstrated that the oil, protein, and carbohydrates in corn distillers dried grains (DDG) can be extracted and used to develop fibers, films, and absorbents.[6,7] The corn protein zein in DDG was found to have similar properties compared to commercially available corn zein. Similarly, the oil in DDG was similar to corn oil. Hemicellulose in DDG was found to have high absorbency, and the cellulose extracted from DDG was used to make films.[7] In another approach, the coproducts of biofuel production have been used to develop thermoplastics without the need to separate the components. For instance, DDG was used as reinforcement and compression molded with synthetic polymers to develop composites.[8]

The nonthermoplastic nature of the components in coproducts of oilseeds is one of the major limitations of using the coproducts for industrial applications. To overcome the poor thermoplasticity, adding plasticizers and/or chemical

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modifications to impart thermoplasticity has been considered. Etherification and esterification were used to modify both the carbohydrates and proteins in corn DDG and develop thermoplastics.[9,10] It was found that acidic conditions during esterification (acetylation) provided DDG acetates with a high degree of substitution and better thermoplasticity than acetylation under alkaline conditions.[9,10] Although coproducts from oilseeds processing such as soy oil and soy protein concentrate have been used for various applications, there are no reports on using soy meal or canola meal for industrial applications.[5] Similar to etherification and esterification, grafting of synthetic monomers is another common approach of making biopolymers thermoplastic. We have shown that grafting methyl methacrylate (MMA) onto chicken feathers makes the feathers thermoplastic and useful in the development of thermoplastic products.[11]

Utilizing the coproducts of biofuel production for high-value applications will help to add substantial value, reduce the cost of biofuel, and make biofuels competitive with fossil fuels. In this research, camelina meal and the components in camelina meal have been characterized for their structure and properties. The potential of using the components in camelina meal for various applications has also been studied. Camelina has been grafted with various acrylic monomers, and the potential of developing thermoplastic products from grafted camelina meal has been investigated.

MATERIALS AND METHODS

Materials. Camelina meal was procured from a commercial camelina seed processor. The meal was used as received for studying the composition and characterizing the structure and properties. In addition to using the raw meal, the meal was Soxhlet extracted using ethanol or acetone. Ethanol extraction was done to remove the oil and study the composition of the oil-free meal. Acetone extraction (which partially removed oil) was performed to avoid interference from oil during calculation of the grafting parameters and to understand the effect of oil on the thermoplasticity of camelina meal and its components. Methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA), initiators, and other chemicals used in the study were of reagent grade and purchased from VWR International, Bristol, CT.

Methods. A schematic of the processes used to extract the components from camelina meal is shown in Figure 1. Initially, the meal was treated with a 4:1 ratio of anhydrous ethanol and repeatedly (until a clear solvent was obtained, typically after four times) Soxhlet extracted to remove oil. After extraction, the ethanol was evaporated and oil was collected for analysis. The oil-free meal was treated with a 0.1% NaOH solution at 30 °C for 1 h with an alkali solution to meal ratio of 20:1 to extract proteins. Treated meal was centrifuged at 8000 rcf for 10 min. Supernatant obtained was collected, and the proteins in the supernatant were precipitated by adding dilute acetic acid. Proteins obtained were washed thoroughly and collected. Oil- and protein-free meal was considered as crude cellulose consisting mainly of hemicellulose, cellulose, and lignin. Enzymes (Spirizyme) and shearzyme were used to remove lignin and starch from the crude cellulose and obtain pure carbohydrates (cellulose and hemicellulose). Enzyme treatment was carried out using a 1:1 ratio of the two enzymes (20% on weight of the raw material) at pH 5.0 and 50 °C for 48 h. After the enzyme treatment, the meal was treated with a 1:10 ratio (meal to alkali) of 5% NaOH solution at 90 °C for 2 h to remove hemicellulose. Finally, the pure cellulose obtained was washed using boiling water, dried, and collected for analysis.

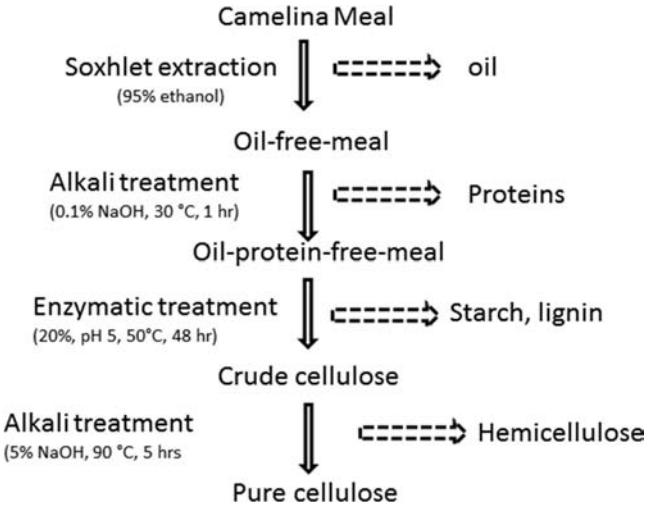

Figure 1. Schematic of the process used to extract the components from camelina meal.

Compositional Analysis. The cellulose and hemicellulose in the samples were measured on the basis of the neutral detergent fiber (NDF) and acid detergent fiber (ADF). NDF is the amount of cellulose, hemicellulose, and lignin, and ADF is the amount of cellulose and lignin. Therefore, the difference between NDF and ADF indicates the amount of hemicellulose. Lignin was determined as Klason lignin according to ASTM standard D 1106-96, and ash was determined according to ASTM E1755-01. At least three replications were done for each analysis, and the average ± one standard deviation is reported. Amino acids in the proteins extracted from the meal were determined. The proteins were hydrolyzed using 6 M hydrochloric acid under argon atmosphere and digested for 20 h at 110 °C. The samples were dried and redissolved in 200 μL of 0.02 M HCl, and later 50 μL of the sample was injected into an amino acid analyzer (Hitachi L-8800A). Corrections were made for dilution errors using norleucine as an internal standard.

Thermal Behavior. The thermal behavior of the components extracted from camelina meal and the grafted films was determined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). For TGA, samples (8−10 mg) were placed in a Sigma T300 analyzer and heated at a rate of 20 °C/min from ambient to 600 °C under nitrogen atmosphere. DSC was performed using a Mettler Toledo thermal analyzer (D822e) under nitrogen atmosphere. Oven-dried samples (7−8 mg) were placed in sealed aluminum crucibles and heated at 20 °C/min from 25 to 250 °C to obtain the DSC curves.

Crystallinity of Cellulose. The percent crystallinity and nature of crystalline peaks in the pure cellulose and crude cellulose extracted from camelina meal was determined using X-ray diffraction. Samples were compressed into pellets and placed in a Rigaku D-max/B$\theta/2\theta$ X-ray diffractometer (Rigaku Americas, Woodlands, TX, USA) with Bragg−Brentano parafocusing geometry, a diffracted beam monochromator, and a copper target X-ray tube set to 40 kV and 30 mA. Samples were scanned from 5 to 45 °C (2θ), and the peaks obtained were analyzed using Microcal Origin. The percent crystallinity was calculated on the basis of the integral area difference between the amorphous regions and crystalline regions in the samples after subtraction of the background and air scatter.

Grafting Acrylates onto Camelina Meal. Camelina meal was grafted with various acrylates, and the grafting conditions were optimized. The acrylates selected were MMA, EMA, and BMA, and the steps involved in grafting the vinyl monomers onto the camelina meal are shown in Scheme 1. Grafting with EMA and BMA was done using conditions that provided a similar grafting ratio when the camelina meal was grafted with MMA under the optimized conditions. Grafting was performed after slowly deoxygenating the flask by passing nitrogen. Reaction temperatures varied from 50 to 80 °C, and reaction time was varied from 0.5 to 2 h using potassium persulfate as initiator and sodium bisulfite as reductant. The initiator and reductant dissolved in water were added along with the monomer (20−60% on weight of camelina meal) into a flask containing the meal. The

Scheme 1. Steps Involved in Grafting Vinyl Monomers onto Camelina Meal

Step 1 Chain initiation

$S_2O_8^{2-} + HSO_3^- \longrightarrow SO_4^{-}\cdot + HSO_3\cdot + SO_4^{2-}$

$SO_4^{-}\cdot + H_2O \longrightarrow SO_4^{2-} + H^+ + HO\cdot$

Camelina Meal — H + $SO_4^{-}\cdot$ / $HSO_3\cdot$ / $HO\cdot$ ⟶ Camelina Meal

"H" in Camelina Meal — H denotes hydrogen atom on — OH, — NH_2, —COOH, — SH.

Camelina Meal + M ⟶ Camelina Meal — M·

M denotes vinyl monomer.

Step 2 Chain propagation

Camelina Meal — M· + M ⟶ Camelina Meal — M — M·

Camelina Meal — M — M· + M ⟶ Camelina Meal—[M]$_{Z}$ M·

Camelina Meal—[M]$_{(n-1)}$M· + M ⟶ Camelina Meal—[M]$_{n}$ M·

Step 3 Chain termination

Camelina Meal—[M]$_{m}$ M· + Camelina Meal—[M]$_{n}$ M· ⟶ Camelina Meal—[M]$_{(m+n)}$ M + Camelina Meal_[M]$_{n}$ M

Camelina Meal—[M]$_{m}$ M· + Camelina Meal—[M]$_{n}$ M· ⟶ Camelina Meal—[M]$_{(m+n+2)}$ / Camelina Meal

grafting reaction was continued with rigorous stirring for the desired time and the predetermined temperature. The graft polymerization was terminated by adding 1 mL of 2% paradioxybenzene. The grafted meal was neutralized by washing in water until the pH of the water was 7, and the grafted meal was later dried in an oven at 50 °C. The grafted meal was then extracted in acetone for 24 h to remove the homopolymers.[11] The grafted meal without homopolymers was used for compression molding to study the effect of monomer concentration and type of monomers.

Effect of Homopolymers. Grafting reaction results in the formation of monomers grafted onto the meal and some of the monomers that react with themselves and form homopolymers. Because formation of the homopolymers leads to lower grafting efficiency and the homopolymers are not expected to be reacted with the meal, it is necessary to understand the effect of the homopolymers on the tensile properties of the grafted camelina meal. To study the effect of homopolymers, films containing various levels of homopolymers were prepared by reacting the monomer (MMA) at 70 °C for 1 h with 5% potassium persulfate and 2% sodium bisulfite on weight of the monomer. Camelina meal was grafted with 1.8 mmol/g BMA, and all of the homopolymers were extracted as described in our previous paper.[11] The homopolymers (0, 25, 50, and 75% on weight of the meal) that were synthesized in a separate experiment were dissolved in acetone, and the grafted camelina meal was added into the homopolymer solution. Acetone was evaporated, and the mixture of homopolymers and grafted camelina meal was then dried as described earlier,[11] powdered, and used to compression mold films at 150 °C for 8 min. To understand the effect of the grafted meal in the films with homopolymers, the homopolymers were also mixed with the ungrafted camelina meal. The mixture was compression molded into films at 150 °C for 8 min.

Evaluating the Grafting of Monomers. The efficiency of grafting the monomers onto camelina meal was determined in terms of percent grafting and percent grafting efficiency, molar grafting ratio (mmol/g), and percent monomer conversion. Percent grafting describes the percentage by weight of the monomers grafted onto the meal; grafting efficiency (%) indicated the weight percent of monomers grafted to the initial weight of the monomers used and includes both the grafted polymers and the homopolymers. The percent monomer conversion was determined by titrating the double bonds in the residual filtrate obtained after grafting.[12] The molar grafting ratio denotes the mole number of monomers grafted onto the camelina meal to the weight of the meal used for grafting. Details of the methods used to calculate the grafting parameters are described elsewhere.[11]

Developing Thermoplastics. Raw camelina meal and camelina meal grafted with acrylic monomers were compression molded into films. The raw camelina meal was mixed with various amounts of glycerol and placed between aluminum sheets and compression molded at 180 °C for 2 min on the basis of our experiences in developing thermoplastics from DDG, feathers, and plant proteins.[9−11] After compression, the films formed were collected to determine their tensile properties. The grafted camelina meal was mixed with 10% glycerol and compression molded at 160 °C for 8 min to form films. Pure (100%) and homopolymers mixed with grafted and ungrafted camelina meal were compression molded at 150 °C for 8 min. The homopolymers flowed through the press when compression molded at 160 °C, and therefore a lower temperature (150 °C) was used to study the effect of homopolymers.

Tensile Properties of the Thermoplastic Films. Compression molded thermoplastic films from camelina meal were conditioned at 21 °C and 65% relative humidity until the samples equilibrated to a constant weight. Tensile tests were performed on the samples according to ASTM D882 using a crosshead speed of 10 mm/min and gauge length of 50 mm. At least 10 samples from three different films were tested, and the average ± one standard deviations is reported.

To determine the wet stability of the films, the films were immersed in distilled water for 30 min at room temperature (21 °C). After 30 min, the films were immediately tested for tensile properties. Average ± standard deviation of the wet tensile properties is reported.

RESULTS AND DISCUSSION

Composition. Camelina meal is mostly composed of carbohydrates and proteins as shown in Table 1. Camelina meal contains much higher amounts of oil (10−12%), proteins, and cellulose than DDG (8−11, 25−30, and 9−16% of oil, protein, and cellulose, respectively).[7] About 20% protein was obtained after the alkaline treatment of the oil-free meal. Some of proteins that were hydrolyzed during the alkali treatment were removed during washing, and some proteins were unextractable and should have remained in the meal. Table 2 shows a comparison of the amino acids in the camelina meal compared to the three common plant proteins. Camelina

Table 1. Composition of Camelina Meal and Components Extracted from the Meal

	NDF	ADF	protein	lignin	ash
camelina	30.7	17.2	40	12.2	5.7
oil- and protein-free	59.1	31.6		9.2	7.6
cellulose	78.6	67.9		19.7	11

Table 2. Comparison of the Major Amino Acids (Grams per 100 g of Protein) in Camelina Proteins with Other Common Plant Proteins[18]

	camelina	soy proteins	wheat gluten	zein
glutamic acid	19.7	19.0	28.7	24.2
arginine	11.9	7.5	3.2	2.4
aspartic acid	8.7	11.5	4.2	4.2
leucine	8.2	8.1	7.2	17.7
cysteine	6.5	1.3	1.7	-
phenylalanine	5.5	5.2	4.4	6.0
glycine	5.5	4.1	3.9	1.3
valine	5.1	5.0	2.9	3.4
alanine	4.8	4.2	3.5	8.4
serine	4.8	5.2	5.7	4.5
lysine	3.9	6.2	1.4	0.5
tyrosine	3.2	3.8	2.8	4.3
histidine	2.8	2.6	1.7	0.9

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proteins had a considerably different amino acid composition compared to the common plant proteins. Most notably, camelina proteins contain about 6.5% of cysteine, similar to that in chicken feathers, whereas soy proteins and wheat gluten have considerably lower amounts of cysteine.[13] Cysteine cross-links proteins through disulfide linkages, and proteins containing high amounts of cysteine are difficult to process (dissolve) and use for the development of products. Camelina proteins also had higher amounts of arginine, whereas other amino acids were comparable to one of the common plant proteins. Proteins from the meal could be used to develop films, fibers, thermoplastics, or composites for various applications.[14−16]

The crude cellulose obtained after removal of the oil and proteins contains 60% cellulose, about 9% lignin, and 7.6% ash, and the remaining components should mainly be hemicellulose and moisture. Removing starch using enzymes and subsequent treatment to remove hemicellulose resulted in pure cellulose consisting of 69% cellulose, 19% lignin, and 11% ash. The composition of the camelina cellulose obtained after purification contained about 20% lignin and was considerably different from the cellulose obtained from DDG.[7] Cellulose from DDG had much lower ash (1.6%) and lignin (0.4%) contents than the cellulose obtained from camelina meal. Previously, we have demonstrated that the cellulose extracted from DDG could be used to develop films or as a dietary fiber.[7] Camelina cellulose could also be useful to develop films or for other applications.

Thermogravimetric Analysis. The TGA curves for the camelina meal, oil- and-protein-free meal, and cellulose obtained from the meal are shown in Figure 3. All three

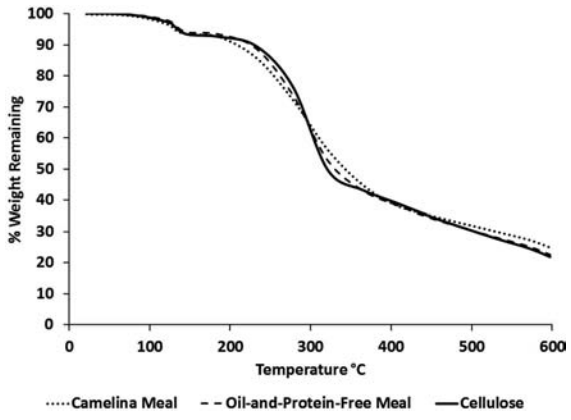

Figure 2. TGA curves of camelina, oil- and protein-free meal, and cellulose extracted from the meal.

samples had very similar weight loss up to about 150 °C. The camelina meal showed a slightly higher weight loss between 230 and 320 °C, and the cellulose sample had a higher weight loss than the other two samples between 320 and 360 °C. These differences should be due to the different constituents in the meal that degrade at different temperatures. At the highest temperature of 600 °C, the weight losses of the meal, oil- and-protein-free meal, and the camelina cellulose were 94, 92, and 89%, respectively. Because the meal had the lowest and the cellulose the highest ash content, the meal had the highest and the cellulose the lowest weight loss. The difference in weight loss (5%) is consistent with the difference in ash content (5.3%). Grafting considerably increased the thermal stability of

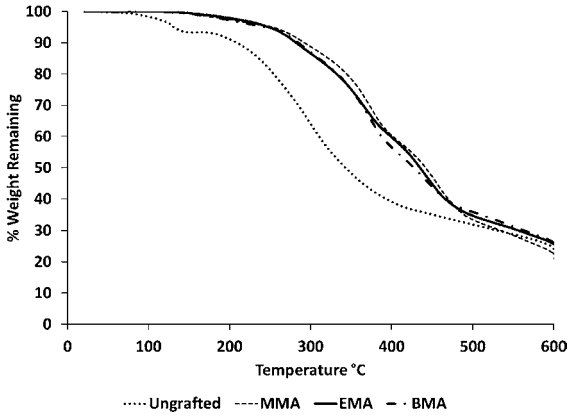

Figure 3. Thermal stability of ungrafted and camelina meal grafted with methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA).

the films up to about 500 °C, as seen from Figure 3. However, there was no major difference in thermal stability between the three monomers grafted onto the meal.

DSC analysis of the camelina samples showed melting peaks at different melting temperatures as seen from Figure 4. The

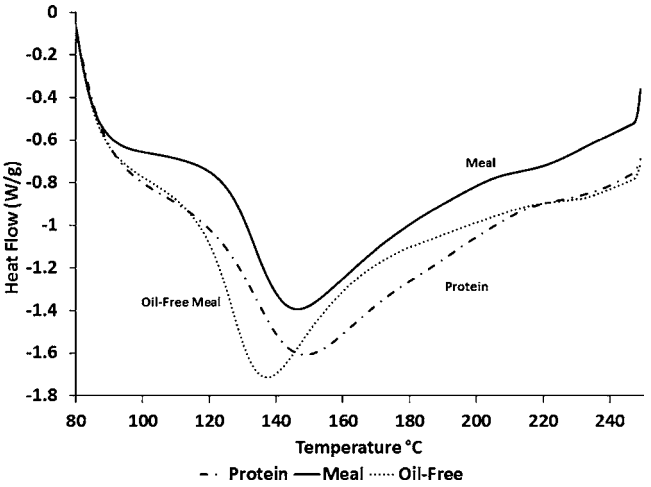

Figure 4. DSC thermograms of the raw meal, oil-free meal, and proteins extracted from the meal.

meal had a very broad melting range with a peak at 146.7 °C and the oil-free meal had a narrow and lower melting peak at 136.7 °C, whereas the proteins extracted from the meal had a broad and slightly higher melting peak at 148 °C. The difference in melting behavior should mainly be due to the variation in the composition of the samples. In addition, oil in the meal could act as a plasticizer and reduce the melting temperature of the proteins and carbohydrates. The ability of the camelina meal and its components to melt indicated that the meal could be compression molded to develop thermoplastic products.

X-ray Diffraction. Figure 5 shows that the pure camelina cellulose had two typical and distinct diffraction peaks belonging to cellulose. The main cellulose peak is seen at a 2θ angle of approximately 22°, and the second broad peak is seen between 15 and 17°. The broad peak due to the presence of noncellulosic impurities is a combination of the two cellulose peaks at 14.9 and 16.6° corresponding to the $^{-}110$ and 110

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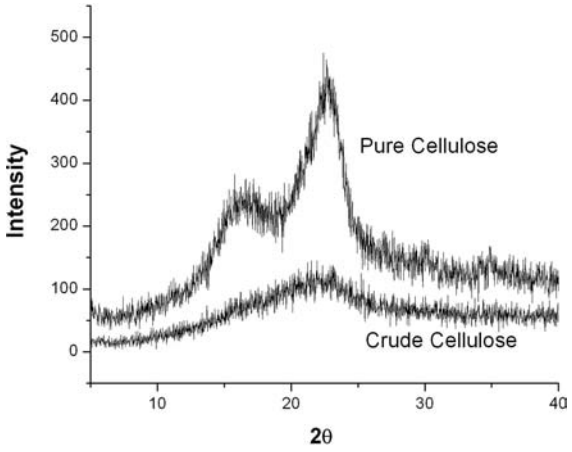

Figure 5. X-ray diffractograms of crude cellulose and pure cellulose extracted from camelina meal.

planes, respectively.[17] The crude cellulose does not show any clear peak except for the broad peak at 22° because of the low cellulose content in the sample. The pure cellulose had a percent crystallinity of 30%, much lower than that in cotton cellulose (65−70%). The lower percent crystallinity would make the camelina cellulose more hydrophilic than cotton cellulose but could affect the mechanical properties of products made from the camelina cellulose.

Tensile Properties of Unmodified Camelina Meal. Tensile properties of films compression molded from the camelina meal with and without glycerol are shown in Table 3.

Table 3. Tensile Properties of Compression Molded (160 °C, 2 min) Camelina Meal with and without Glycerol

% glycerol	peak stress, MPa	breaking elongation, %	modulus, MPa
0	3.0 ± 1.0	0.7 ± 0.3	1241 ± 400
5	2.8 ± 1.1	0.8 ± 0.4	1063 ± 194
10	2.3 ± 0.6	1.3 ± 0.4	566 ± 70
20	0.4 ± 0.1	1.0 ± 0.4	93 ± 26

Camelina meal could be compression molded into films without the need for additional plasticizers because oil in the meal acted as a plasticizer. The role of oil as a plasticizer was confirmed by using meal after extraction of the oil for compression molding. It was not possible to compression mold the meal without oil even after the addition of 20% glycerol. Even with the oil in the meal, the films obtained without glycerol had low elongation (0.7%) but high strength and modulus. Adding glycerol increased the elongation up to 1.3% but decreased the strength and modulus. At 20% glycerol, the meal had good thermoplasticity and formed thin films, but the films had relatively lower strength and modulus. Although the camelina meal was compression molded into films with good strength, the films had low elongation even after using glycerol compared to films made from other biopolymers such as wheat gluten and soy proteins.[15,16] Because camelina meal is a mixture of proteins, carbohydrates, and oil, some of the components, especially the carbohydrates, may not melt under the compression conditions used and acted as reinforcement, increasing the strength but decreasing the elongation of the films. DDG, which also contains oil, proteins, and carbohydrates, did not melt even after using glycerol.[18] Although the unmodified camelina meal could be compression molded into films with good tensile properties, the films had poor wet stability. Compression molded camelina films disintegrated when immersed in water and were too weak when conditioned at high humidities. Therefore, grafting of acrylic monomers was performed to improve the thermoplasticity and water stability of the camelina meal.

Effect of Amount of Homopolymers on Tensile Properties. The effect of different amounts of homopolymers mixed with grafted and ungrafted camelina meal on the tensile properties of the films obtained is shown in Figure 6 and Table 4. Without any homopolymers, the films obtained from the grafted camelina meal had considerably low tensile strength (7 MPa) and elongation (2.5%) due to the poor thermoplasticity of the grafted meal. Increasing the amount of homopolymers to 25% increased the strength substantially to 48 MPa, but there was a marginal increase in the breaking elongation to 3%. Further increase in homopolymer content to 50% did not show any considerable change in the strength or elongation of the films. There was a considerable decrease in the strength (1.7 MPa) but increase in elongation (42.7%) when the homopolymer content was 75%. The strength decreased further from 2 to 1 MPa but elongation increased substantially to 257% from 43% for the films made from 100% homopolymers. The homopolymers are thermoplastic and have high elongation, and therefore adding homopolymers provided better thermoplasticity and higher elongation to the films. The homopolymer itself had low strength but very high

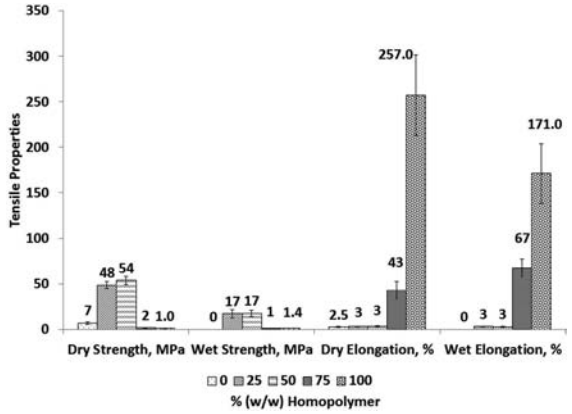

Figure 6. Effect of homopolymer content on the dry and wet tensile properties of camelina meal grafted with butyl methacrylate (BMA) at a grafting ratio of 1.8 mmol/g.

Table 4. Effect of the Form of Homopolymers in the Films on Tensile Properties of Grafted (1.8 mmol/g BMA) and Ungrafted Camelina Meal

	homopolymer + grafted camelina		homopolymer + ungrafted camelina	
% of homopolymer	peak stress, MPa	elongation, %	peak stress, MPa	elongation, %
0	7.0 ± 1.4	2.5 ± 0.7	7.0 ± 1.4	2.5 ± 0.7
25	48.4 ± 3.7	3.0 ± 0.6	1.7 ± 0.3	1.7 ± 0.2
50	53.7 ± 4.4	3.1 ± 0.7	1.7 ± 0.3	1.8 ± 0.3
75	1.7 ± 0.1	42.7 ± 9.7	1.3 ± 0.3	2.1 ± 0.6
100	1.0 ± 0.2	257 ± 44	1.0 ± 0.2	257 ± 44

elongation and, therefore, the films with 75% homopolymers had low strength but relatively much higher elongation.

Although the grafted camelina meal without homopolymers was compression molded into films with good strength and elongation, the films were too weak in water and could not be tested. Without homopolymers, the grafted meal did not melt completely and swelled considerably when immersed in water and lost most of its strength. Improved thermoplasticity with the addition of homopolymers provided the films with good dry strength and, therefore, higher wet strength than the films without homopolymers. In addition, adding the hydrophobic homopolymers decreased the hydrophilicity of the films, which also leads to better wet tensile properties.

Homopolymers were added into the ungrafted meal and compression molded into films to understand the effect of grafting on the thermoplasticity and mechanical properties of the films. As seen from Table 3, films made from homopolymers and ungrafted camelina meal had poor tensile properties. There was no significant change in the strength or elongation of the films when the homopolymer content was increased from 25 to 75%. This suggested that the films developed were like composites, where the ungrafted meal acted as reinforcement and the homopolymers as matrix. The ungrafted meal did not melt and merely acted as filler for the homopolymers. There was considerable incompatibility between the homopolymers and the ungrafted meal, leading to films with poor tensile properties. Grafted meal partially melts and the homopolymers had better compatibility with the grafted meal, providing good tensile strength and elongation to the films containing grafted meal and homopolymers compared to the films made from the ungrafted meal and homopolymers. Therefore, both grafted monomers and an optimum level of homopolymers are necessary to obtain films with good tensile properties.

Effect of Monomer Concentration on Tensile Properties. Figure 7 shows the influence of the initial concentration of monomer used on the dry and wet tensile properties of camelina meal grafted with MMA compared to the camelina meal compression molded without grafting (0% monomers). Increasing monomer concentration increased the percent grafting ratio, which was 1.7, 2.8, and 5.0 mmol/g when grafted using 20, 40, and 60% monomers. MMA grafted camelina meal showed considerably higher (twice) tensile strength than the unmodified camelina meal even when grafted using low (20%) monomers. Further increase in monomer concentration did not show any significant change in the tensile strength, although the grafting ratio increased considerably. Elongation of the grafted films was higher than that of the films made from ungrafted camelina meal, but there was no statistically significant change in elongation with increasing monomer concentration/grafting ratios. Grafting improved the thermoplasticity, and therefore the films made from the grafted camelina meal had better tensile properties than the films made from ungrafted meal.

The wet tensile properties of the camelina films showed a different trend from the dry tensile properties with change in monomer concentration. Increasing monomer concentration increased the wet strength but decreased the breaking elongation at high monomer concentrations. At 20% monomer concentration, the wet strength was 0.2 MPa and elongation was 2.6%. Increasing the monomer concentration to 60% increased the strength to 0.5 MPa but decreased the elongation to 1.8%. Increasing the monomer concentration increased the percent of MMA grafted onto the meal. With higher MMA, the films are less hydrophilic, and therefore the wet tensile strength increased. The wet elongation of the films is higher than their dry elongation because water acts as a lubricant and allows the polymers to stretch during tensile testing. The wet elongation decreased at high monomer concentration (60%) compared to the elongation at 20 and 40% concentration due to the lower moisture absorption of the samples with higher amounts of MMA.

Effect of Type of Acrylic Monomer on Tensile Properties. Tensile strength and elongation of the camelina films grafted with three different types (MMA, EMA, and BMA) of acrylic monomers with similar grafting ratios (1.7, 1.8, and 1.8 mmol/g, respectively) and with all of the homopolymers removed are shown in Figure 8. Although the average strength of the camelina films grafted with MMA, EMA, and BMA showed an increasing trend, there was no statistically significant difference. Wet strength of the EMA grafted

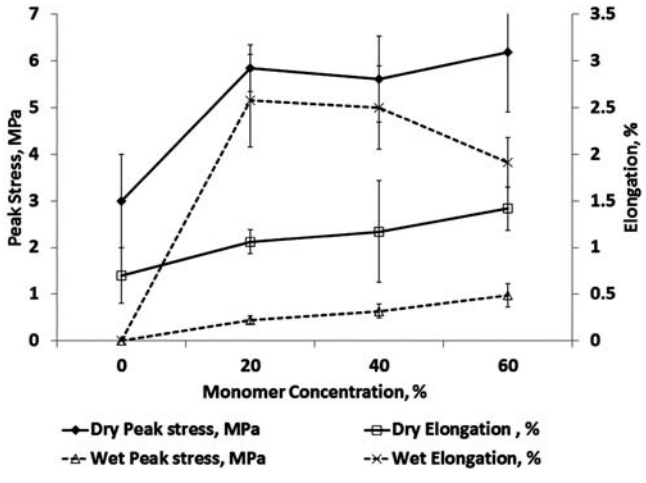

Figure 7. Effect of monomer concentration on the dry and wet tensile properties of camelina meal grafted with methyl methacrylate (MMA). Grafting was performed for 1 h at 70 °C, and the grafting ratio was 1.7, 2.8, and 5.0 mmol/g when the percent monomer used was 20, 40, and 60%, respectively.

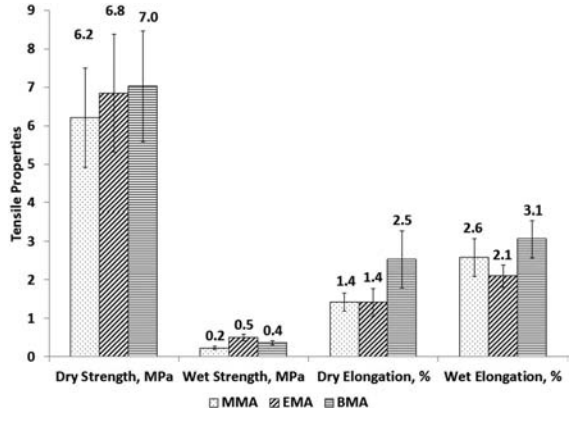

Figure 8. Effect of type of monomer on the dry and wet tensile properties of camelina meal grafted with methyl methacrylate (MMA). Grafting was performed for 1 h at 70 °C, and the grafting ratios for the methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) grafted films were 1.7, 1.8, and 1.8 mmol/g, respectively.

(highest) and BMA grafted films was higher than that of MMA grafted films probably due to the lower hydrophilicity of EMA and BMA. The dry elongation of the BMA grafted films was more than twice that of the MMA and EMA grafted ones mostly likely due to the longer length of polymer chains and therefore better flexibility of BMA compared to MMA and EMA. No particular trend was observed in the wet elongation of the films. Results from Figure 8 indicate that BMA provided better thermoplasticity and higher strength and elongation than MMA and EMA at similar grafting ratios.

Influence of Grafting Parameters on Mechanical Properties of Films. The influence of the main grafting parameters on the tensile properties of the films is depicted in Figure 9. As seen from the depiction, the grafting parameters

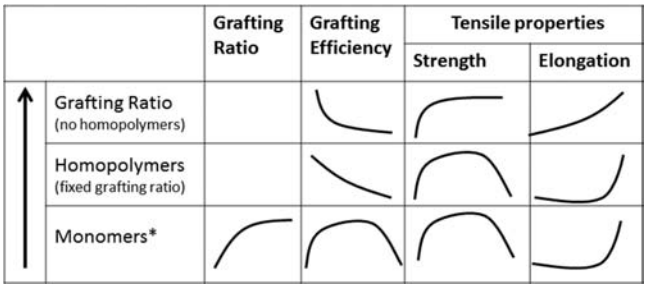

Figure 9. Effects of grafting conditions on grafting and tensile properties. * Monomers added during the reaction influence grafting ratio and homopolymers.

play an important role in determining the tensile properties of the films. Without any homopolymers, increasing grafting ratio continually increased the elongation of the films, but the tensile strength had an optimum level above which the strength decreased. Increasing the amount of homopolymers at fixed grafting ratio showed that an optimum level of homopolymers was necessary to obtain good strength and elongation. High homopolymers led to high elongations but considerably low strength and vice versa. Changing the monomer concentrations during the reaction changed both the grafting ratio and percent homopolymers and therefore affected the tensile properties. Adding excessive amounts of monomers not only decreased the grafting efficiency but led to the formation of high percent homopolymers. As with the percent homopolymers, the addition of monomers should be controlled to an optimum to obtain films with good strength and elongation, save chemicals, and reduce the cost of grafting.

This research showed that camelina meal and the components in camelina meal can be potentially used for food, fuel, fibers, thermoplastics, and other applications. Up to 19% oil, 20% protein, and 40% carbohydrates were extracted. Camelina meal and the proteins extracted exhibited melting peaks without any plasticizers. The meal was directly compression molded to form thermoplastics, but the films formed were unstable in water. Camelina grafted with various acrylates showed good thermoplasticity and ability to be compression molded into films with good dry and wet tensile properties. BMA grafted meal had high dry and wet tensile strengths, but the amount and form of homopolymers considerably affected the tensile properties. Results showed that an optimum level of grafting ratio and percent homopolymers is necessary to obtain good tensile properties. Camelina meal is an inexpensive raw material that has the potential to be used to develop various bioproducts.

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Notes

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