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ORIGINAL ARTICLE

Comparison of Canola and Soy Flour with Added Isocyanate as Wood Adhesives

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Abstract Canola is widely grown in the northern latitudes for its vegetable oil, generating large quantities of residual, low value canola flour used as animal feed. The common wood adhesive poly(diphenylmethylene diisocyanate) (pMDI) should react with the wide variety of functional groups in proteins. Therefore, it would seem that canola flour with added pMDI could be an effective adhesive. Two main questions are addressed in this study: How do the wood adhesive properties of canola flour compare to the better-studied soy flour? How well do proteins, which contain an abundance of functional groups, cure with the very reactive pMDI? These questions were addressed using the small-scale adhesive strength test ASTM D-7998, with various adhesive formulations and bonding conditions for canola flour plus pMDI compared to soy adhesives. The more challenging wet cohesive bond strength was emphasized because the dry strengths were usually very good. Generally, soy adhesives were better than canola ones, as was the polyamidoamine-epichlorohydrin cross-linker compared to pMDI, but these generalizations can be altered by the conditions selected. Three-ply plywood tests supported the small-scale test results.

Keywords Canola flour · Soy adhesive · Wood adhesive · Poly(diphenylmethylene diisocyanate) · Shear strength · Water resistance

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Introduction

Proteins have for thousands of years been used as adhesives, including for wood bonding (Adhikari et al., 2017; Frihart and Lorenz, 2018; Lambuth, 2003). Fossil fuel-derived adhesives, with superior performance, especially in water resistance, displaced proteins in the mid-20th century. Concerted efforts have been made to use more bio-based adhesives in recent years (He, 2017; Hemmilä et al., 2017).

Most of the research on defatted oilseed residue has been on soybeans because of their dominance in the market (Adhikari et al., 2017; He, 2017; Lusas, 2000; Statista, 2019; Vnučec et al., 2017; Wool and Sun, 2005), as worldwide soybean production was 360.08 (in Million Metric Tons) compared to rapeseed production with 70.91 (in Million Metric Tons) in 2018/2019. Although rapeseed is the second most abundant oilseed, defatted rapeseed has largely been ignored as an industrial material (Adhikari et al., 2017; Li et al., 2017a). Rapeseed has historically had low value due to toxins in both the oil and the defatted solids. However, a variety called canola has been developed to have low toxin levels (Canola, ; Tan et al., 2011). Despite the canola/rapeseed has among the lowest utility of the defatted oilseeds. Canola/rapeseed grows well in colder climates, while soybeans grow in warmer ones. Because of the large amount of canola grown in Canada, Europe, and other areas, knowing the adhesive potential of canola is important for better use of this bio-resource.

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Canola flour, like soy, is defatted by pressing or solvent extraction, leaving meals that are ground into meal/flour. In contrast to soy, canola meal can only be fed to animals or used industrially since it is not suitable in human foods (Li et al., 2017a; Mieth et al., 1983). Table 1 shows that canola flour has less protein, the presumed main adhesive component, than soy.

The low protein content in the canola flour is probably why most of the research has been on the isolated proteins rather than the meal or flour (Li et al., 2012a; Li et al., 2017a; Manamperi et al., 2011; Tzeng et al., 1990). However, because each oilseed has its own protein structures and properties, cohesive strength may not necessarily correlate with the protein content.

Since plant flour adhesives do not give sufficient wet bond strength by themselves, some type of additional co-reactant or cross linker is needed (Adhikari et al., 2017; Bjorksten, 1951; Frihart and Lorenz, 2018; Frihart and Lorenz, 2019; Hettiarachchy and Kalapathy, 1998; Shi et al., 2017; Vnučec et al., 2017). Some cross linkers, such as aldehydes, phenol-formaldehyde (PF), polyamidoamine-epichlorohydrin (PAE) resin, and magnesium oxide, are simply mixed with aqueous flour dispersions. Up to 30% soy flour can be added to either poly(diphenylmethylene diisocyanate) (pMDI) or PF adhesive with little property loss (Hand et al., 2018). PAE is used in the commercial soy adhesive Soyad™ (Allen et al., 2010). Unlike soy, there is little available information on the bonding properties of canola flour with pMDI or PAE. In this paper, we compare the wood adhesive properties of canola flour to soy flour, with pMDI or PAE, to explore the possibilities of canola flour adhesives.

Experimental Methods for Canola and Soy Testing

Materials

Defatted canola flour (*Brassica napus L.*) and Prolia™ 200-90 soy flour were obtained from Behpak Industrial Co (Behshahr, Mazandaran, Iran) and Cargill Inc. (Cedar Rapids, IA), respectively. Columbia Forest Products supplied the hard maple (*Acer saccharum*) veneer, while white oak (*Quercus alba*) veneer for plywood was supplied by Armstrong flooring company (Lancaster, PA, USA). The cross-linkers pMDI (Rubinate M) and PAE (CA1920 A) were provided by Huntsman, (The Woodlands, TX, USA), and Solenis (Wilmington, DE, USA), respectively.

Table 1 Composition of defatted canola flour (Li et al., 2017a) and soy flour (Wolf, 1970)

Constituent	Canola flour (%)	Soy flour (%)
Protein (N × 6.25)	35	55
Carbohydrates	35	34
Remaining Fat	2	2
Ash	6	6
Other material (Glucosinolates, erucic acid, phytic acid, phenolics, etc. in canola flour., fiber in soy flour)	22	3

Automated Bonding Evaluation System Testing

Soy or canola flour was dispersed in water at the required amount, and after mixing for about 5 min, the cross linker was added and the mixture was stirred for at least 30 min, except as noted. Adhesive was then applied to 5 mm on the end of one piece of hard maple (*Acer saccharum*) veneer (117 × 20 × 0.6 mm), which was overlapped 5 mm with another piece of veneer. Test pieces were hot pressed in the Automated Bonding Evaluation System (ABES) equipment (AES, Corvallis, OR) at 0.2 MPa for 120 s at 120, 150, or 180 C, see Fig. 1 (ASTM_International, 2015). The bonded wood test pieces were equilibrated at 21 C and 50% relative humidity at least overnight before testing dry or wet after soaking in water for 4 hours at room temperature. Five specimens dry and wet were tested in tensile shear with the ABES. The average and one standard deviation are reported.

Plywood Testing

White oak veneers with dimensions 300 mm × 300 mm × 2.1 mm were used. Three-layer plywood panels were made with a laboratory hot press (Carver- 3856, Wabash, IN, USA). The adhesive was applied to both sides of the middle cross ply layer by coating one side and placing it with the grain perpendicular to the first layer; then flipping the assembly so the second side of the middle layer could be coated with adhesive and finally attaching the third layer with the grain parallel to the first layer. The glue spread rate was 226 g m^{-2} based on wet mass for each side. Prior to hot pressing, the plywood panels had a closed assembly time under light pressure for 15 min, and then the panel was placed in a hot press at 120, 145, or 170 C, and pressed at 0.862 MPa (125 psi) for 5 min.

The plywood panels were conditioned at 26 C and 30% RH for 7 days. Then panels were cut into shear test pieces according to EN 314-1 standard to determine dry and wet shear strength (EN 314-1, 2004). Shear test was performed with the lathe checks pulled closed (Fig. 2a) to reduce data variability compared to pulling both closed and open (Fig. 2a and b). Each sample had a bonded area of 25 mm × 25 mm. Both wet and dry shear strength of plywood test pieces were determined with a MTS Insight (MTS Systems

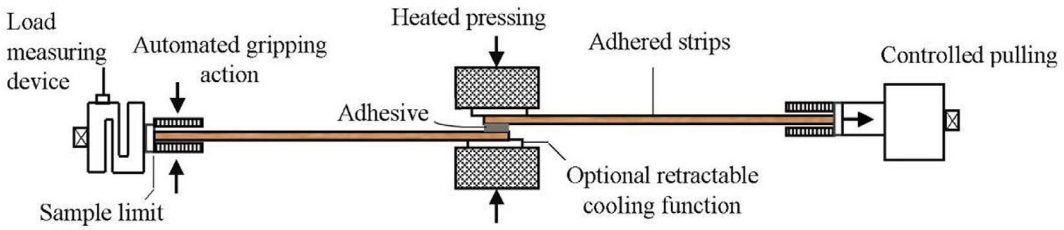

Fig 1 Schematic illustration of bonding and testing with ABES (ASTM_International, 2015)

Corporation, Eden Prairie, Minnesota, USA) mechanical testing machine. For the wet shear strength, the test pieces were soaked in room temperature water for 24 hours prior to testing and tested wet. Error bars show standard deviation of five replicates for each test.

Water-Resistance Testing

The water resistance of the plywood test pieces was determined with a three-cycle soaking/drying test according to ANSI/HPVA HP-1-2009 (Institute and Plywood, 2009). Eighteen plywood test pieces (5.08×12.7 cm^2) were cut from each panel, and then soaked in water at (24 ± 3) ^{o}C for 4 hours, and dried at 49–52 C for 19 hours. This soaking/drying cycle was repeated three times. All test pieces were inspected to observe any delamination after the first and third cycle of testing. According to the standard, if delamination was found in only 5% of the test pieces, i.e., 1 out of the 18 test pieces after the first soaking/drying cycle as well as only 15% of test pieces, i.e., 3 out of 18 test pieces after the third soaking/drying cycle, a plywood panel meets the water resistance requirement for interior applications. Definition of delamination based on ANSI/HPVA HP-1-2009 is any continuous opening between two layers, which is longer than 50 mm (two inches) and deeper than 6.25 mm (0.25 in.) and wider than 0.075 mm (0.003 in.).

Infra-Red Analysis

Canola dispersions with 5, 15, 30 wt% pMDI or without additives were freeze-dried (Labconco, Kansas City, MO, USA). Canola adhesives with 30 wt% pMDI (based upon dry canola flour weight) were cured in an oven at 120 C to a constant weight. The dried and cured canola adhesives were ground into fine powders, and FTIR spectra were recorded on a Perkin Elmer Spectrum two FT-IR spectrophotometer equipped with Perkin Elmer UATR–TWO diamond ATR (Waltham, MA, USA) from 450 to 4000 cm^{-1} with a 4 cm^{-1} resolution, using 16 scans.

Scanning Electron Microscope Imaging

The fractured surface of shear-tested (plywood) test pieces and wood surfaces were sputter coated with gold and observed with a LEO EVO 40 (Carl Zeiss Microscopy, Ltd, Cambridge, UK) scanning electron microscope (SEM).

Results and Discussion

ABES Testing

While the plywood tests are very valuable for validating final formulations, they are less useful in developing

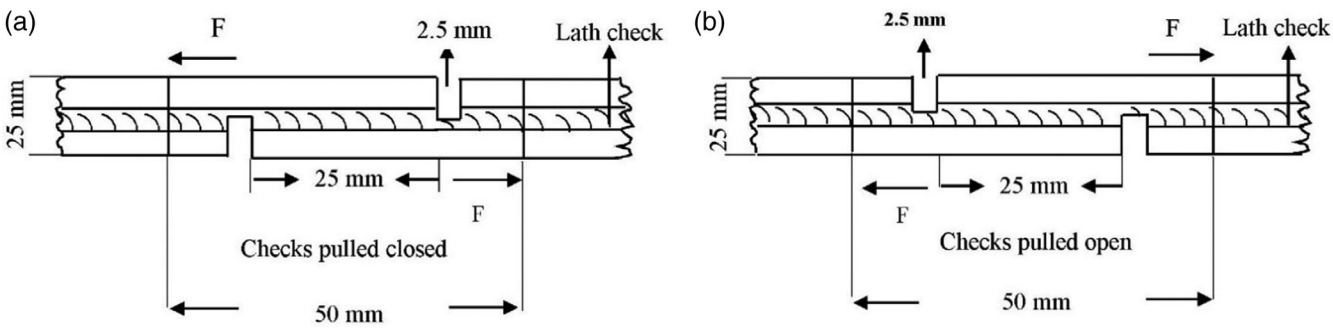

Fig 2 Visualization of lathe check direction in plywood testing. (a) Middle ply with lathe checks pulled closed. (b) Middle ply with lathe checks pulled open

adhesive formulations and an understanding of strength development because they are sensitive to veneer quality, adhesive viscosity, adhesive penetration, open and closed assembly time, etc. Because the objective of this study is understanding the effect of the changes in formulation and bonding temperatures, our initial work used the small-scale test ASTM D-7998 (ASTM_International, 2015) using an ABES machine, which emphasizes cohesive strength of the adhesive. With the smooth maple veneer, ABES specimens are less sensitive to gap filling, wood penetration, and lathe check issues than are standard plywood tests.

We concentrated on interior plywood applications because soy adhesives have found their great success in this area. For the preliminary work, canola was tested with various chemicals that have been used to improve soy flour performance. These were first tested using the ABES so that reliable comparisons could be made between canola and soy with and without various additives. The emphasis was on making canola adhesives with pMDI that compared favorably to commercial soy flour with PAE.

Fig. 3 shows that canola was much lower in dry shear strength than soy, and that both are low in wet strength. A number of methods have been claimed for increasing the strength of soy (Frihart and Lorenz, 2019; Shi et al., 2017; Vnučec et al., 2017) with PAE being the most commercially common method; thus, ABES test pieces were bonded with both canola and soy cross-linked with PAE and pMDI. The pMDI was initially added to canola or soy flour after the water, which was our typical method for laboratory modification of soy. However, since it was later hypothesized that the poor strength increase was due to pMDI reacting rapidly with water, we also tried adding pMDI to flour before the water, as discussed in more detail below. Addition of pMDI to flour before the water greatly improved both dry and wet strength, and compares well to PAE-cross-linked flour adhesives. However, much of the research was done adding the pMDI to the canola after the water, which is easier commercially. In none of these comparisons did the canola give dry or wet strengths as high as the soy with PAE.

Because canola with pMDI showed acceptable strength and pMDI is a widely used wood adhesive for particulate composite panels (Frazier, 2003), further investigation was warranted. The literature of pMDI with protein for wood bonding is very limited and the studies that are available react pMDI with low molecular weight, purified proteins (Adhikari et al., 2017; Cheng et al., 2019). Several concentrations of pMDI from 5 to 30 % were tested in preliminary experiments. With regard to the results, two concentrations of pMDI 10 and 20% were selected to compare. Higher pMDI concentrations at a certain point provide no further strength improvement, so the improvement is self-limiting and the reason for this is not clear. Two parameters likely to be important are the amount of pMDI used and the bonding temperature, since the water amount was determined by the adhesive viscosity. As is often the case with protein wood adhesives, the wet shear strength (water soak) was too low for commercial utility (Frihart et al., 2009). Thus, we focused on wet strength, using the ABES method.

According to the literature (Gao et al., 2011), isocyanate groups can react with residual amino groups and free hydroxyl groups of proteins (Fig. 4a, b). Also, the water in the adhesive reacts with isocyanate (Fig. 4c).

For the PAE cross-linker, its reactions are shown in Fig. 5. Fig. 5a shows the reaction between azetidinium group in PAE and the remaining secondary amines in the

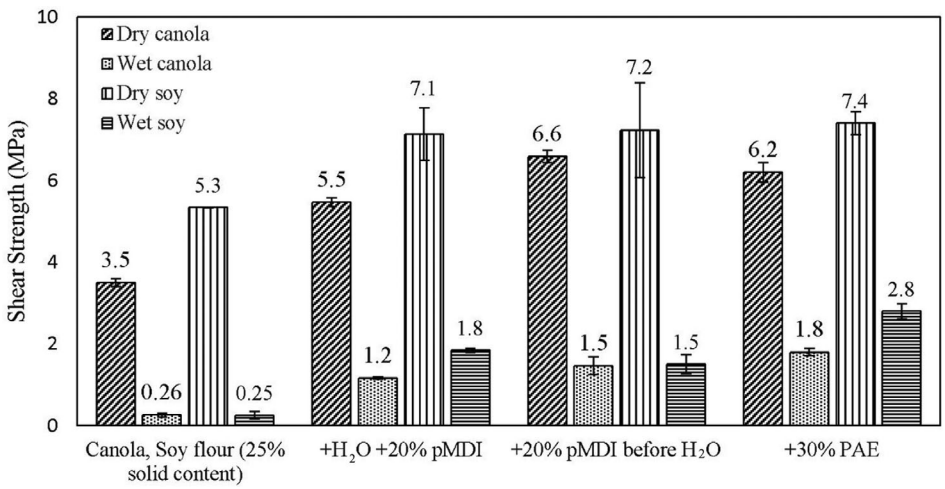

Fig 3 ABES shear strengths of modified canola and soy adhesives bonded at 120 C, where the H_2O and pMDI were added in the order stated. The percent soy or canola represents the final mixture weight percent and the weights of additives were based on the dry canola and soy weights

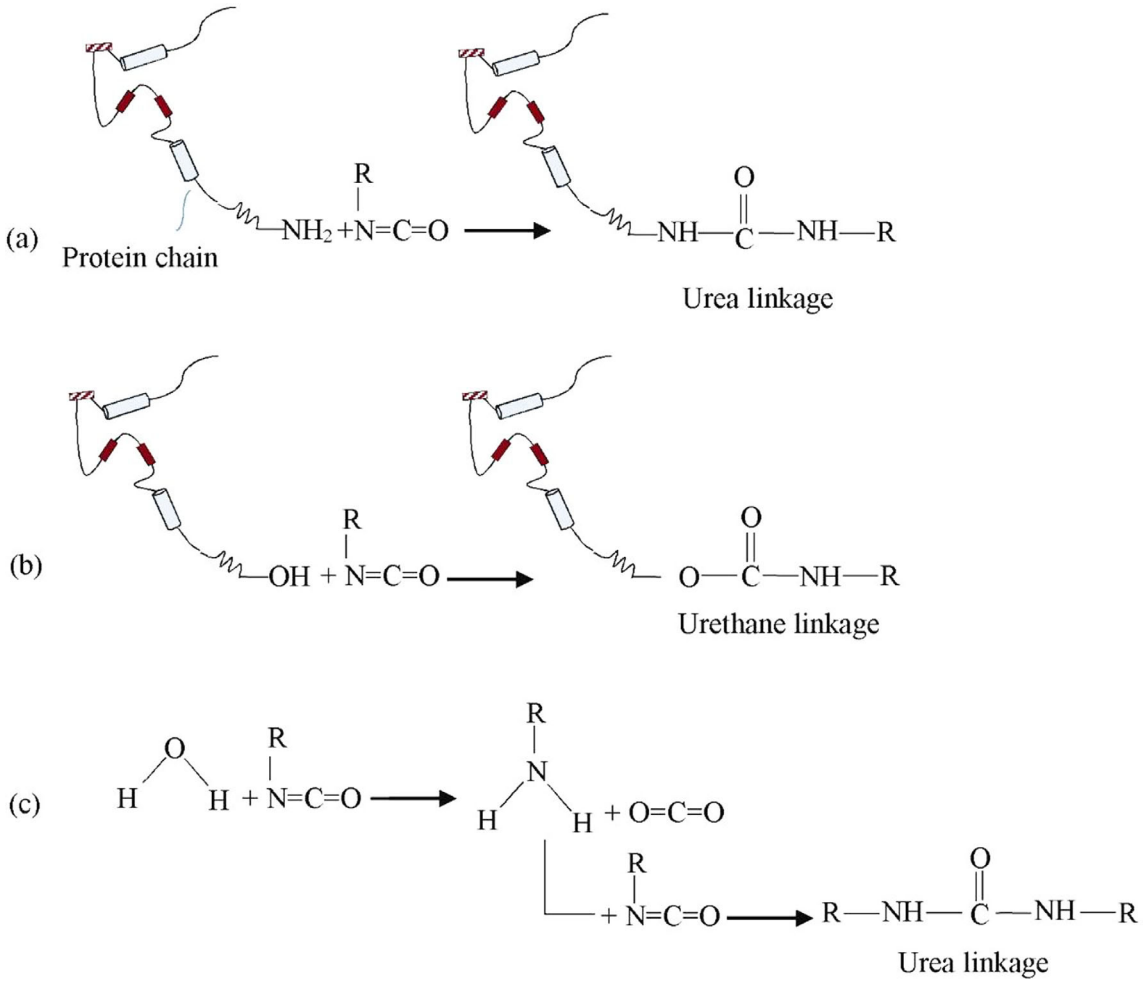

Fig 4 Illustrations of reactions between isocyanate and protein (a, b), and water (c)

PAE resin, resulting in homo-cross-linking, normally at pH above 6. Fig. 5b shows how the azetidinium group might react with carboxylic acid groups. Fig. 5c shows the cross-linking mechanism with various amino groups in canola or soy flour proteins and the azetidinium group (Li et al., 2004). The reaction of PAE with the carboxylic acids of carbohydrates is well known (Espy, 1995), but the reaction of PAE with amines on proteins is more speculative.

It is expected that pMDI and PAE are likely to form covalent bonds with both carbohydrate and carboxylic groups in wood as well as those carboxylic and amino groups exposed on the protein surface. These bonds should produce good wet strength. However, unlike the PAE, the pMDI can react with the abundant water present to form urea compounds instead of linking the proteins and carbohydrates. Thus, canola and soy adhesives were also made with pMDI, based on the weight of dry flour, which was 25% in the final formulation, added before and after the water.

The resulting strength data in Fig. 6 show that adding the different amounts of pMDI to either flour before the water always gave better wet shear strengths, but the effect was greater with canola and slightly exceeded the soy in wet strength. This information agrees with the concept that despite the high abundance of reactive groups in the oil

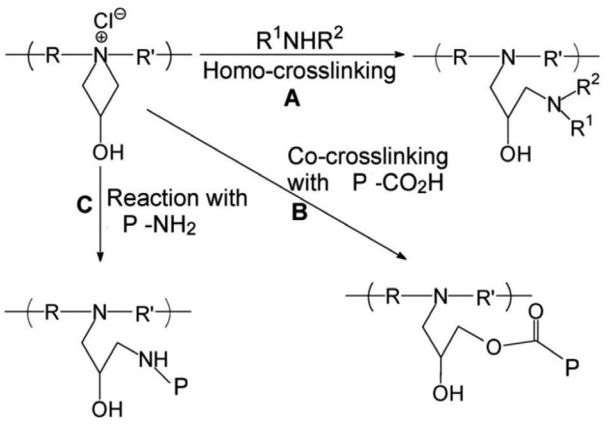

Fig 5 Major cross-linking mechanism between PAE and proteins (P). (a) Self-reaction, (b) protein carboxylic groups, (c) protein amino groups (Li et al., 2004)

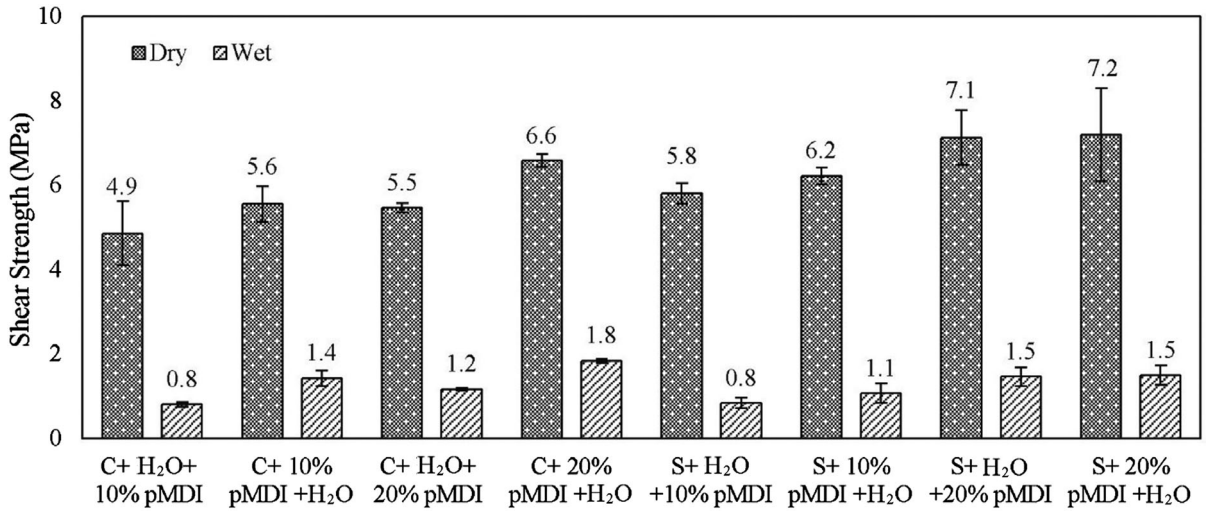

Fig 6 ABES shear strength of canola (C) and soy (S) flours, where the H_2O and pMDI are added in the order stated. The percent soy or canola represents the final mixture weight percent and the weights of additives were based upon the canola and soy weights

seed proteins, these groups are probably less accessible being buried in the globular proteins while the water is very accessible for reaction. Giving the pMDI a chance to react with the proteins prior to competition with the water results in better cross linking.

Although improvement was observed in the canola bond strength with pMDI added before adding the water, we also wanted to look at the effect of bonding temperature with pMDI added to soy and canola flour after the water similar to our prior PAE studies (Frihart et al., 2016). Prior work has shown that soy adhesives are stronger when bonded at, or exposed to, higher temperatures without and with added PAE (Frihart et al., 2016). This was attributed to improved film coalescence, with the heat providing molecular mobility needed to entangle proteins and form additional bonds. Therefore, we investigated the effect of press temperature on canola/pMDI adhesives compared with soy/pMDI adhesives using ABES bonding temperatures of 120, 150, and 180 C bonded for 2 min adding pMDI after the water.

Fig. 7 shows that the dry and wet strength increased for soy and pMDI with the increase in bonding temperature, at both pMDI levels, consistent with previous work (Frihart

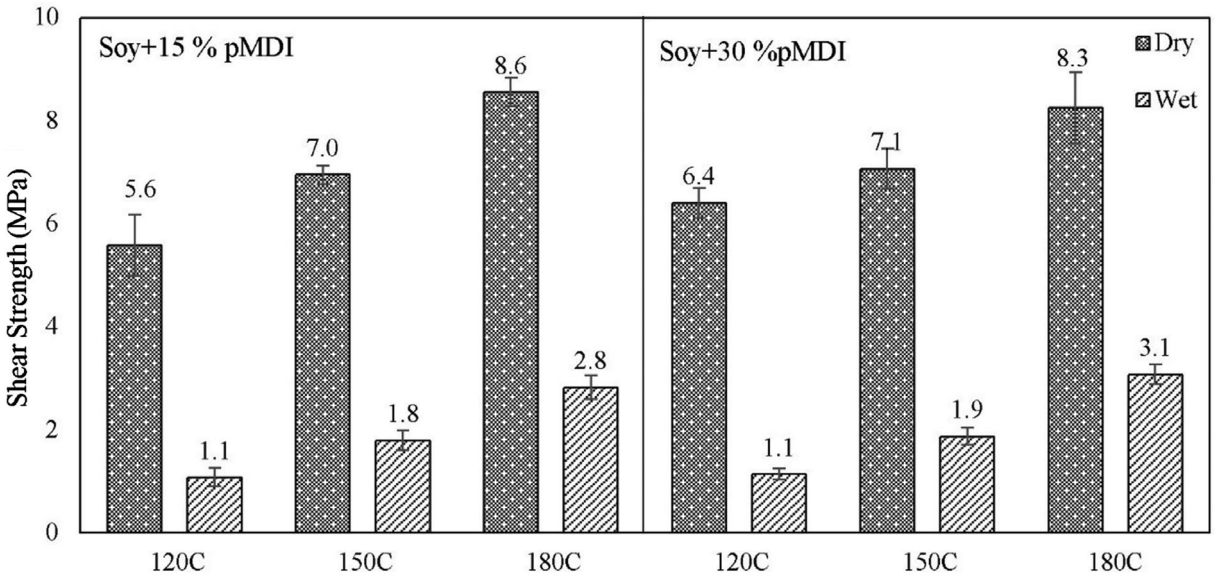

Fig 7 Dry and wet ABES shear strength of soy flour with two added amounts of pMDI

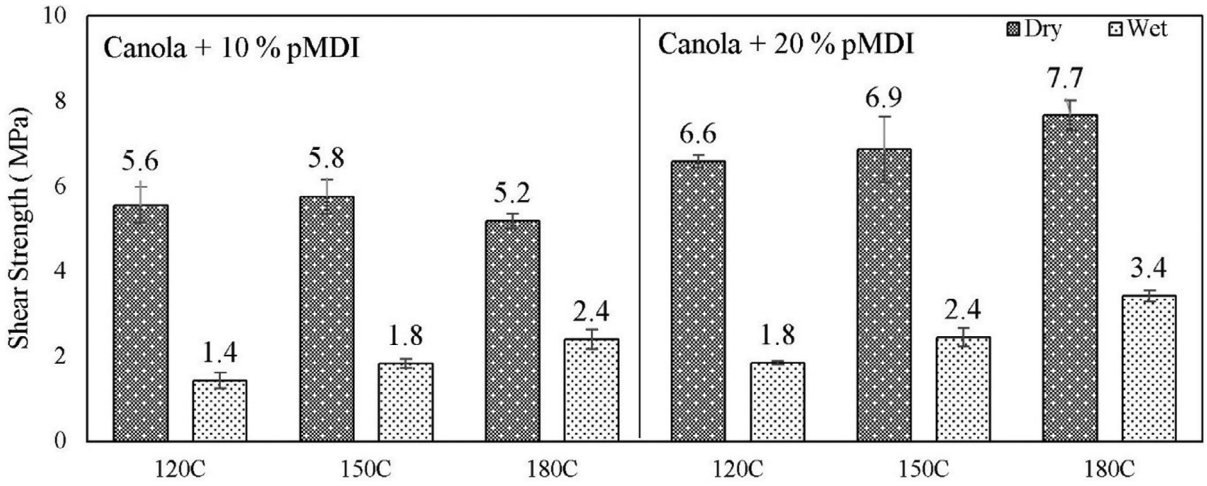

Fig 8 Dry and wet ABES shear strength of canola flour with two added amounts of pMDI

et al., 2016). Surprisingly, there was almost no change in both the wet and dry performance between 15% and 30% pMDI. While the positive effect of higher bonding temperatures was not surprising, the lack of greatly improved wet strength by doubling of the pMDI was unexpected. The lack of additional effectiveness could indicate that at 15%, there is enough pMDI to react with all the readily available sites in the soy flour.

Fig. 8 shows that canola had a much weaker response to temperature than did soy. There was no statistical difference in dry strength among the three bonding temperature with 10% pMDI. The increase in strength with temperature for wet canola at 10% pMDI and both wet and dry data at 20% pMDI, were statistically significant but smaller in magnitude than the changes observed with temperature in Fig. 7 for soy flour adhesives. If coalescence is the mechanism behind the increase in strength with temperature, this suggests that improving coalescence is not as useful with canola than with soy.

Fig. 8 also shows that the higher level of pMDI in canola has probably not reached saturation; 20% pMDI appears to be more effective than 10%. Interestingly, the canola with 20% pMDI bonded at 120 C appears to be comparable or better than the soy with 30% pMDI.

Since increasing the pMDI amount for canola increased the wet bond strength, we wanted to see if a similar effect existed with PAE at several different amounts, as shown in Fig. 9. The data clearly show that the canola with the PAE

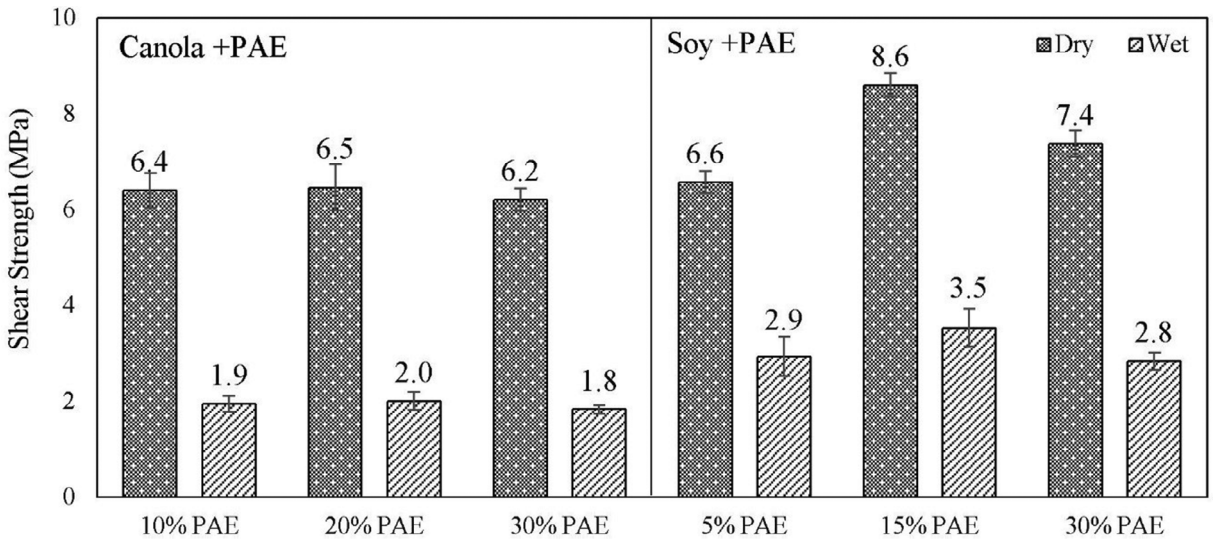

Fig 9 ABES shear strength of canola and soy flour with added PAE

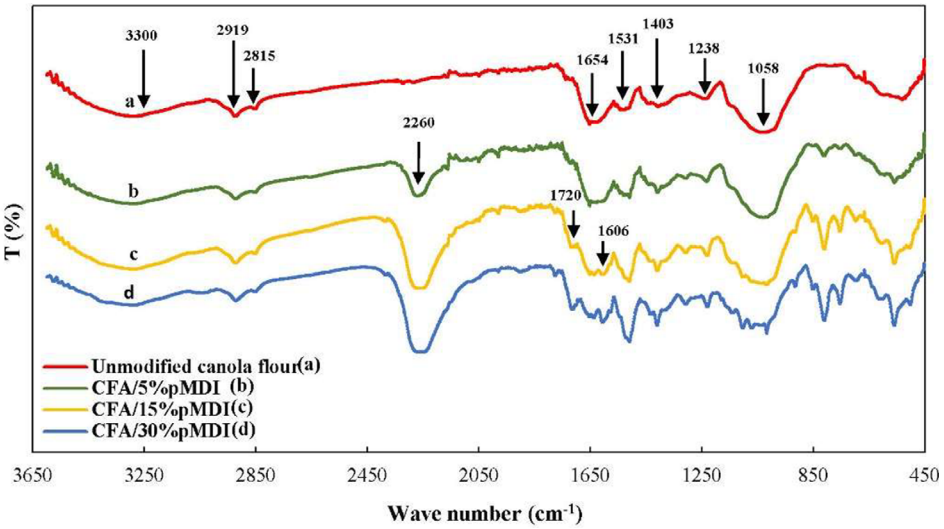

Fig 10 FTIR spectra of freeze-dried modified and unmodified canola adhesives

does not give the wet or dry strength that is observed with soy plus PAE. In addition, both canola and soy reached a point of diminishing returns as the highest PAE amount did not improve strength. However, the same conclusion may not be observed with a thicker bondline and the non-parallel ply orientation that exists in plywood bonding.

ATR-FTIR Spectroscopic of Canola Flour Adhesives

The improved wet strength in the ABES testing of the pMDI with canola flour led to appropriately characterize the possible interactions between canola and pMDI using ATR-FTIR spectroscopy. The initial adhesive mixture of canola and pMDI was freeze-dried to compare changes with the cured adhesive. The FTIR results of freeze-dried canola adhesives are shown in Fig. 10. In comparison to the FTIR spectra of the different soy adhesives which have been discussed in the literature (Gui et al., 2013; Lei et al., 2014; Li et al., 2017b), the spectra and peaks of canola flour adhesive were very close to those of the soy adhesive because they are both from oilseed plants.

Fig. 10 shows the following absorption peaks; a peak was observed at 3300 cm^{-1}, which was attributed to the free and bound O—H and N—H groups (Lei et al., 2014; Li et al., 2017b). The absorption peaks at 2919 and 2851 cm^{-1} were allocated to stretching of —CH_2— groups on proteins

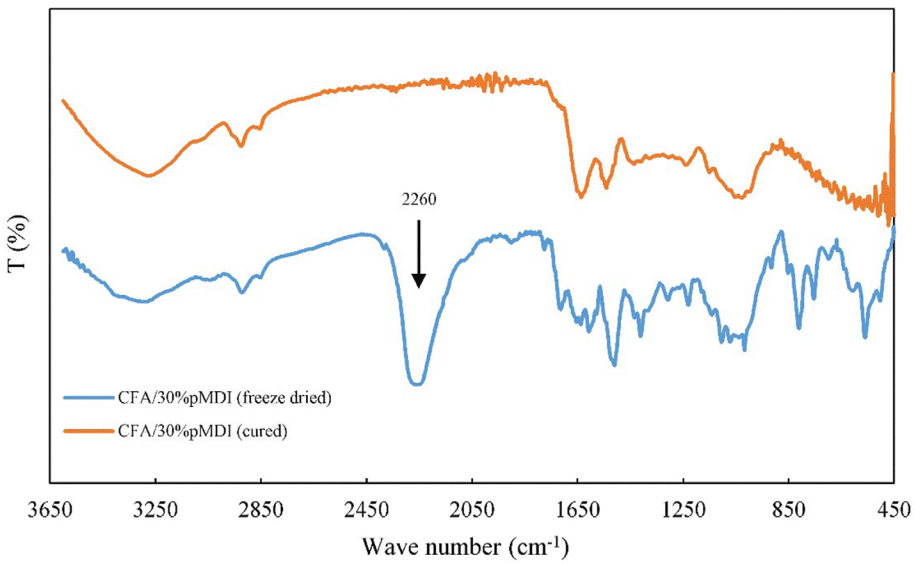

Fig 11 FTIR spectra of cured and freeze-dried canola adhesives modified 30% pMDI

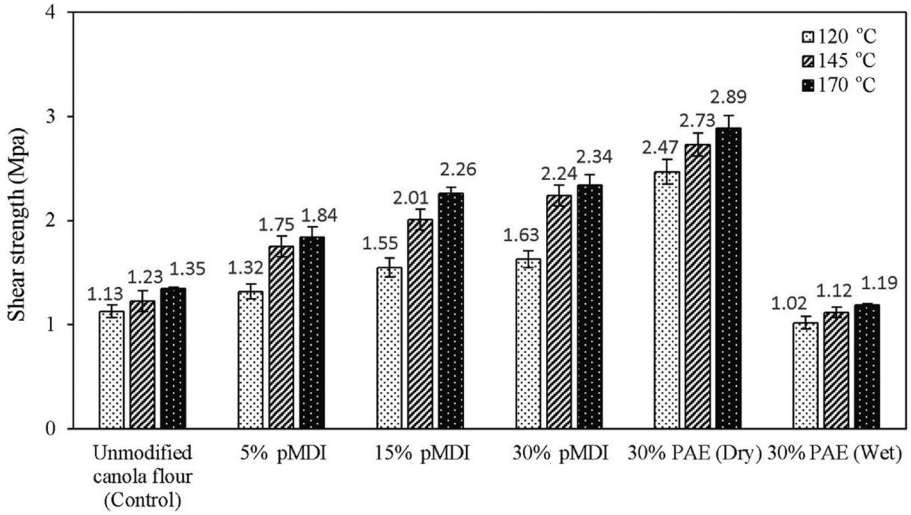

Fig 12 Shear strength of plywood panels bonded with canola flour adhesives modified with pMDI or PAE (wet shear test pieces of canola plus pMDI did not have enough integrity for testing)

(Li et al., 2017b). The bands of amide, the characteristic group of protein, observed at 1654, 1531, and 1238 cm^{-1} were assigned to the amide I (C═O stretching), amide II (N─H bending) that main bands of peptide linkage (Schmidt et al., 2005) and amide III (C─N stretching and N─H bending) (Lei et al., 2014; Li et al., 2014; Li et al., 2017b; Zhang et al., 2014). With addition of pMDI to the canola adhesive, a new absorption peak appeared at 2260 cm^{-1} which was attributed to N═C═O stretching of the pMDI (Gordon and Ford, 1972) and was largest for canola plus 30% pMDI. These bands were not observed for unmodified canola flour adhesive. For canola adhesive plus 15% and 30% pMDI, two new absorption peaks were observed at 1720 cm^{-1} (Kurimoto et al., 2000) and 1606 cm^{-1} (Arunkumar and Ramachandran, 2017) that were assigned to carbonyl groups (C═O stretching) of urethane linkage and urea linkage, respectively and were larger for canola plus 30% pMDI.

Fig. 11 shows the FTIR results of cured and freeze-dried canola plus 30% pMDI with the disappearance of the absorption peak at 2260 cm^{-1} in cured canola/30% pMDI compared to freeze-dried uncured adhesive. This disappearance confirmed that isocyanate groups reacted with water to form a polyurea or protein functional groups forming cross-linked networks between proteins. Moreover, curing of the adhesives resulted in decrease of absorption peaks at 1058, 1238, 1403, 1531 cm^{-1} due to the reactions, which occurred between functional groups and formation of cross-linking networks.

Table 2 Cohesive wood failure of plywood panels (%)

Sample	120 C	145 C	170 C
Unmodified canola adhesive	12	15	20
Canola/5% pMDI	17	20	27
Canola/15% pMDI	20	25	32
Canola/30% pMDI	30	37	40
Canola/30% PAE (Dry)	57	62	63
Canola/30% PAE (Wet)	5	5	10

Plywood Shear Strength of Canola Flour Adhesives

Despite the limited wet shear strength, it was valuable to make plywood because the selectivity of pMDI between reacting with the protein/carbohydrate vs. the water may be altered due to the thicker adhesive film and slower heating of the bondline in plywood relative to ABES specimens. The effect of press temperature and various levels of added pMDI or PAE with canola has been examined, using

Table 3 Water resistance of plywood panels

Sample	1st cycle	3rd cycle	Pass/Fail
Unmodified canola	18[a]/18[b]	18/18	Fail
Canola/5% pMDI	15/18	18/18	Fail
Canola/15% pMDI	13/18	18/18	Fail
Canola/30% pMDI	11/18	18/18	Fail
Canola/30% PAE	0/18	4/18	Fail

[a]The number of failed test pieces upon completion of the soaking/drying cycle. If only one sample failed in first cycle and only three test pieces failed after the third cycle, then the test pieces are considered to pass.

[b]The number of all test pieces used in soaking/drying cycle.

plywood shear strength. The dry shear strengths of canola flour adhesive plus pMDI or PAE and the wet shear strength of canola flour with PAE are shown in Fig. 12. It can clearly be seen that higher pMDI concentrations resulted in greater dry shear strength due to the importance of building a better bridge between the rough plywood surfaces, but the wet test pieces of canola with pMDI could not be tested since the test pieces delaminated after water soaking. Also the PAE at 30% had higher dry strengths than pMDI at 30%. In this research, it seems that the isocyanate did not build a good adhesive matrix with canola flour. Although the dry shear strengths increased with increasing temperature and amount of pMDI, they were insufficient to provide water resistance.

The shear strength was improved following an increase in press temperature. Similar results for curing canola protein adhesives were observed in the literature (Li et al., 2012b). Moreover, increasing press temperatures

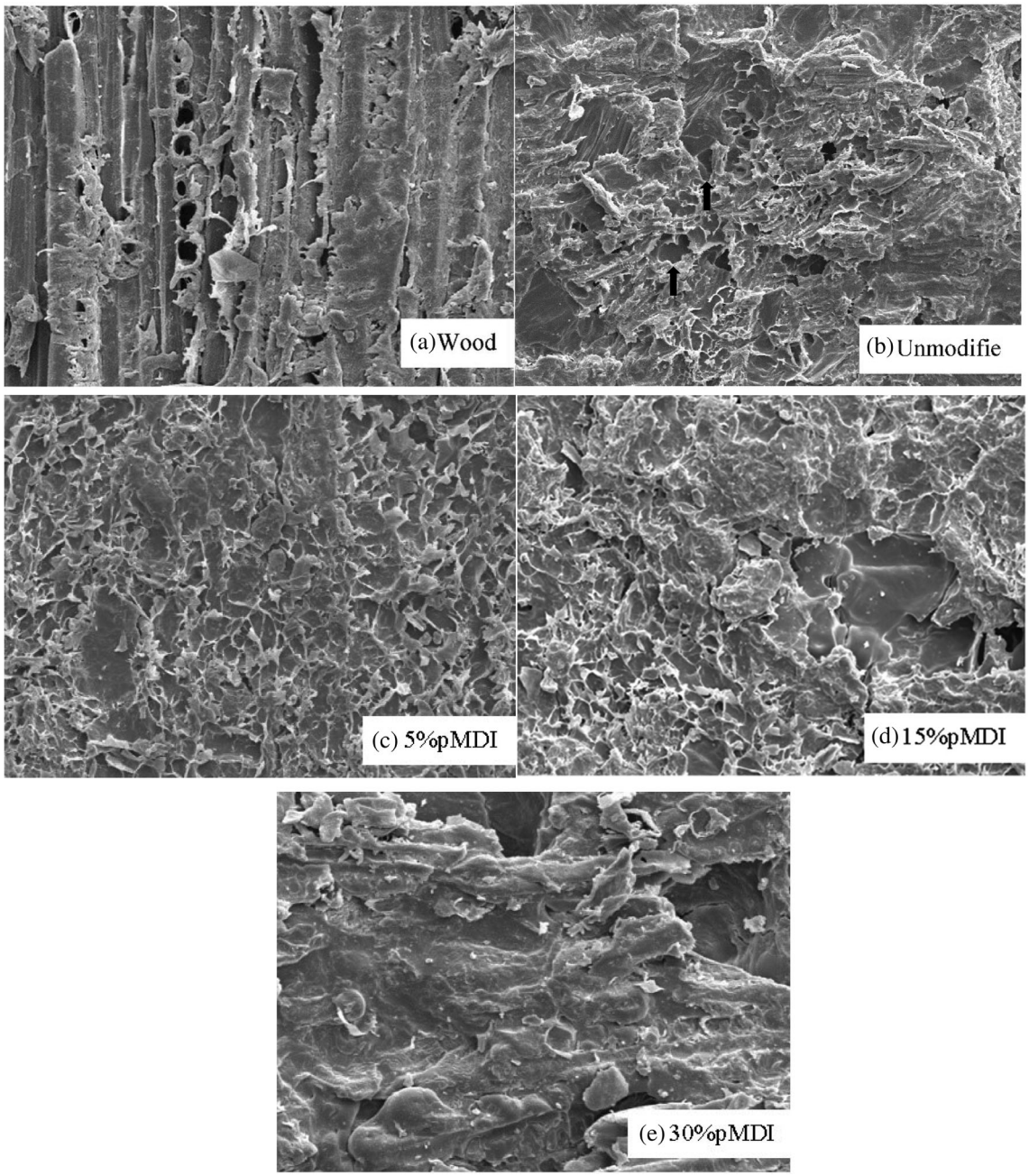

Fig 13 SEM images of wood fractured surface (10 μm), (a) wood surface, (b) unmodified canola, (c) canola/5% pMDI, (d) canola/15% pMDI, and (e) canola/30% pMDI

are reported to have a remarkable effect on the protein molecules, evaporation of solvent, and the probability of chemical and physical reaction between proteins and wood surface (Li et al., 2012b). According to EN 314-2, cohesive wood failure is applied to determine bonding quality of plywood panels with shear strengths lower than 1 MPa. However, the shear strength of canola adhesives in Fig. 12 was more than 1 MPa and there is no requirement for a wood failure, the cohesive wood failures are shown in Table 2.

Delamination Resistance of Plywood Panels

The delamination water-resistance results for plywood panels are shown in Table 3 with all panels made at 120 C. The sample bonded with unmodified canola flour adhesive (control) delaminated after the first cycle. The water resistance of canola flours was improved when pMDI was added to the dispersion. The pMDI is a good cross-linker, which could form bridges between canola proteins and carbohydrates. Although increasing the pMDI concentration improved performance, and the number of test pieces that failed gradually decreased with each cycle, the performance was far from satisfactory even at the highest pMDI levels and the test pieces did not pass three cycles of soaking/drying. Thus, we know that pMDI gives some improvement, but it is far from the required performance.

Although PAE plus canola flour also failed, the number of test pieces that failed was much lower than the pMDI plus canola. The much poorer performance of the pMDI plywood compared to ABES may relate to the greater time for exposure to water before the adhesive cures.

SEM Analysis

To try to understand more about the pMDI when it reacts, we looked at test pieces of the failed plywood bondlines using scanning electron microscopy (SEM). The representative images of fractured adhesion interface of the shear tested test pieces are shown in Fig. 13. Wood surface without adhesives showed a regular oriented structure (Fig. 13a). There were a large number of holes on the surface of test pieces bonded with unmodified canola (Fig. 13b), suggesting steam bubbles formed in the bondline during hot pressing. In addition, the many smooth surfaces with thin vertical walls (arrows) appear to show that fracture passed through many bubbles. The large number of bubbles in the bondline would be consistent with the low observed strength. These bubbles were also widespread in the 5 and 15% pMDI specimens (Fig. 13c, d). In contrast, few bubbles were observed in the 30% pMDI specimen (Fig. 13e). It is noteworthy that none of the canola, unmodified or modified, adhesive failure surfaces look in anyway like the wood surfaces; thus, failure is cohesive within the adhesive (Fig. 13b–e). SEM observation confirmed that canola flour/pMDI adhesives could cover the wood surface very well, formed a cross-linked glue line during the hot press process, and improved the dry shear strength of the adhesives. However, based on shear strength results in this research, it seems that the isocyanate did not build a good enough matrix of the adhesive between the wood surfaces, and it was insufficient to provide water resistance to the canola, although the dry shear strength increased with additions of 5%, 15%, and 30% pMDI to canola.

Conclusions

Shear strength of canola and soy flour adhesives usually improved when pMDI was added in increasing amounts, presumably because of pMDI cross-linking. Good results were achieved for dry shear strength, but not for the wet shear strength of canola and soy adhesives. Compared to pMDI, PAE was generally a better reactant and resulted in increased dry and wet shear strengths of canola or soy adhesive. Press temperature also had an important effect on shear strength so that higher press temperatures led to increased shear strength. By increasing the temperature from 120 to 170 C for plywood, the shear strength of plywood test pieces bonded with increasing amounts of pMDI were improved. Even though FTIR and SEM results showed that chemical reactions apparently occurred among functional groups to form cross-links between canola flour proteins, the lack of good adhesive network formation between the wood surfaces led to reduction of wet shear strength. Although PAE is relatively stable in water, the rapid reaction of pMDI with water leads to self-curing and can occur before the pMDI has time to penetrate the globular protein and react with the protein functional groups. Thus, it was found that adding the pMDI to the canola or soy flour before the water addition led to improve strengths. In addition, although soy and canola flour both contain globular proteins, their reactions with cross-linkers and heat result in some variations in strength development.

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Conflict of Interest The authors declare that they have no conflict of interest.

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