

Glyoxal Cross-Linked Polyvinyl Alcohol-Microcrystalline Cellulose Blend as a Wood Adhesive with Enhanced Mechanical, Thermal and Performance Properties

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Abstract: Toxicity and limited availability of petrochemicals for wood adhesive have opened research for alternative materials that are sustainable and renewable. Cellulose is one such material that is incorporated in other matrices for reinforcing and enhancing properties. This work investigates the properties of wood adhesive prepared by blending polyvinyl alcohol (PVA) and microcrystalline cellulose (MCC) in water. The blend is further modified by cross-linking with a dialdehyde, glyoxal at 0.1 wt. % and 0.2 wt. % for enhancing properties. Cross-linking occurs by the acetal bond formation with free hydroxyl groups of MCC and PVA. The effect of cross-linking was studied by various tests, including viscosity and pH measurements, Fourier-transform infrared (FTIR) spectroscopy, and contact angle measurement. Enhancement of mechanical property and thermal property of cross-linked blends were evidenced from pencil hardness of the films, improvement in storage modulus by dynamic mechanical analysis (DMA), and increase in glass transition temperature by differential scanning calorimetry (DSC). The performance property of cross-linked wood adhesive was measured by wet tack analysis and tensile lap shear test with a canarium wood substrates after 6 hr. and 24 hr. of bonding showed excellent results. Glyoxal cross-linked blends show enhancements in adhesion with improved thermo-mechanical properties.

Keywords: Microcrystalline cellulose; Biopolymer; Polyvinyl alcohol; Blend; Glyoxal; Cross-linking; DMA analysis; DSC analysis; Wood adhesive.

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1. Introduction

Overexploitation of petrochemicals has seen a negative impact on the environment, with visible changes like global warming and climate change. Researchers investigated alternatives to the petroleum-based products and found that bio-based materials are one such alternative [1]. Bio-based

materials have the advantage of being renewable and sustainable with possibilities of further modification [2, 3]. Considering the increasing demand of wood products for construction and building materials, the wood adhesives have been in high demand. Conventional systems based on

formaldehyde adhesives have the disadvantage of toxicity [4]. Carcinogenicity from the formaldehyde emission from wood panels has resulted in the exploration of 'green' biobased materials [5, 6]. Hence bio-based adhesives were introduced to the adhesive industry. Compared to formaldehyde-based wood adhesives, polyvinyl alcohol (PVA) stabilized polyvinyl acetate (PVAc) wood adhesives, which are water-based, have a very low impact on nature [7, 8]. PVA is a water-soluble and biodegradable polymer that has excellent adhesion properties, which is one of the promising water-based adhesives [9]. Moreover, chemical modifications are done on PVA for enhancing its properties prior to its incorporation on PVAc emulsion [8]. To enhance the adhesion properties of PVA, modifications are done by the addition of fillers [10], chemical modification of PVA [11, 12], blending with other polymers [13], and so on.

Microcrystalline cellulose (MCC) is a polysaccharide biopolymer obtained by isolation from cellulosic biomass by the chemical and physical method [14]. Amorphous regions are selectively hydrolyzed, resulting in the isolation of crystalline regions. Inherent binding properties of cellulose have made them a potential candidate in the adhesive sector [15]. Wood adhesives made from cellulose have shown eco-friendliness with enhanced mechanical properties by its reinforcing nature, barrier properties along with the reduction of cost [16, 17]. Enhancement in adhesion properties has shown in commercial adhesives by the incorporation of cellulose [18–21]. PVAc wood adhesive containing nanocellulose shown reinforcing property, an increase in bond strength, and thermal stability [22]. By incorporating cellulose on the PVA matrix, enhancement of compressive properties was observed, and as concentration increased, properties were also increasing [23]. For further improvement of various properties, chemical modifications are done [2]. Cross-linking of cellulose is one such modification [24, 25]. The presence of hydroxyl groups in PVA and cellulose acts as a site for cross-linking reaction, which gives enhancements in thermal and mechanical properties [24, 26–28].

2. Materials and Methods

2.1. Materials.

Polyvinyl alcohol (PVA), of molecular weight 99,000 to 105,000 g/mol and having 87 to 89 % degree of hydrolysis was obtained from Kuraray

Since PVA and cellulose can be blended in water, the preparation of adhesive does not need any organic solvent. The cross-linking process involves the joining of molecules by covalent bonds. The presence of hydroxyl groups in both PVA and MCC provides a site for chemical modification [29]. Dialdehydes have found to be effective cross-linkers for PVA and cellulose separately and combined [27, 30–33]. The smallest dialdehyde, glyoxal, can attack the hydroxyl groups of PVA and cellulose [34, 35]. Glyoxal cross-linked PVA has many applications [31]. The hydroxyl groups from PVA and MCC react with aldehydes via the formation of acetal bonds [36]. Since, the dialdehyde, glyoxal at 90 °C reacts with the hydroxyl groups, forming an acetal bond between MCC and PVA. The medium required for this reaction to occur acidic, which is inherently present in the solution [37]. With these possibilities, the expected cross-linking mechanism of PVA and MCC with glyoxal is shown in Figure 1.

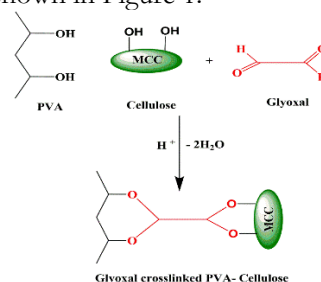


Figure 1. Cross-linking mechanism of PVA and MCC with glyoxal.

Though the studies on cross-linking PVA/MCC with various cross-linkers have observed an enhancement in mechanical and thermal properties, making MCC as a functional filler. However, investigations on the inherent binding properties of PVA and cellulose and its effects when introducing a cross-linker to the blend are scarcely reported. The novelty of this work is to understand and to study the performance properties of the adhesive prepared by blending PVA and microcrystalline cellulose (MCC) in water and cross-linking the system with a dialdehyde, glyoxal. The study further investigates the bonding strength, thermo-mechanical and performance properties of cross-linked adhesive.

Cooperative Limited, India. Glyoxal (~ 40 % content in water) and microcrystalline cellulose (MCC) (powder, the particle size of 51 µm, and bulk density 0.6 g/mL (25 °C) were purchased from

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Sigma-Aldrich. Deionized water is used for all the formulations that were prepared in the lab. To remove the moisture, all the chemicals used in work were conditioned at 30 °C.

2.2. Preparation method.

Polyvinyl alcohol (PVA) and microcrystalline cellulose (MCC) powder were added to deionized water in a sealed kettle. The samples are mixed with a mechanical stirrer at 170 rpm and heated to 60 °C with the help of a water bath. Finally, in the final stage of the adhesive's preparation, cross-linker, glyoxal is added to the sample at 0.1 wt.% and 0.2 wt.%. After adding the cross-linker, the temperature is raised to 92-95 °C, keeping the stirring at constant. To study the difference between cross-linked and non-cross-linked adhesive blend, a blank sample (standard) is also prepared without adding the cross-linker. The sample is heated for 2.5 hr. in the water bath. Table 1 shows the formulations for the blended adhesive. The blend adhesive samples were labeled as MCC G Cross 0.1, and MCC G Cross 0.2 for PVA/MCC blend with 0.1 wt.% glyoxal and 0.2 wt.% glyoxal. The standard blank sample was labeled as MCC blank.

Table 1. Formulation for preparing the blended samples.

Blend sample name	PVA wt. %	MCC wt. %	Glyoxal wt. %	Water wt. %
MCC blank	15	3	0	82
MCC G Cross 0.1	15	3	0.1	81.9
MCC G Cross 0.2	15	3	0.2	81.8

2.3. Characterization and testing.

2.3.1. Viscosity and pH.

A Brookfield DV1 Viscometer was used for calculating the viscosities of the samples at 20 rpm.

pH was measured using a digital pH meter, CL 54 + Toshcon Industries, India. To reduce the error, viscosity and pH measurements were repeated 3 times. The values were taken at 30 °C and 60 % relative humidity.

2.3.2. Fourier Transform Infra-Red Spectroscopy (FTIR).

Infrared spectra of cross-linked PVA and MCC blends were measured on a PerkinElmer FTIR spectrum 100 instruments in the range 4000–400 cm⁻¹ with 30 scans using the reflectance process. Prior to the test, a background spectrum was also taken to minimize the error, and the whole test was done at 30 °C and 60 % relative humidity.

2.3.3. Differential Scanning Calorimetry (DSC).

A Perkin Elmer instrument Q 100 DSC has been used for measuring the glass transition temperature (T_g) of the samples. 1 mg of sample films having 1000 µm thickness was used in the test. During the measurement, an oxygen-free nitrogen stream of 40 mL/min was maintained through the cell. The DSC analyses were done with a heating rate of 20 °C min⁻¹.

2.3.4. Dynamic mechanical analysis (DMA).

Dynamic mechanical analysis (DMA) of the blend samples were performed using DMA Q 800. Sample films of 200-micron thickness were cut in a specific dimension and loaded in the DMA sample holder. The conditions for the test included the start temperature of -30 °C with soak time for 5 min. The end temperature was 150 °C, with a ramp rate 5 °C/min. A single point frequency of 1 Hz with a strain 0.1 % was given during the analysis. DMA works in the principle that, by applying sinusoidal stress, the corresponding strain in the material was measured and the complex modulus. By varying the temperature of the sample or the frequency of the stress, it correlates to viscoelastic nature. Hence by this approach locating the glass transition temperature (T_g) of the material, as well as identifying the transitions corresponding to cross-linking between the molecules, are made possible.

2.3.5. Contact angle measurement.

The contact angle was measured using a Rame-Hart Goniometer instrument, Germany. To measure the contact angle, the samples were cast over glass substrates with a thickness of 50 micrometers. A syringe containing deionized water was allowed to produce 1 drop (0.05 ml) over the sample coated glass substrate, and the reading was taken after 5 seconds. The test was conducted at a temperature of 30 °C and 60 % relative humidity. Variations in the hydrophobicity in formulations can be analyzed using contact angle measurements.

2.3.6. Pencil hardness test.

The blended samples were cast over a glass plate with a thickness of 1000 micrometers. The test was conducted using ASTM D 3363 standard. QHQ-A portable pencil hardness tester with lead pencils of various hardness values were used in the test.

2.3.7. Wet tack.

A probe tack analyzer from Rohit Instruments, Pidilite R & D lab, Mumbai, India, was used for the wet tack analysis. 2-3 mg of blended samples were

kept in between the metal cylinder and the surface of the instrument. The sample is squeezed as the cylinder comes in contact with the surface. The wet tack is measured by calculating the resistive force offered as the cylinder retracts back. The cylinder movements are at a speed of 5 mm/min. The analysis is conducted at a temperature of 30 °C and 60 % relative humidity. The data is repeated for 3 times and reported with a unit of gram force (gf).

2.3.8. Tensile shear strength.

For measuring the bond strength of prepared adhesive blend, tensile shear strength of steamed beech wood samples was measured on Universal

Testing Machine (model: H25KT Tinius-Olsen, USA). The test method was done according to ASTM D906 test method. The adhesive blend sample was applied on one end (2.5 cm × 2.5 cm) of the two canarium wooden pieces, which were held by grips (total load - 5 kg cylinder + 2.5 kg arm) and pulled at a controlled speed of 5 mm/min. For a better understanding of tensile strength development with respect to time, the test was performed after 6 and 24 hr. The whole test was conducted at a temperature of 30 °C with 60 % relative humidity.

3. Results and Discussion

The result obtained from various characterizations is shown in Table 2.

Table 2. Data obtained from various tests.

Sample name	MCC Blank	MCC G Cross 0.1	MCC G Cross 0.2
Viscosity (cps)	400 ± 19	650 ± 28	800 ± 33
pH	4.6 ± 0.3	4.5 ± 0.1	4.5 ± 0.4
Glass transition temperature (° C)	59.53	59.73	61.30
Contact angle (°)	28.1 ± 1.3	42 ± 1.9	52.9 ± 2.1
Pencil hardness value	H	4H	6H
Wet tack (gmf)	2048 ± 18	2204 ± 26	2297 ± 25

3.1. Viscosity and pH.

The effect on viscosity by the cross-linking between the hydroxyl groups of PVA and MCC with the addition of glyoxal is evident in from the viscosity data shown in Table 2, and Figure 2. pH remained almost same on adding glyoxal to the blend.

An increase in viscosity was observed in the PVA/MCC blends with 0.1 wt.% and 0.2 wt.% of glyoxal concentration. Glyoxal acts as a cross-linker, as shown in Figure 1, which connects two polymer chains by forming acetal bonds at the hydroxyl groups of PVA/MCC blend and hence forming a network structure [32]. The cross-linked structure consolidates the samples and reduces the mobility of chains, thus increases the viscosity. By increasing the concentration of glyoxal, the chances of developing the cross-links increase with further limits the chain mobility, hence a rise in the viscosity was shown.

3.2. Fourier Transform Infra-Red Spectroscopy (FTIR).

The bands occurring at 3400 cm⁻¹ show the characteristic peak of the PVA/MCC blends for stretching vibration bands of the O–H group showing the free hydroxyl groups. For blend samples with 0.1 wt.% and 0.2 wt.% glyoxal, the peak intensity reduces, and this trend is reflected in all the peak intensities. The possible reason can be due to the cross-linking, the free hydroxyls are consumed, and hence a structural change occurs [34, 35]. The two bands at 2850 and 2750 cm⁻¹ of C–H stretching related to aldehydes. The presence of carbonyl group was observed at 1720–1740 cm⁻¹.

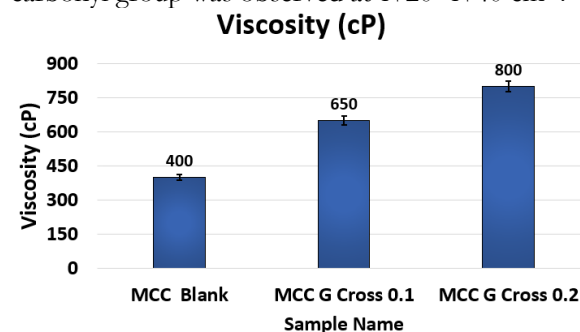


Figure 2. Viscosity of samples.

These bands are overlapping and broadening PVA bands in these regions. In addition to that, by cross-linking PVA with glyoxal, the O–H stretching vibration peak (3330–3350 cm⁻¹) was relatively decreased when compared to non- cross-linked PVA/MCC blend [38]. Other peaks are C–H group stretching vibration at 2935 cm⁻¹, 1340–1450 cm⁻¹ corresponds to C–H asymmetric bending vibration, and O–H deformation vibration of PVA and MCC as shown in Figure 3.

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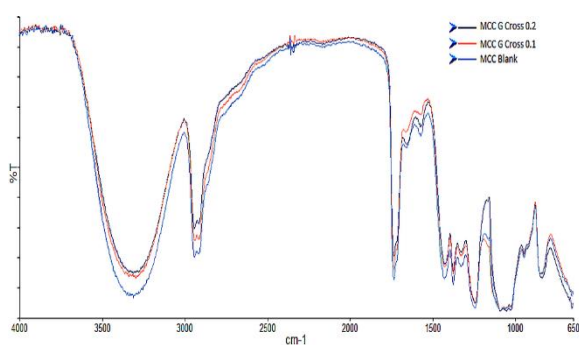


Figure 3. FTIR spectra of PVA/MCC blends with and without glyoxal.

3.3. Differential Scanning Calorimetry (DSC).

The glyoxal acts as a cross-linker for PVA/MCC blend, which has led to subsequent glass transition temperature change, as shown in Table 2. The glyoxal, being a dialdehyde, reacted with the hydroxyl groups and thus forming a cross-linked network [35]. Hence by cross-linking, an increase in the chain length of the polymers occurred. Also, the network structure reduces the voids between the blends, which results in lowering the chain mobility. Thus, the glass transition temperature (T_g) increases as the mobility decreases in the formation of cross-links. Also, the chances of forming the cross-links increase with an increase in cross-linker concentration. This has contributed to the increase in T_g with an increase in glyoxal content shown in Figure 4.

The FTIR curves further substantiates cross-linking reaction by showing a decrease in the hydrogen bonding of the adhesive with a subsequent increase in cross-linker. A similar trend is observed for T_g , showing an increase in T_g with an increase in the concentration of cross-linker.

3.4. Dynamic mechanical analysis (DMA).

Thermomechanical study was performed by DMA analysis, and Table 3 shows the results. The thermogram of storage modulus is shown in Figure 5 indicates an increase in the storage modulus in the glassy region for samples with 0.1 wt.% and 0.2 wt.% glyoxal compared to the blank. The loss of modulus data is shown in Figure 6, and it is seen that the peak value increased with a shift to higher temperature on incorporating glyoxal. Increment in storage modulus relates to the stiffening of chains [12, 39, 40], hence combining the observations from viscosity data, the cross-linking is thus evidenced.

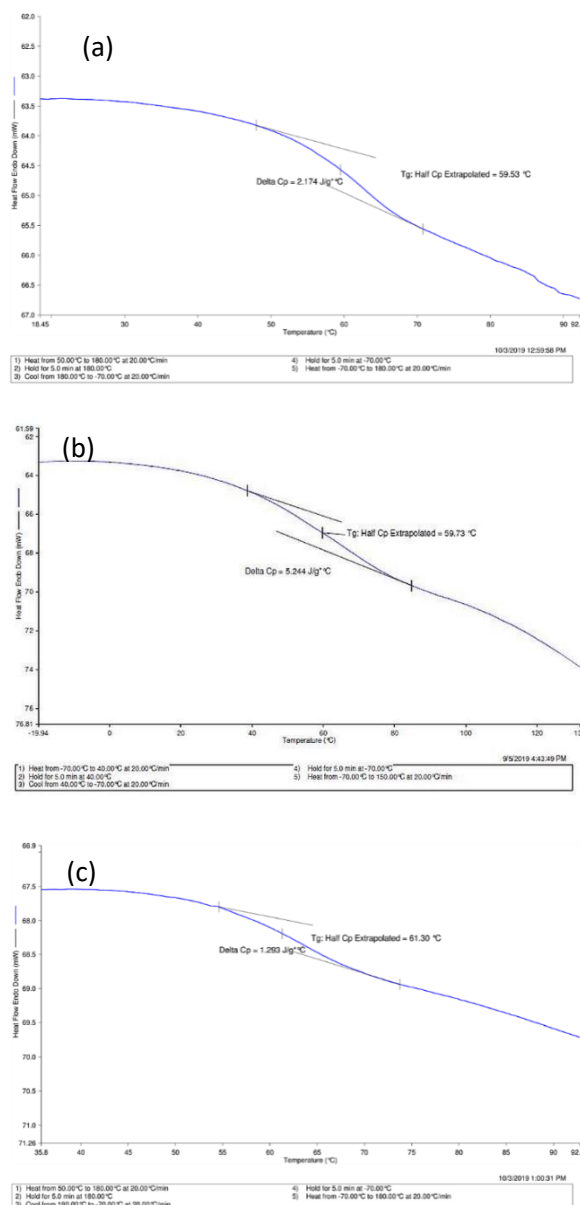


Figure 4. DSC graph for (a) MCC blank; (b) MCC G cross 0.1; (c) MCC G cross 0.2.

Table 3. Data obtained from DMA test.

Sample Name	MCC blank	MCC G Cross-0.1	MCC G Cross-0.2
Storage Modulus at glassy region (MPa)	5039	5976	10143
Storage Modulus at the rubbery region at 100 °C (MPa)	141.8	149.3	219.4
Loss Modulus (E'') (MPa)	503.7	511	883.2

Also, by this cross-linking, reinforcement occurs by the intermolecular binding as covalent bonds are introduced. The cross-links formed supplements the natural intermolecular hydrogen bonds to improve mechanical properties. Hence from DMA analysis, by the addition of cross-linker, enhancement of thermomechanical properties is evidenced as compared with blank samples.

3.5. Contact angle measurement.

The contact angle of sample film with water droplet correlates with the hydrophobic or hydrophilic nature of the material, and the results obtained are shown in Table 2. Since PVA and MCC blend is rich in hydrophilic hydroxyl groups. Hence the blank sample shows the lowest contact angle. The contact angle of the sample with water is shown in Figure 7.

Glyoxal acts as a cross-linker by connecting polymeric chains. As the cross-linking uses hydroxyl groups of the blend, the observation from contact angle measurement justifies the increment in the contact angle of cross-linked samples. As concentration increases contact angle also increases, showing the increase in cross-links formed. This observation is in line with the test results of viscosity, FTIR, DSC, and DMA conforming to the cross-links formed.

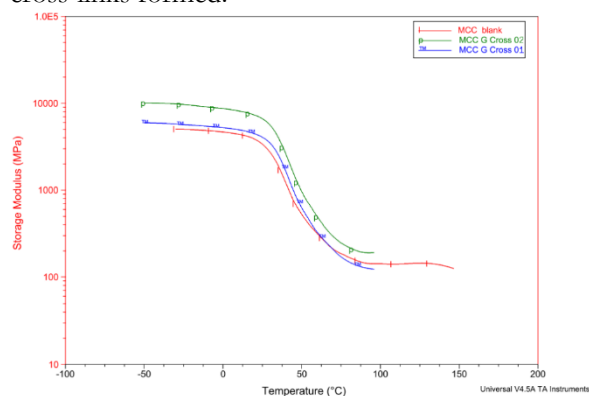


Figure 5. Thermogram of storage modulus (E').

3.6. Pencil hardness test.

The pencil hardness value of a film relates to its mechanical property [35]. Table 2 shows the value obtained from the test and is seen that the film hardness is getting enhanced with the increase in the concentration of glyoxal. The introduction of glyoxal into the blend created cross-linked network structure that connected polymer chains and reduced the voids between them.

The crystalline cellulose contributed to enhancement in harder parts in the blend. As a

result, the polymeric chains in the cross-linked blends become stiff with lower mobility and better cohesion compared to the blank sample.

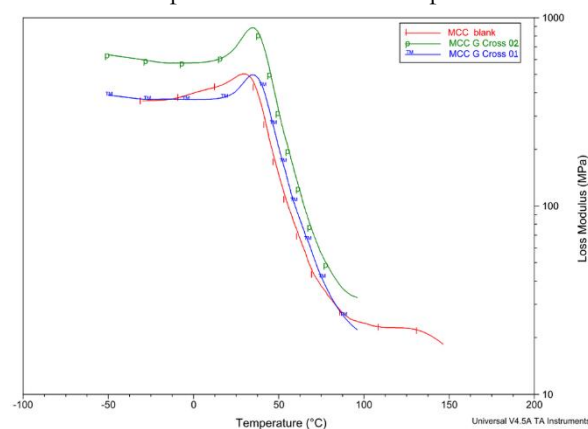


Figure 6. Thermogram of loss modulus (E'').

This made it difficult to penetrate using pencils of lower hardness values. Hence pencil hardness test results show the enhancement in mechanical properties of the cross-linked blends.

3.7. Wet tack analysis.

The adhesive needs to have good tack property for better adhesion with the substrate. The wet tack analysis can relate to the performance property of an adhesive [41]. From the results shown in Table 2, the cross-linked blends showed enhanced tack property compared to the blank, and the increment is proportional to the concentration of glyoxal. Formation of cross-links in the blend created covalent bonds between the polymeric chains, reducing the voids; this resulted in better cohesion. Therefore, by the introduction of cross-linking, the blends showed better cohesive property, which can contribute to the enrichment in the performance property of the adhesive.

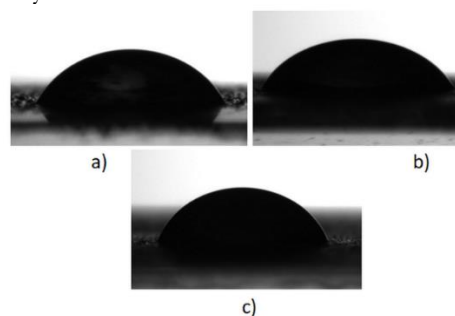


Figure 7. Contact angle images of a) MCC blank b) MCC G cross 0.1 and c) MCC G cross 0.2.

3.8. Tensile shear strength.

The blended PVA/MCC and cross-linked blends were analyzed for evaluating the bond strength by applying the samples to steamed beech



wood specimens by ASTM D 906 test method. Lap shear strength of the adhesive samples is shown in Figure 8.

The cross-linking with PVA and MCC molecule causes cohesion between the blend as evidenced from wet tack data shown in Table 2. Cohesive force creates interaction between the chains and reduces free volume, imparting better bond strength with the wood surface. To study the extent of bond strength, adhesive applied wood substrates tested at two intervals 6 hr. and 24 hr. The results obtained from the tensile test indicates that, by increasing glyoxal content, better adhesion occurs in the canarium wood specimen. Moreover, as time increases, the development of tensile strength of bonded wood substrates occurs. The results from the tensile test and wet tack analysis

show that the cross-linker has an essential role in enhancing the performance properties of the prepared wood adhesives.

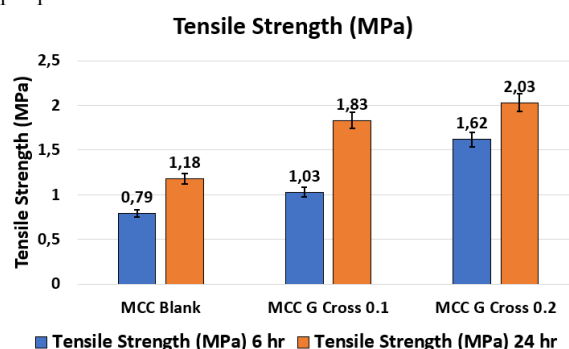


Figure 8. Tensile shear strength values after 6 hr. and 24 hr. for various samples.

4. Conclusions

The need for employing cellulose as an effective bio-filler needs modification of cellulose and the matrix. As the work described here is focused on utilizing MCC for preparing eco-friendly adhesive for wood consolidation using water as the solvent. From the study, glyoxal acts as an effective cross-linker for PVA/MCC blend. The cross-linking of PVA/MCC blends has been evidenced from viscosity analysis, the formation of ether linkages from FTIR, the increment of T_g compare to blank non-cross-linked sample, contact angle data, and DMA analysis. As the concentrations of glyoxal increases, cross-linking increases, which limited the mobility of polymer chains resulting in an increase in the

storage modulus values, as shown by DMA. Pencil hardness data correlates to the improvement in the mechanical property of the films on increasing the cross-linker content. The performance properties of the samples were measured by wet tack analysis and tensile lap-shear test of bonded canarium wood substrates. The results showed a drastic improvement in the adhesive strength with the increase in cross-linker concentration. Therefore, the work concludes with the fact that cross-linking of PVA/MCC with glyoxal can be a potential tool for preparing sustainable wood adhesive with enhanced thermo-mechanical and performance properties.

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Conflicts of Interest

The authors declare no conflict of interest.

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