International Journal of Research in Advent Technology, Vol.6, No.6, June 2018
E-ISSN: 2321-9637
Available online at www.ijrat.org

Carboxymethyl Lignin Bio Polymer and Microcrystalline Cellulose as a Surface Coating Additive to Improve the Properties of Paper on Starch Surface Sizing

Amjath Khan F[1], A. Zahir Hussain[2], S.N.H Noorul Huq[3]
[1,3]*Research & Development, Tamilnadu newsprint and papers limited (TNPL), Karur, Tamilnadu, India, theamjath@gmail.com*
[2]*Department of chemistry, Jamal Mohamed college, Tiruchirappalli,Tamilnadu, India, azahirhussainchem@yahoo.co.in*

Abstract- The water soluble Carboxymethyl lignin (CML) biopolymer was synthesized from lignin with the assistance of microwave. This lignin biopolymer was isolated from spent liquor, a kraft pulping biomass. This CML biopolymer derived from lignin was applied on starch surface size coating of fine paper along with microcrystalline cellulose (MFC). The application of CML biopolymer and MFC on paper coating with and without starch was characterized in terms strength properties (Tensile index, TEA and elongation), Barrier properties ($Cobb_{60}$, Water Vapor Transmission rate), Optical properties (Brightness and Opacity) and printing properties (Surface strength for Printability and wax pick No). The effect of application of CML on surface sizing with and without starch were discussed and reported. Starch coating with addition of CML and MFC yields considerable improvement in terms of surface properties and print properties of paper substrate.

Keywords: Lignin derivative, Carboxymethyl lignin, micro fibrillated cellulose, starch, paper surface.

1. INTRODUCTION

In papermaking, sizing improves the fibre-fibre contacts by the fulfilling the empty pores and spaces and thus conferring better superficial strength and increasing the resistance to water penetration[1]. In paper coating and converting, starch is the most common natural and cost effective additive. Native and modified starch (cationic, oxidized, and enzyme modified) is used mainly for dry strength improvement of paper and reduce dusting. And also starch plays a vital roles as a flocculation aid for retention and dewatering, as a natural binder in coating formulas and strength additive in corrugated board production. The paper industry consumes around 10% of all produced starches and most of it goes to the surface applications like surface sizing and coating[2].

Besides the cost and natural abundance, main disadvantages of starch are associated with the rheological behavior which allows only small coat weight, limited barrier properties, the sensitiveness to water and microbial attack of the applied films[3]. Therefore, in recent times numerous researches have aimed to develop new bio-based materials, which can provide good barrier and strength properties for paper.

Cellulose derivative, Carboxymethyl cellulose (CMC) was used as strength additives, as thickeners and binders in surface sizing and coating formulation in paper and packaging[4]. Several works have been reported the efficiency of chitosan derivatives as process and functional additives. Quaternary chitosan was investigated as retention, drainage and flocculation aid[5].

Micro fibrillated cellulose (MFC)

The preparation of Micro fibrillated cellulose (MFC) derived from wood was introduced by Turbak et al.[6] The microfibrils are 1–50 nm thick and have a length of several micrometers. Their strength, flexibility and aspect ratio suggest a host of tentative possibilities to utilize MFC in large-scale applications

The MFC and NFC are materials produced generally by mechanical, chemical and biochemical (Enzymatic) pretreatments of the cellulosic fiber pulp. The treated pulp was then subjected disintegration into micro fibrils with the aid of high pressure homogenizer. The micro fibrils are of several micrometers long and 20-60 nm in diameter[7, 8]. The pretreatments lead also to an increase in the content of carboxylic acid groups on the fibre surface. The MFC is obtained as a viscous, aqueous gel, consisting of cellulose micro/nano fibril aggregates. The micro/Nano fibrillated celluloses present high intrinsic tensile properties and high aspect ratio, which result in good reinforcing potential when used in composite materials[7, 9].

Furthermore, they have the ability to form dense films, with MFC structures, which can provide gas barrier effects similar to those of synthetic polymer films Therefore, further development in obtaining and application of MFC nanocelluloses could offer alternatives to synthetic polymer films for barrier properties of paper, along with mechanical strength improvement.

Carboxymethylated lignin (CML)

Carboxymethylated lignin (CML) is a lignin derivative with hydrophilic carboxyl groups engrafted by carboxymethylation modification. In recent times a limited number of works only reported in literature regarding the synthesis and applications of CML. Linhuo Gan et al., prepared the water-soluble carboxymethylated lignin by using wheat straw alkali lignin (WAL) as the raw material[10]. Leandro G. da Silva et.al, synthesized carboxymethyl lignin (CML) from acid hydrolysis of sugarcane bagasse in the process of bio-ethanol production and complexed the CML with the Fe^{3+} ion (CML-Fe) for the removal of Brilliant Red 2BE textile dye[11]. Cerrutti et al., Studied the lignin obtained from sugarcane bagasse in a bioethanol producing plant was carboxymethylated to yield the water-soluble carboxymethyl lignin(CML), which was then used as stabilizing agent in aqueous alumina (Al2O3) suspensions[12]. El-Zawawy et al., evidenced that the modified lignin (CML) with Cobalt (III) and some metal ions find an application as remarkable filler in polystyrene polymer composites which can be used in packaging applications[13]. Carboxymethyl lignin (CML) is the most important water soluble derivative, with many applications in the dispersant and adsorption. However, water soluble lignin derivatives was never investigated in surface sizing of paper and packaging products.

Lertsutthiwong et.al reported that chitosan as a Surface Sizing Agent for Offset Printing Paper. Blending of oxidized starch with a small quantity of chitosan significantly improved the sizing quality of the paper[14].

Fang et al. reported 98% reductions of WVTR for 7.4 g/m^2 two-layer coatings based on chitosan and poly (vinylydene chloride) composites [15]. In this work, we are looked into the functional application of CML biopolymer, MFC and combination of both in surface application of paper with starch. With this consideration, the MFC and CML biopolymer were investigated in coating formulas as additive to supplement starch, for the improvement of barrier, strength and printing properties of paper substrate.

2. EXPERIMENTAL SECTION

Materials

Kraft lignin is isolated from spent liquor of sugarcane bagasse pulping. Native starch was procured from M/s SPAC starch industries, Salem, Tamilnadu, India. Amylase enzyme was purchased from M/s. Texbio science, Chennai, India and all the other chemicals were of analytical grade and used as received without further purification.

Isolation of lignin and microwave preparation of Carboxymethyl lignin (CML)

Lignin was precipitated from black liquor bio-mass obtained from Kraft pulping of sugarcane residue (Bagasse) using 20% Sulphuric acid. The precipitate obtained was thoroughly washed with water and filter. The residue was dried and weighed. The crude lignin was purified using 1, 4 dioxane.

Preparation of carboxymethyl lignin is followed by our earlier work and as per the procedure[16] with some modification under microwave environment. About 15g of Kraft lignin dispersed in 450mL isopropyl alcohol and stirred for about one hour. About 50mL of 40% NaOH was added into the reaction mixture and further stirred for 30 min prior to adding 18g of Monochloroacetic acid (MCA). The mixture was covered with aluminum foil and placed in a microwave oven at 180KW power for 30 minutes. The solid phase was separated and washed with 100mL of ethanol, neutralized with acetic acid (90%) and filtered using a Buchner funnel. The product was washed five times by soaking in 300mL of ethanol (70 %) for 10 minutes to remove undesirable by products. The final product was washed with 300mL of absolute methanol. The carboxymethyl lignin (CML) obtained was dried overnight at room temperature.

Preparation of micro fibrilated cellulose(MFC)

Bleached bagasse chemical pulp (CBP) was procured from an ‘A’ grade mill in India and made the concentration about 50g/l. Then the pulp was pretreated with cellulase enzyme followed by saturated mechanical beating with laboratory PFI mill, Germany with the load of 177kN. Then refined pulp subjected to mechanical shearing by Polytron high shear homogenizer. The resulted micro fibrillated pulp suspension was preserved with formaldehyde and used as a MFC

Coating substrate:

60 g/m^2, A4 size, non surface sized machine made paper was purchased from an 'A' grade mill in India and the same sheets used in all the experiments.

Preparation of surface sizing recipe

Coating recipe of surface sizing starch was prepared by cooking dry starch powder, CML biopolymer and MFC with the solid content of 8%w/w in water bath of 85°C for 30 minutes under stirring. When the gelatinization starts, the amylase enzyme was introduced at the dose of 0.001% of starch to reduce the viscosity. After complete cooking, the cooked starch solution was kept at thermostat to maintain temperature about 55^{O}C.

Coating method

Coating recipe was applied with a metering rod (ROD #3) using an Auto bar coater, GIST Co Ltd, GmpH from Frank PTI with the speed of 20mm/min. Coating speed was set to achieve total solid deposition (Coat weight) of 3.0 g/m^2 in one passes by each coating recipe. Coated samples were dried at 25 ºC in overnight and cured at 100^{O}C in hot air oven then used for testing.

Characterization of board samples

Sample conditioning:

All paper tests were carried out under conditioned atmosphere (23 °C and 50% relative humidity) according to TAAPI Standard T 402 sp-08. All samples were exposed to conditioned atmosphere for 24 hours prior to testing.

Water absorption capacity:

Water absorption capacity was evaluated by Cobb method, according to IS 1060 (Part-I), at 60 seconds contact time between the paper surface and water ($Cobb_{60}$ Index, g/m^2).

Water vapor transmission rate (WVTR):

WVTR defined as the amount of water vapour transmitted from one face of the sample to the other per unit time and unit area, under specific conditions. In these experiments, the WVTR was measured by a gravimetric method, according to ISO 2528 standard. The samples were sealed with paraffin wax on top of aluminum cups containing anhydrous $CaCl_2$. The cups were exposed to conditioned atmosphere (23 °C and 50% RH) for 96 hours and weighed at regular time intervals. The mass uptake was used to calculate the WVTR. Five samples were tested for each coating type.

Tensile strength properties:

The load–elongation curves of coated sheets were registered at constant strain. The clamp separation was 100 mm and the strain rate was 10 mm/s. Tests were carried out by using L&W make Tensile tester in machine direction according to the method IS 1060 (Part-I),. Ten samples were tested for each coating type and the corresponding tensile index, elongation at break (stretch) and tensile energy absorption were reported.

Optical Properties

Optical properties such as Brightness (%ISO) and Opacity % were tested with L&W, ELREPHO spectrophotometer according to the method IS 1060 (Part-I, II), the reflectance @ 457nm was measured as brightness of the sheets.

Surface strength- VVP

Surface strength of the coated sheets were determined by using the IGT-printability tester a print is made on the paper to be tested with pick test oil at an increasing speed. The first damaging of the print is observed and from a table the speed where picking begins is read. The VVP (viscosity velocity product) is calculated as the product of the speed where picking begins and the viscosity of the pick test oil used.

WAX pick number was tested with Dennison wax sticks as per the stated in the method IS 1060 (Part-III).

3. RESULTS AND DISCUSSION

Water absorption capacities of the coated sheets are shown in the (Fig.1). The Cobb of CML /Starch coated sheets are on par with starch surface sized sheets (25-26g/m^2). Surface sized with MFC/Starch sheets were found to be have more water absorptive (Cobb is 38g/m^2) in nature than CML/S coated sheets, this increase of water absorption can be attributed with hydrophilic character of MFC.

The water absorption capacity increases in CML/Starch with MFC addition. Hence combination of CML/MFC/Starch will have an optimum water absorption properties.

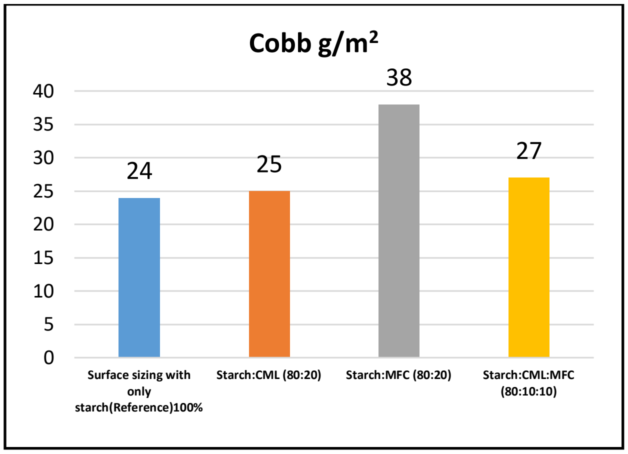

Figure.1

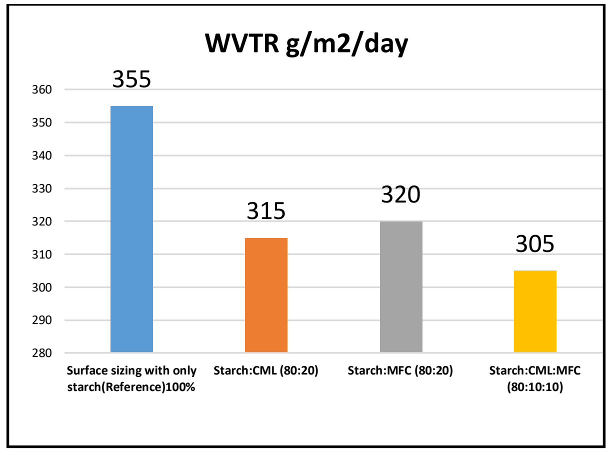

Figure.2

Water vapor transmission rate (WVTR)

The property like WVTR was revealing some key points on CML and MFC surface coated sheets (Fig.2). Unlike starch coating ($355 g/m^2/day$), CML/Starch ($315 g/m^2/day$) and MFC/Starch ($320 g/m^2/day$) combination had significant influence on the WVTR, though both are hydrophilic and have similar values of $Cobb_{60}$ index. In fact, all coatings containing CML and MFC have lesser WVTR values (10-15% lesser WVTR) than individual starch coatings.

The efficiency of the coating of CML/MFC combinations on reduction of WVTR is appears promising considering with other polymers in literature.

Optical properties

Since the CML/Starch has light brown color, the optical properties of CML/Starch coated sheets were found to be slightly deviated in terms of brightness. As per shown in the (Fig.3) about 2-3.5 points (from 86.5 to 84.7%ISO) have been decreased in brightness. This can be compensated by adding of suitable optical whitening agent. MFC/Starch coating with starch has not influenced the brightness considerably. On the other hand the opaqueness of the paper sheets has been significantly increased with addition of CML and MFC and the combination of both. For the lower substance (gsm) paper product the opacity can be increased by addition of CML in starch.

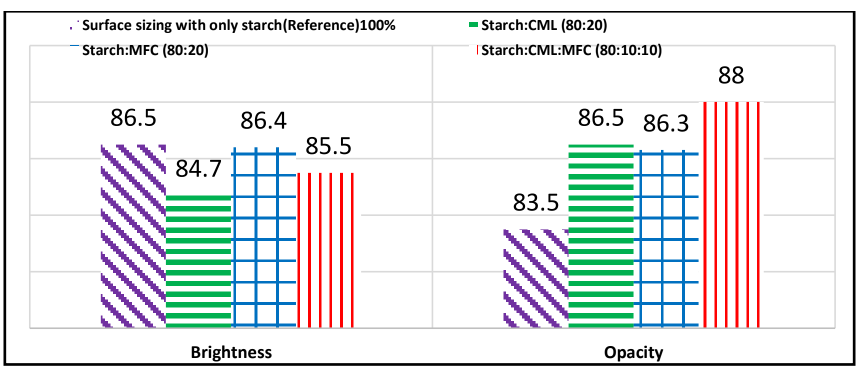

Figure.3

Surface strength of the Paper

Surface strength of paper sheets were evaluated by testing VVP. The VVP values of CML/Starch coated sheets (1552 m.poise /S) were higher than that of only starch coated (1352 m.poise /S) and MFC/Starch (1152 m.poise /S coated sheets). The picking and continuous delamination of surface occurs in CML/Starch coated sheets are far apart than the picking occurs in starch coated sheets. The pick start and delamination of the samples are shown in (Fig 6).

There is no significant impact on surface strength by MFC as a coating additive rather it accelerates the picking of fibre from the surface of the paper. . Unlike exclusive MFC, the combination CML and MFC has resulted a significant improvement in surface strength 1360 m.poise /S. The surface strength of the tested paper sheets reveals that the film formation efficiency of CML/Starch combination found to be good and the paper will run on web offset printing with increased mileage.

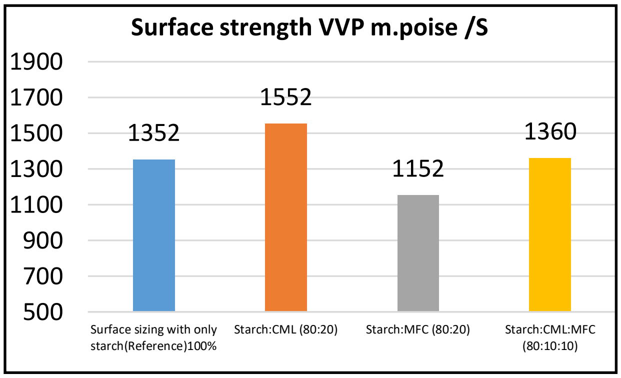

Figure.4

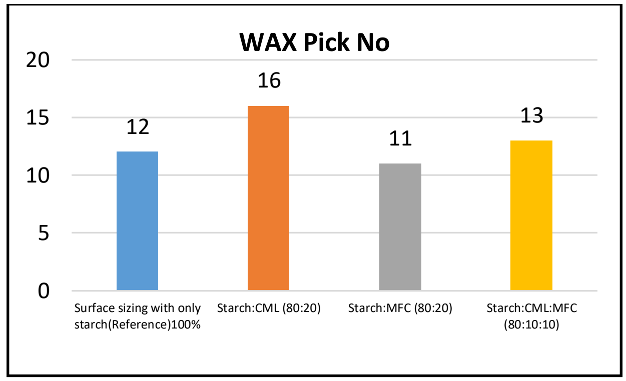

Figure.5

Wax stick test resembles the surface strength results (Fig.5). For wax pick no of CML/Starch coated sheets is 13 which is better than starch coated sheets. Unlike CML, the MFC coated sheets were poorly picked in 11.

Starch coated paper	CML/S coated paper	MFC/S coated paper	CML/MFC/S coated paper

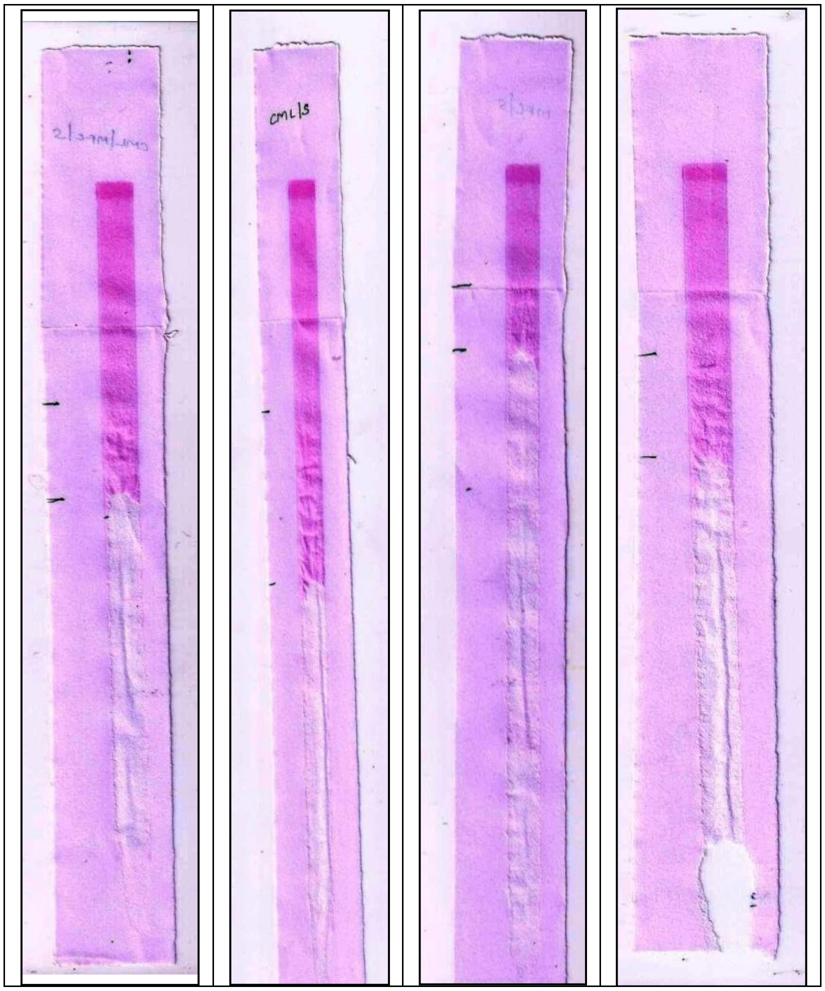

Figure.6

Strength properties

The tensile index (Nm/g), Elongation at break (stretch, %) and tensile energy absorption (TEA, J/m^2) were registered for all formulations in machine direction. As Figure 6 illustrates, CML/S coated sheets showing a slight increase in TI (5.4% higher than the reference),

A more consistent improvement of tensile strength properties is illustrated by the 10-15% increase of tensile energy absorption (TEA) in the case of CML/S film coatings (Fig.7). The TEA value is an indication of the ability of paper to withstand repetitive stress and strain (Fig.9). The TEA values obtained for surface coatings based on MFC combinations are 175 and 189 J/m^2 (Fig.8) which is lower than CML/S coating (199 J/m^2). This may due poor film formation ability and crystallanity of the MFC fibrils. The results are demanding more investigations on finding out solutions for a more uniform distribution of the cellulose micro fibrils (MFC) in a biopolymer matrix.

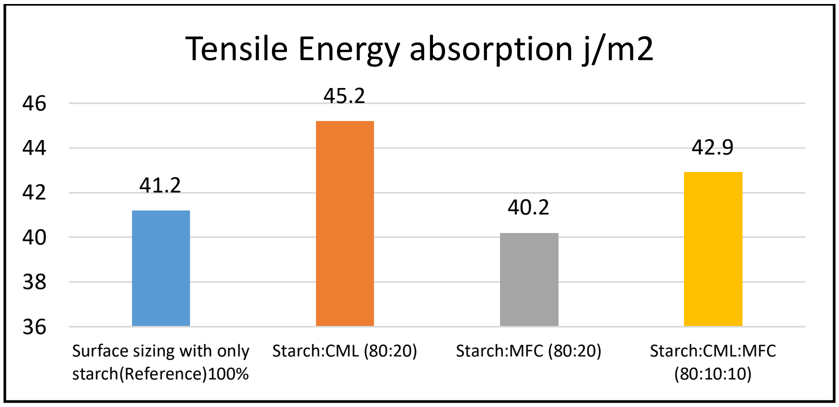

Figure.7

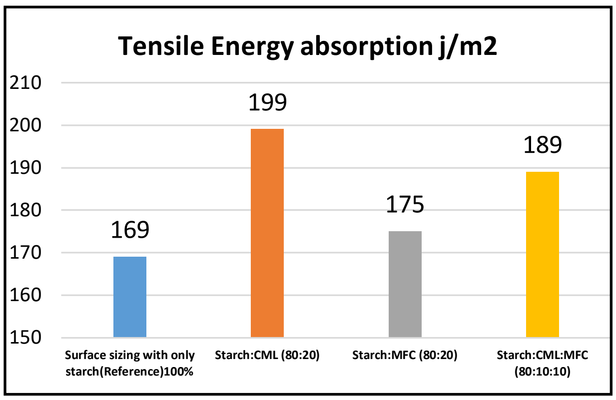

Figure.8

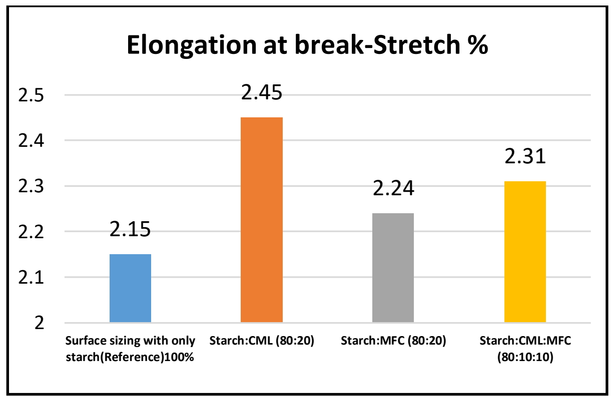

Figure.9

4. CONCLUSION

Lignin derivative, carboxymethyl lignin (CML) and micro fibrillated cellulose (MFC) show wide differences in barrier properties when applied as additive in starch coating of paper. Combination of MFC/Carboxymethyl lignin (CML) coatings maintained the hydrophilicity of paper surface and evidenced by the values of Cobb index. The WVTR drops by 15% for the CML/ Starch coatings than starch coating due to a compact and uniform film morphology of CML/Starch.

When applied along with starch coating, both CML and MFC have positive influence on the mechanical strength properties. Tensile energy absorption – TEA increases by 17% for the CML/S coating which reflects in tensile index of CML/Starch coating and TI increased by 10%. About 11% increase was recorded for MFC/Starch coating. Similar trends has been observed for elongation at break. In context with surface strength, CML/Starch coating increases the strength by 15%. Surface strength of the paper was effected by the addition of MFC in starch. This surface strength could be attributed by the corresponding wax pick number. CML/Starch combination on application in coating paper will run on web offset printing with increased mileage. There is significant impact observed in terms of opacity of paper when using CML and MFC. The experimental data observed on this study provide promising results, which validate the multi functionality of lignin derivative, Carboxymethyl lignin (CML) as papermaking additives.

ACKNOWLEDGEMENTS

The authors are thankful to Jamal Mohamed College, Tiruchirappalli, India and Tamilnadu Newsprint and Papers Limited (TNPL), Kagithapuram, Karur, India for providing research facilities, co-operation and constant encouragement to carry out the work.

REFERENCES

[1] Verboeff.J., Hart, J.A,e Gallay,W (1963)sizing and mechabnism of water penetration of water into paper, Pulp.Pap.Mag. Can. **64**, T509.

[2] W. J. Auhorn, in "Handbook of Paper and Board", edited by H. Holik, published by Willey-VCH, Weinhem, 2006, **68-69**

[3] C. Johansson, L. Järnström, C. Breen, Biopolymer based barrier material and method for making the same, WIPO Patent WO/2010/077203, July 8, 2010.

[4] T. Lindström, L. Wågberg, T. Larsson, in Transactions of the 13th Fundamental Research Symposium, Cambridge, 11-16 September, 2005, Vol. **1-3**, pp. 457-562.

[5] R. Miranda, R. Nicu, I. Latour, M. Lupei, E. Bobu et al., Chem. Eng. J., **231**, 304 (2013).

[6] Turbak AF, Snyder FW, Sandberg KR (1983) Microfibrillated cellulose, a new cellulose product: properties, uses and commercial potential. J Appl Polym Sci Appl Polym Symp **37**:815–827

[7] N. Lavoine, I. Deslonges, A. Dufresne, J. Bras, Carbohyd. Polym., **90**, 735 (2012).

[8] L. Wågberg, G. Decher, M. Norgren, T. Lindström, M. Ankerfors et al., Langmuir, **24**, 784 (2008).

[9] I. Siró and D. Plackett, Cellulose, **17**, 459 (2010).

[10] Linhuo Gan1, Mingsong Zhou1,, Xueqing Qiu1, Advanced Materials Research. 2012; **550-553:**1293-1298.

[11] Leandro G. da Silva and Reinaldo Ruggiero Chemical Engineering Journal. 2011; **168**: 620–628.11

[12] B.M. Cerrutti, C.S. de Souza, A. Castellan, R. Ruggiero and E. Frollini: Ind. Crops Prod. 2012; **36**:108.12

[13] El-Zawawy. W.K, Materials Chemistry and Physics 2011;**131**: 348–357.

[14] Lertsutthiwong, Pranee; Nazahad, Mousa M; Chandrkrachang, Suwalee; Stevens Willem F; Appita Journal, **57**, **4**, 2004;274-280.

[15] Z. Q. Fang, G. Chen, Y. Liu, X. Chai, *Appl. Mech. Mater.*, **200**, 180 (2012).

[16] W.K. El-Zawawy et al. / Materials Chemistry and Physics, 2011, **131**, 348–357.