

Carboxymethyl Cassava Starch/Polyurethane Dispersion Blend as Surface Sizing Agent

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Surface sizing agent (SSA) is a material used to improve the surface quality of the paper. It is one of the compulsory components in the paper-related industries to impart surface smoothness, printability, water resistivity and brightness. An environmental friendly surface sizing agent based on carboxymethyl cassava starch/polyurethane dispersion (CCS/PUD) blend had been developed. A local cassava starch (CS) was modified with anionic reagent, sodium monochloroacetate (SMCA) via etherification, in a presence of sodium hydroxide (NaOH) to form sodium carboxymethyl cellulose (CCS). Later CCS was blended with 30 wt% polyurethane dispersion (PUD) to enhance its water resistivity. The CCS/PUD blend was applied onto the surface of a hand-made paper prior to being tested and characterised. Fourier transform infrared analysis had verified the successful of etherification process by showing peaks at $3,400\text{ cm}^{-1}$, $1,635\text{ cm}^{-1}$ and $1,440\text{ cm}^{-1}$, corresponding to carboxymethyl substituent. The highest degree of substitution (0.76) was obtained from the system that used 6 g SMCA at fixed 1 : 7 CS : water ratio and 4 mL NaOH. Meanwhile, CCS/PUD-coated paper had improved water resistivity corresponded to higher water contact angle at 73° , in comparison with the CCS-coated paper (62°) and the uncoated paper (40°). This was supported with low surface energy showed by CCS/PUD-coated paper (33.9 mJ/m^2).

1. Introduction

Sizing of paper is a process of imparting some degree of water resistance to the paper. Internal or external sizing agents are applied during the papermaking operation where the external sizing agent gives better resistance to the water penetration because it is applied onto the surface of the paper compared to an internal sizing agent (Liu et al., 2011). The surface sizing also improves the smoothness and printability due to the possible formation of hydrogen bonding between the agent or the printing ink with the hydroxyl groups of cellulose of the paper (Bock et al., 1994). Starches are traditional sizing agents used in paper industry. Native starch has limited usage due to its hydrophilic character which swells and gelatinises when heated in water (Ali et al., 2013). The fluctuation in viscosity causes the starch paste has poor stability, poor tolerance to acidity and low resistance to shear pressure (Garcia-Ubasart et al., 2012). The starches need to be modified to change their physical and/or chemical properties such as changing the shape and composition of the constituent amylose and amylopectin molecules (Ramaswamy et al., 1995).

Waterborne polyurethane (PUD) has emerged as an important class of polymeric materials in many applications such as paint and ink industries due to its environmental nature (Gao et al., 2011). PUD has alternating sequences of the soft and the hard segments where the hard segments generate glassy crystalline regions while the soft segments form amorphous regions (Jung et al., 2010). The co-existence of this morphology has imparted excellent toughness, abrasion resistance, and mechanical flexibility (Krol et al., 2011). PUD proved to be an excellent surface sizing agent. It was found that the surface properties of the sized paper such as water resistant, smoothness and glossiness were improved due to the emulsion had filled the fiber interspaces and formed a layer of the continuous film after drying on top of the paper (Siau et al., 2004). Due to its expensive price, PUD is normally blended with cheaper polymers such as polyacrylic (Vincent et al., 2014) or corn starch (Guo et al., 2011).

In this research, native cassava starch (CS) was selected to be used as a surface sizing agent due to its local available, cheap and has remarkable characteristics including high paste viscosity, high paste clarity, and high freeze-thaw stability (Parra et al., 2004). CS was modified through a simple etherification process at atmospheric pressure with an anionic SMCA to form ether carboxymethyl cellulose (CCS). Later CSS was blended with PUD in order to improve water resistivity and surface smoothness. The degree of substitution (DS) of carboxymethylated starch and wettability (surface energy) of dried film were analysed.

2. Experimental

2.1 Sample Preparation

Native cassava starch (CS) and sodium monochloroacetate (SMCA) were purchased from Sigma-Aldrich. Ethanol (99 % purity) and sodium hydroxide (NaOH) were obtained from Merck while polyurethane dispersion (PUD) was purchased from DSM (Neorez R-974). All chemicals were used as received.

Pre-gelled cassava starch was prepared by mixing 2.0 g of native cassava starch and 150 mL of distilled water in a 250 mL reaction flask. Then, 4 mL ethanol and 4 mL of sodium hydroxide were added dropwise and stirred for 30 minutes. Then the pre-gelled starch was placed in the water bath equipped with a horizontal shaker. The etherification of starch into carboxymethyl starch (CCS) was started with the addition of 5.0 g sodium monochloroacetate (SMCA). The mixture was heated to 60 °C for 3 h. Later, the mixture was cooled to room temperature. The same steps were repeated for 6.0 g and 7.0 g SMCA. The etherification of cassava starch is following the reaction scheme as shown in Figure 1.

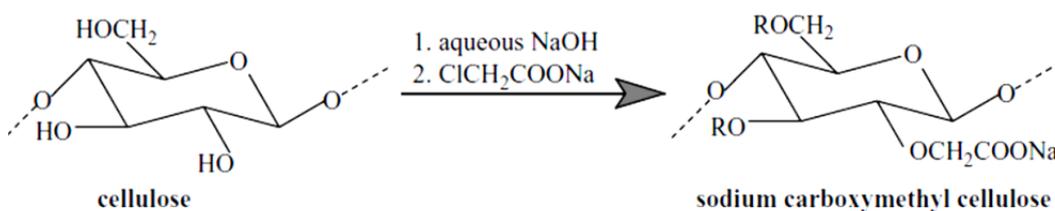


Figure 1: Reaction scheme of etherification of cellulose into carboxymethyl cellulose (Heinze and Pfeiffer, 1999)

To prepare CCS/PU blend, about 30 wt% of PU was added to the mixture and stirred for 30 min at 600 rpm using a stainless steel blade.

All SSAs were applied onto the hand-made papers using a roller brush with the average thicknesses of 1 mm. The coated papers were left to dry at room temperature.

2.2 Determination of Degree of Substitution

Absolute degree of substitution of CCS was determined by potentiometric back titration as described by Pushpamalar et al. (2006) and Elomaa et al. (2004). The carboxymethyl groups in the CCS were first converted to the acid form by acidifying with 2 M nitric acid. The acidified starch was then recovered by precipitation with ethanol, filtration, washing with methanol and drying in the oven. The dried starch was then treated with an excess amount of 0.5 N sodium hydroxide. The solution was then back-titrated with 0.3 N hydrochloric acid. The DS was then calculated based on Eq(1) and Eq(2).

$$\text{Carboxymethyl content (\% CM)} = [(V_0 - V_n) \times 0.058 \times 100] / M \quad (1)$$

$$\text{DS} = 162 \times \% \text{ CM} / [5800 - (57 \times \% \text{ CM})] \quad (2)$$

where,

V_0 = mL of HCl used to titrate blank;

V_n = mL HCl used to titrate sample;

M = sample amount (g).

2.3 Fourier Transform Infrared spectroscopy

Fourier transform infrared (FTIR) analysis was done to determine the successful of the etherification of CS into CCS. The samples were characterised using FTIR-ATR spectrophotometer model Perkin Elmer 1000 with ranges of the wavelength of 4,000 cm⁻¹ to 370 cm⁻¹.

2.4 Wettability Analysis

The contact angle was measured using a drop test method according to ASTM D724 with a VCA Optima. About 20 μl of water and di-iodomethane (D-IM) were dropped onto the sample using a micro syringe. The spreading of the drop was later examined using an image analyser. For each sample, at least five measurements were recorded at different parts of the coated surface. The surface free energy (γ) of the sample was calculated based on a Fowkes method using Eq(3) to Eq(5) (Zenkiewicz, 2007).

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (3)$$

$$\gamma_s^d = 0.25\gamma_1(1 + \cos \theta)^2 \quad (4)$$

$$\gamma_s^p = \frac{[0.5\gamma_1(1 + \cos \theta) - (\gamma_s^d \gamma_1^d)^{0.5}]^2}{\gamma_1^p} \quad (5)$$

Where,

For water; $\gamma_1^d = 21.8 \text{ mJ/m}^2$; $\gamma_1^p = 51 \text{ mJ/m}^2$;

For di-iodomethane; $\gamma_1 = \gamma_1^d = 50.8 \text{ mJ/m}^2$.

3. Results and Discussion

3.1 Effect of SMCA on the Degree of Substitution

In this study, the amount of NaOH and CS : water ratio were fixed at 4 mL and 1 : 7. Only the amounts of SMCA were varied at 5.0 g, 6.0 g and 7.0 g. It was found that the highest DS value i.e. 0.76 was obtained at 6.0 g SMCA as shown in Figure 2. The increase was due to greater availability of SCMA which provided sufficient amount of acetate ions to take part in the substitution reaction with OH groups of starch. Further increased the amount of SMCA at 7.0 g had decreased the value at 0.44. The decrease was related to the access amount of SMCA that triggered the secondary reaction with sodium hydroxide to form sodium glycolate ($\text{HO-CH}_2\text{COONa}$), thus reducing the efficiency of substitution to CCS. The same observations were reported by other researchers (Bhattacharyya et al., 1995; Barai et al., 1997).

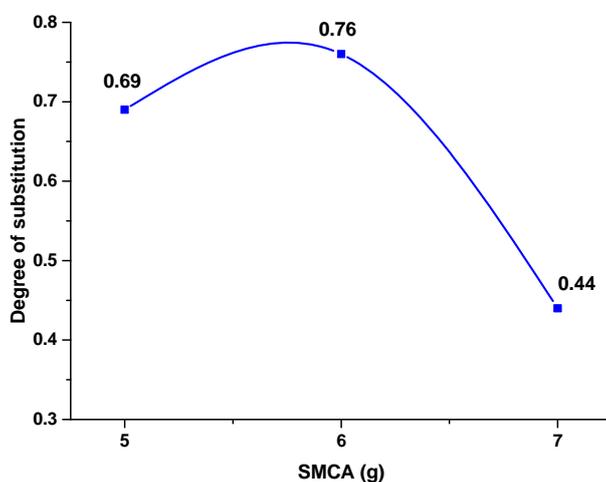


Figure 2: Degree of substitution of CCS at different amount of SMCA

3.2 Fourier Transform Infra-red Spectroscopy

The successful of etherification process of CS into CCS were verified with the detection of absorption peaks of carboxymethyl substituent as showed in Figure 3. Carboxyl groups and its salt have wavenumbers in the range of $1,600 - 1,640 \text{ cm}^{-1}$ and $1,400 - 1,450 \text{ cm}^{-1}$ (Adinugraha et al., 2005). The peak observed at $1,635 \text{ cm}^{-1}$ was related the stretching of a carboxyl group (COO^-) while the peaks detected at $1,411 \text{ cm}^{-1}$ and $1,344 \text{ cm}^{-1}$ were corresponded to $-\text{CH}_2$ scissoring and $-\text{OH}$ bending. Those peaks did not appear in the native CS

spectrum. The vibration band of α -1,4-glycosidic linkage (C-O-C) at 926 cm^{-1} , the stretching band of primary alcohol ($-\text{CH}_2\text{OH}$) at $1,078\text{ cm}^{-1}$ and the water adsorbed in the amorphous regions at $1,641\text{ cm}^{-1}$ are the characteristic groups of native CS, which were similarly obtained by Marques et al. (2006), as well as Braihi et al. (2014). The band of $-\text{CH}_2\text{OH}$ group was undetected in CCS spectrum, implying the group underwent the substitution reaction with SMCA. The waveband of urethane linkages at $1,535\text{ cm}^{-1}$ was detected in CCS/PUD spectrum, indicating the presence of PUD in the blend. The broad absorption bands observed at $3,360 - 3,311\text{ cm}^{-1}$ were belong to the stretching frequencies of the $-\text{OH}$ groups of all samples.

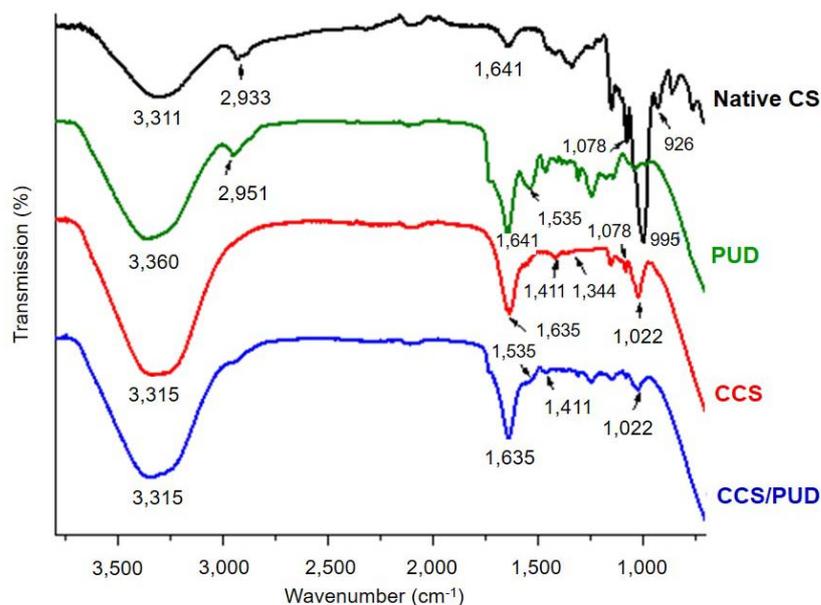


Figure 3: FTIR spectra of CS, CCS and CCS/PUD

3.3 Surface Wettability

Surface wettability of coated papers was plotted in Figure 4. The CCS/PUD-coated paper had a water contact angle at 73° , compared to the CCS-coated paper (62°) and uncoated paper (40°). These results manifested that the water resistivity of the uncoated paper increased at about 41 % and 66 % with respect to the CCS- and CCS/PUD-coated papers. The increase in CCS was related to the 76 % of OH groups in CS had been substituted with the carboxymethyl groups, thus reducing the hydrophilicity of the sample. While the presence of hydrophobic PUD in the CCS/PUD blend contributed to the increase of water resistivity of the sample. The ability of PUD to form a continuous film on the surface of the sized paper and the formation of hydrogen bonding between PUD and the surface of the paper were also the reasons behind the increase (Guo et al., 2011). The result obtained was in compliance with the calculated surface energy of CCS/PUD-coated paper that had lower value i.e. 33.9 mJ/m^2 . Substrate with low surface energy has low adhesion force between the substrate surface and SSA liquid phase, thus preventing the liquid from wetting the surface of the substrate (Cognard, 2006). Although PUD-coated paper showed the highest value of water resistivity at 86° , it is uneconomical to use 100 % PUD due to its expensive price. The surface properties of SSA coated papers are summarised in Table 1.

Table 1: Surface properties of papers coated with various type SSAs

Coated paper surface	Contact angle ($^\circ$)		Surface Energy (mJ/m^2)*
	Water	Di-iodomethane	
Uncoated	40.0	50.6	50.5
CS	45.0	56.8	45.9
CCS	62.0	60.4	37.3
CCS/PUD	73.0	70.9	33.9
PUD	86.0	62.7	33.1

*Calculated using Fowkes Method: $\gamma_s = \gamma_s^d + \gamma_s^p$

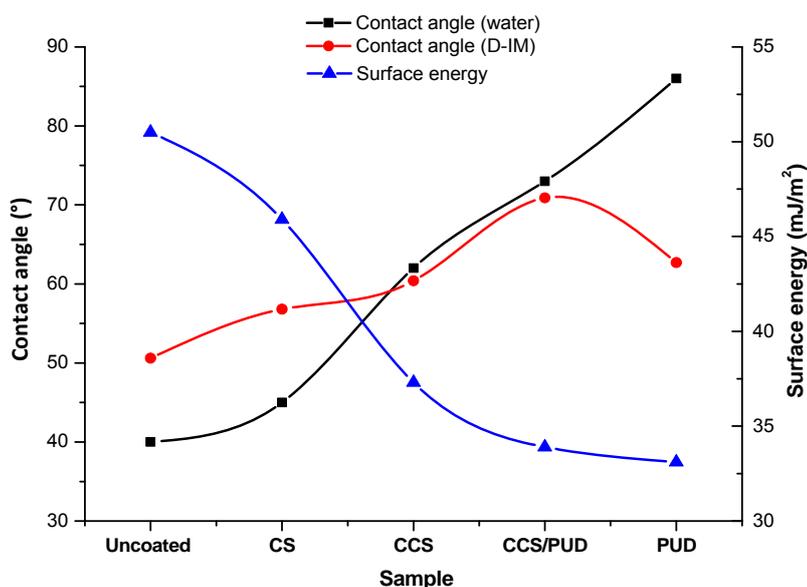


Figure 4: Surface wettability of papers- coated with various SSAs

4. Conclusion

The etherification of cassava starch (CS) into carboxymethyl starch (CCS) had been successfully prepared as proven by FTIR spectra. Paper coated with CCS had improved water resistivity due to the substitution of OH group of CS with the ether CCS ($>\text{CH}_2\text{COO Na}^+$). Paper coated with CCS/PUD blend showed a superior water resistivity (73°) with low surface energy i.e. 33.9 mJ/m^2 .

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References

- Adinugraha M.P., Marseno D.W., Haryadi M., 2005, Synthesis and characterization of sodium carboxymethylcellulose from cavendish banana pseudo stem (*Musa cavendishii* LAMBERT), *Carbohydrate Polymers* 62, 164–169.
- Ali R.R., Rahman W.A.W.A., Kasmani R.M., Ibrahim N., Mustapha S.N.H., Hasbullah H., 2013, Tapioca starch biocomposite for disposable packaging ware, *Chemical Engineering Transactions* 32, 1711-1716.
- Barai B.K., Singhal R.S., Kulkarni P.R., 1997, Optimization of a process for preparing carboxymethyl cellulose from water hyacinth (*Eichornia crassipes*), *Carbohydrate Polymers* 32, 229-231.
- Bhattacharyya D., Singhal R.S., Kulkarni P.R., 1995, A comparative account of conditions for synthesis of sodium carboxymethyl starch from corn and amaranth starch, *Carbohydrate Polymers* 21, 247-253.
- Bock M., Casselmann H., Blum H., 1994, Progress in Development of Waterborne PUR Primers for the Automotive Industry Waterborne, higher-solids and powder coatings symposium, New Orleans, Louisiana, USA.
- Braih A.J., Salih S.I., Hashem F.A., Ahmed J.K., 2014, Proposed cross-linking model for carboxymethyl cellulose /starch superabsorbent polymer blend, *International Journal of Materials Science and Applications* 3 (6), 363-369.
- Cognard P., 2006, Adhesives and Sealants, General Knowledge, Application Techniques, New Curing Techniques: Handbook of Adhesives and Sealants, Vol. 2, Elsevier, New York.

- Elomaa M., Asplund T., Soininen P., Laatikainen R., Peltonen S., Hyvarinen S., Urtti A., 2004, Determination of the degree of substitution of acetylated starch by hydrolysis, ¹HNMR and TGA/IR, *Carbohydrate Polymers* 57, 261-267.
- Gao X.Y., Zhu Y.C., Zhou S., Gao W., Wang Z.C., Zhou B., 2011, Preparation and characterization of well-dispersed waterborne polyurethane/CaCO₃ nanocomposites, *Colloids Surface A: Physicochemical Engineering Aspects* 377, 312-317.
- Garcia-Ubasart J., Colom J.F., Vila C., Hernandez N.G., Roncero M.B, Vidal T., 2012, A new procedure for the hydrophobization of cellulose fibre using laccase and a hydrophobic phenolic compound, *Bioresources Technology* 112, 341-344.
- Guo Y., Li S., Wang G., 2011, Properties and application of waterborne polyurethane/starch composite surface sizing agent, *Advanced Materials Research* 317-319, 15-18.
- Heinze T., Pfeiffer K., 1999, Studies on the synthesis and characterization of carboxymethylcellulose, *Macromolecular Materials and Engineering* 266 (1), 37-45.
- Jung D.H., Kim E.Y., Kang Y.S., Kim B.K., 2010, High solid and high-performance UV cured waterborne polyurethanes, *Colloids Surface A: Physicochemical Engineering Aspects* 370, 58-63.
- Krol P., Krol B., Pielichowska K., Pikus S., 2011, Comparison of phase structures and surface free energy values for the coatings synthesised from linear polyurethanes and from waterborne polyurethane cationomers, *Colloid Polymer Sciences* 289, 1757-1767.
- Liu Q.X., Li J.L., Xu W.C., 2011, Preparation and properties of cationic starch with high degree of substitution, *Materials Science Forum* 663-665, 1264-1267.
- Marques P.T., Lima A.M.F., Bianco G., Laurindo J.B., Borsali R., Le Meins J.F., Soldi V., 2006, Thermal properties and stability of cassava starch films cross-linked with tetraethylene glycol diacrylate, *Polymer Degradation and Stability* 91,726-732.
- Parra D. F., Tadini C. C., Ponce P., Lugao A. B., 2004, Mechanical properties and water vapor transmission in some blends of cassava starch edible films, *Carbohydrate Polymers* 58, 475-481.
- Pushpamalar V., Langford S.J., Ahmad M., Lim Y.Y., 2006, Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste, *Carbohydrate Polymers* 64, 312-318.
- Ramaswamy H.S., Basak S., Abbatemarco C., Sablani, S.S, 1995, Rheological properties of starch as influenced by thermal processing in an agitating retort, *Journal of Food Engineering* 25 (3), 441-454.
- Siau C.L., Karim A.A., Norziah M.H., Wan Rosli W.D., 2004, Effects of cationization on DSC thermal profiles, pasting and emulsifying properties of sago starch, *Journal of the Science of Food and Agriculture* 84, 1722-1730.
- Vincent B.J., Natrajan B., 2014, Waterborne polyurethane from polycaprolactone and tetramethylxylene diisocyanate: synthesis by varying NCO/OH ratio and its characterization as wood coatings, *Open Journal of Organic Polymer Materials* 4, 37-42.
- Zenkiewicz M., 2007, Methods for the calculation of surface free energy of solids, *Journal of Achievements in Materials and Manufacturing Engineering* 24 (1), 137-145.