

RHEOLOGICAL PROPERTIES OF PALM-BASED CARBOXYMETHYL CELLULOSE SOLUTIONS

NOR ZULIANA YUSOF^{1*}; ZAFARIZAL ALDRIN AZIZUL HASAN¹; NUR ELIYANTI ALI OTHMAN¹ and YUSRABBIL AMIYATI YUSOF¹

ABSTRACT

Palm empty fruit bunches have been value added into carboxymethyl cellulose (CMC). However, its potential as rheological modifiers in cosmetic and personal care has yet to be explored. Therefore, the aim of this study was to investigate the rheological performance of the CMC solutions (1%, 2%, 3% and 4%) against two commercially available CMC (cotton-based and wood-based CMC). Our study revealed that all the CMC solutions studied gave flow behaviour index of less than 1, which indicated the pseudoplastic or shear-thinning properties. Among the three CMC studied, 2% and 3% CMC from palm empty fruit bunches (PEFB-CMC) and cotton-based CMC exhibited viscoelastic solid properties where the storage modulus (G') was larger than loss modulus (G'') on amplitude sweep test. On the other hand, all the wood-based CMC did not exhibit any viscoelastic solid properties. In addition, the 2% palm-based CMC exhibited higher gel strength as compared to 2% cotton-based CMC solution, while the wood-based CMC exhibited fluid-structure through frequency sweep test. The palm-based CMC exhibited potential application as rheological modifier in consumer products particularly for the development of cosmetic and personal care products.

Keywords: palm-based carboxymethyl cellulose, shear-thinning properties, viscoelastic solid.

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INTRODUCTION

The conventional sources of cellulose include cotton linters and wood pulp. However, there are continuous global efforts to search for cellulose biomass from other sources as an alternative feedstock to expensive cotton linters and wood pulp, which nowadays are discouraged due to environmental regulations (Varshney and Naithani, 2011). Nonetheless, cellulose can also be extracted and is readily available in large quantities from non-wood alternatives. One such viable source is oil palm empty fruit bunch (OPEFB) fibre, a by-product of the oil palm industry (Wan Rosli *et al.*, 2011). OPEFB is considered the cheapest natural fibre with good properties and exist abundantly in Malaysia (Padzil *et al.*, 2020). Oil palm fibre comprises of 40%-50% cellulose,

20%-30% hemicellulose and 15%-20% lignin (Rosnah *et al.*, 2002; Ariffin *et al.*, 2008). Several studies on cellulose extraction from OPEFB with the yield of 64% (Nazir *et al.*, 2013), 58.5% (Ching and Ng, 2014), 43.22% (Sisak *et al.*, 2015), 37% (Rosnah *et al.*, 2012) and 34.1% (Astimar *et al.*, 2002) were reported.

Cellulose is not water-soluble, it should be modified to enable it to be applied as a thickener, a gelling agent or a stabilising agent (Hutomo *et al.*, 2012). In order to make water-soluble cellulose, cellulose is derivatised through the etherification process to produce carboxymethyl cellulose (CMC), hydroxyethyl cellulose, hydroxypropyl cellulose, methylcellulose and hydroxypropyl methylcellulose (Rowe *et al.*, 2013). CMC is the most important water-soluble cellulose derivative with many applications in the food, pharmaceutical, cosmetics, detergent, textile, paper, and many other industries. It is a white to off-white, non-toxic, odourless and biodegradable powder. CMC is used to enhance the viscosity, to control the rheology of a solution, to avoid separation of water

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from a suspension, and to improve the surface of barrier properties (Stigsson *et al.*, 2001).

CMC is one of the thickeners used in various products such as creams, lotions and toothpaste formulation (Benchabane and Bekkour, 2008). Furthermore, due to its polymeric structure that acts as a film-forming agent, it has also been used to improve moisturising effects (Benchabane and Bekkour, 2008). The rheological properties of CMC depend on the concentration of polymer and the degree of substitution, which varies from 0.5-1.2 (Barba *et al.*, 2002). Rheological properties such as flow behaviour are important and it can be correlated with the spreadability and flow of cosmetic products from the bottle (Niraula *et al.*, 2004). CMC is regarded as polyelectrolyte, and once it is dissolved in water, the molecule is separated into sodium cations and anionic polymer. CMC dispersions exhibited thixotropic and viscoelastic behaviour at high CMC concentrations (Ghannam and Esmail, 1997).

The palm-based CMC from OPEFB has been reported to potentially contribute towards the development of an oil palm-based specialty chemical industry (Rosnah *et al.*, 2004; Eliza *et al.*, 2015; Parid *et al.*, 2018). A study conducted by Amin *et al.* (2007) suggested that CMC from OPEFB can be used as a film-coating agent for pharmaceutical industry.

So far, very little attention has been paid to the role of palm-based CMC in various applications, especially in Malaysia. Therefore, palm-based CMC has huge potential in the development of sustainable cosmetic and personal care. This article described the rheological properties of palm-based CMC solutions.

MATERIALS AND METHODS

Materials

Palm-based CMC (PH 2000) is a yellowish-white powder obtained from Waris Nove Sdn. Bhd., Pahang, Malaysia. Two commercial CMC from other sources; cotton and wood were also used in this study for comparison. The two commercial CMC were cotton-based CMC sodium salt, C5013 (Sigma-Aldrich, Missouri, USA) and wood-based CMC, Walocel™ CRT 2000 PA (The Dow Chemical Company, USA).

Scanning Electron Microscope Measurement and Degree of Substitution Determination by Energy Dispersive X-ray Analysis

The morphology of palm-based CMC was examined by Hitachi S-3400N Scanning Electron Microscope (SEM) (Hitachi, USA) equipped with Energy Dispersive X-ray (EDX) (Bruker XFlash 6I10)

analysis. The test parameters used were as follows; Chamber pressure: 10 Pa; High voltage: 20.00 kV; Tilt: 0.00; Take-off: 35.00; Amplification time: 102.4; Resolution: 133.44. The powdered samples were analysed without coating and carbon cement adhesive. The degree of substitution was calculated using EDX data and the following Equation (1) (Singh and Kathri, 2012):

$$\text{Degree of substitution} = \frac{162 \times \% \text{ Sodium}}{2300 - (80 \times \% \text{ Sodium})} \quad (1)$$

where 162 is the molecular weight of the anhydrous glucose unit, 80 is the net increment in the anhydrous glucose unit for every substituted sodium carboxymethyl group, and 23 is the molecular weight of Na.

Characterisation of CMC by Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded using Perkin Elmer FTIR Spectrum 100 equipped with Universal ATR Attachment, recording the spectra over a wavenumber range of 650-4000 cm⁻¹. The average value of eight scans with 4 cm⁻¹ resolution was collected for each sample.

Preparation of CMC Solutions

Palm-based, cotton-based and wood-based CMC solutions were prepared at 1%, 2%, 3% and 4% (w/v) solution in ultrapure water (ELGA PURELAB Flex 3, High Wycombe, United Kingdom) by dissolving the CMC powder in ultrapure water with gentle magnetic stirring for 30 min at ambient temperature.

Viscosity Measurement

Viscosity measurement of CMC solutions was carried out using DV-III Ultra Rheometer (Brookfield Eng. Lab. Inc., Middleborough, USA). The measurements were performed at room temperature, speed 30 rpm and more than 10% torque. The viscosity of solutions was measured at Day 1, after Day 7 and Day 30 of storage at room temperature.

Rheological Measurement

The rheological measurements were performed using a stress-controlled rheometer (Anton Paar MCR300, Anton Paar GmbH, Graz, Austria). The geometry used was a cone plate with a diameter of 50 mm and a gap height of 1.000 mm. Rheological measurements were carried out at ambient temperature with a fresh sample each time. Samples were placed on the rheometer plate and equilibrated for 5 min before measurements.

Rotational test. The flow properties of CMC solutions were measured in continuous flow conditions, with a controlled shear rate test, by recording viscosity values at increasing shear rate (0-100 s⁻¹).

Oscillation test. Amplitude sweep studies were examined in a log strain ramp from 0.1%-1000% at an angular frequency of 10 rads⁻¹. Amplitude sweep is designed to measure the viscoelastic properties of samples without the disruption of the internal structures. A sinusoidal stress as a function of the angular frequency (ω) and the stress amplitude was applied to the samples. Frequency (small deformation) measurements were performed within the linear viscoelastic region by varying frequency from 0.1-100 rads⁻¹.

RESULTS AND DISCUSSION

We have carried out the EDX analysis of SEM of palm-based CMC, cotton-based CMC and wood-based CMC. The SEM images with 100 μ m magnification, along with the EDX analysis, are shown in *Figure 1*. The results are tabulated in *Table 1*. Palm-based and cotton-based CMC showed a similar morphology structure; long-shaped with relatively smooth surface (*Figures 1a* and *1b*). However, the surface morphology of wood-based CMC is different where the particles are compactly gathered together (*Figure 1c*).

The degree of substitution (DS) is an important CMC parameter, which could influence its performance, such as its solubility in water. The theoretical maximum of the DS value for CMC is 3.0, but the DS value of commercially available CMC grades is generally in the range of 0.4-1.5 (Heinze and Koschella, 2005). *Table 1* listed the calculated DS value based on the wt % sodium (Na) from EDX analysis. Cotton-based CMC recorded the highest wt %Na (13.08) and gives calculated DS value of 1.69, followed by palm-based CMC with wt %Na (9.88) and calculated DS value of 1.06. While, wood-based CMC recorded wt %Na (8.94) and gives calculated DS value of 0.91. The calculated

DS value was compared to the DS value given from the certificate of analysis (CoA) of each CMC (*Table 1*), provided by the CMC's supplier which usually determined according to ASTM D1439 test method. The method evolves the conversion of the CMC to free acid then again forming CMC by adding excess alkali and finally titrating the excess alkali with standard hydrochloric acid. Then, the DS value was determined by the used volume of the standard alkali (ASTM, 1995). Calculated DS values for palm-based and wood-based CMC are close to values reported by CoA. However, cotton-based CMC recorded a higher calculated DS value as compared to CoA (*Table 1*). According to Singh and Khatri (2012), the EDX analysis has a limitation to predict the exact DS value if the sample is not pure. Free sodium chloride (NaCl) in the sample would be reflected in the wt %Na value and so in the DS value. According to Borsa and Racz (1995), CMC has good water solubility above DS value of 0.6. Palm-based, cotton-based and wood-based CMC have DS value above than 0.6 and it was observed that all CMC soluble in water and gives clear solution.

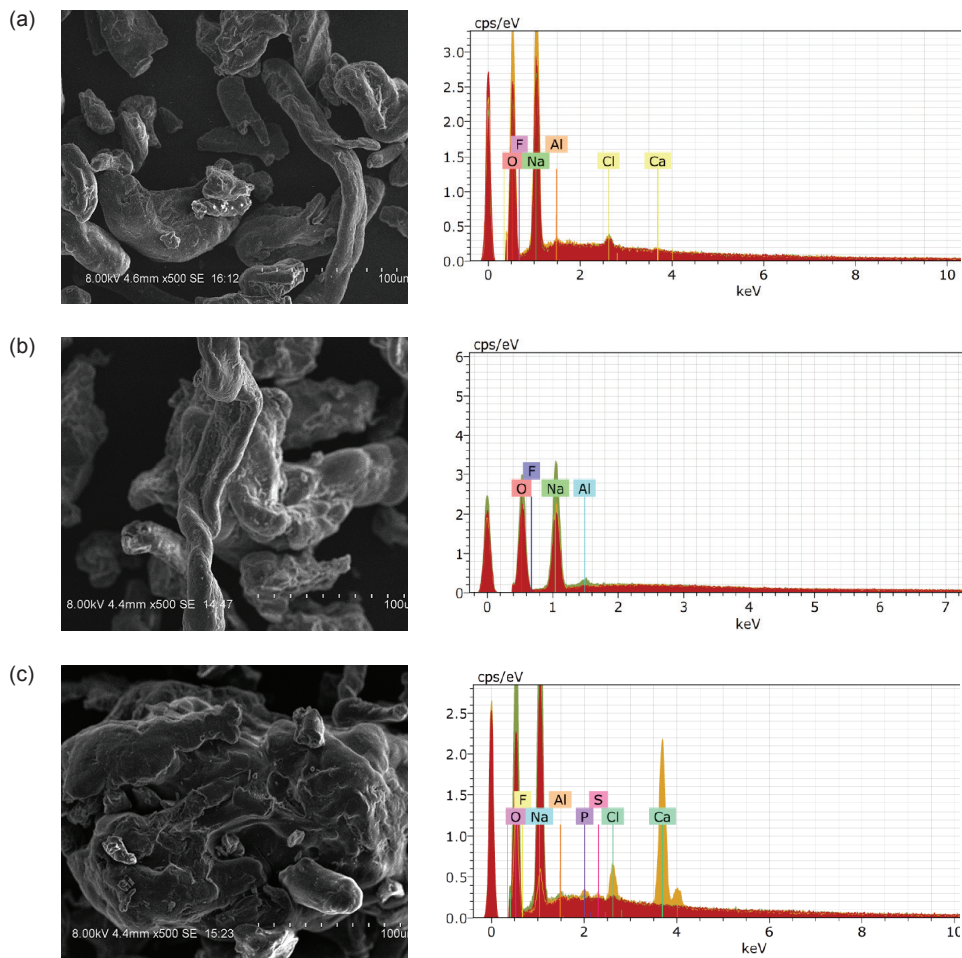
Figure 2 depicts the FTIR spectra of palm-based, cotton-based and wood-based CMC. The spectra pattern was similar to the spectra of CMC from OPEFB as reported by Eliza *et al.* (2015) and spectra of CMC as prepared by Ramli *et al.* (2015). In this study, it was clearly shown that all CMC have a broad band located within the region of 3600-3200 cm⁻¹, attributable to an -OH stretching vibration consistent with the polyhydroxylated saccharide backbone. The band at 2921.69 cm⁻¹ is attributed to CH stretching vibration (3000 cm⁻¹). All CMC recorded a weak absorption band at 2887-2933 cm⁻¹ consistent with the C-H stretching within each glucose unit. The strong absorption band observed at 1585.88, 1586.61 and 1589.90 cm⁻¹ are due to presence of carboxyl group -C(O)O, while the peaks at 1412 and 1415 cm⁻¹ are relevant to CH₂-stretching. The ether groups (-O-) stretching was observed at peak 1000-1200 cm⁻¹ (Eliza *et al.*, 2015; Ramli *et al.*, 2015).

A non-Newtonian fluid is a fluid whose flow properties differ in many ways from those of

TABLE 1. DEGREE OF SUBSTITUTION OF PALM-BASED, COTTON-BASED AND WOOD-BASED CMC BY EDX ANALYSIS AS COMPARED TO CoA

CMC	EDX analysis (wt. %Na)	Calculated DS	DS value from CoA
Palm-based	9.88 ± 1.73	1.06	>0.70
Cotton-based	13.08 ± 2.97	1.69	0.89
Wood-based	8.94 ± 4.29	0.91	0.82-0.95

Note: DS - degree of substitution; CoA - certificate of analysis; CMC - carboxymethyl cellulose; EDX - energy dispersive X-ray.



Note: CMC - carboxymethyl cellulose.

Figure 1. Scanning electron microscope (SEM) images with Energy Dispersive X-ray (EDX) of sample (a) palm-based CMC, (b) cotton-based CMC, and (c) wood-based CMC.

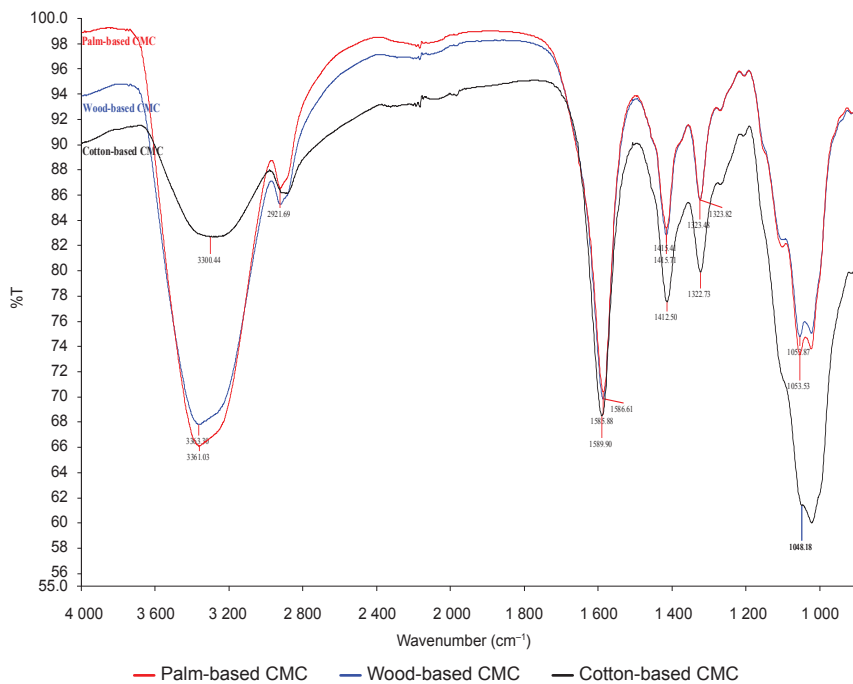


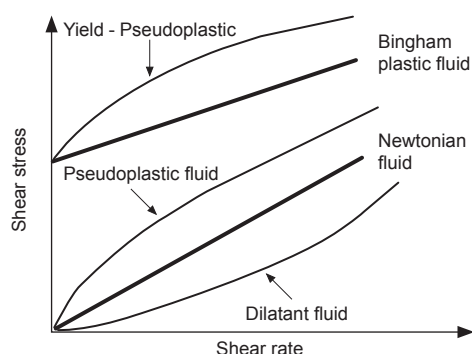
Figure 2. Infrared spectra of palm-based, cotton-based and wood-based carboxymethyl cellulose (CMC).

Newtonian fluids. In practice, many fluid materials exhibit non-Newtonian fluid behaviour such as salt solutions, toothpaste, starch suspensions, paint, shampoo *etc.* Figure 3 shows the flow curves of different types of time-independent non-Newtonian fluid (Nguyen and Nguyen, 2012). The rheology of a non-Newtonian fluid is often described by the power law equation as in Equation (2).

$$\tau = K\gamma^n \tag{2}$$

where τ is the shear stress, K is the flow consistency index, γ is the shear rate and n is the flow behaviour index. The larger the deviation of n from 1, the more non-Newtonian is the behaviour of the fluid. For a Newtonian fluid, n is equal to 1, for a dilatant or shear-thickening fluid, n is greater than 1 and for pseudoplastic or shear-thinning fluid, n is less than 1. The smaller the value of n , the greater is the degree of shear-thinning (Holdsworth, 1971). Table 2 summarises the value of n and description of the flow behaviour of palm-based, cotton-based and wood-based CMC solutions.

The values of flow behaviour index (n) for palm-based CMC, cotton-based CMC, and wood-



Source: Nguyen and Nguyen (2012).

Figure 3. Types of time-independent non-Newtonian fluid.

TABLE 2. VALUE OF n AND DESCRIPTION OF FLOW BEHAVIOUR OF CMC SOLUTIONS

CMC	% solution in water (w/v)	Flow behaviour index (n)	Flow consistency index (K)
Palm-based	1	0.50	3.52
	2	0.34	33.28
	3	0.24	131.19
	4	0.19	344.57
Cotton-based	1	0.57	2.42
	2	0.35	28.76
	3	0.17	202.03
	4	0.15	378.87
Wood-based	1	0.90	0.12
	2	0.77	1.04
	3	0.64	5.77
	4	0.54	19.96

Note: CMC - carboxymethyl cellulose.

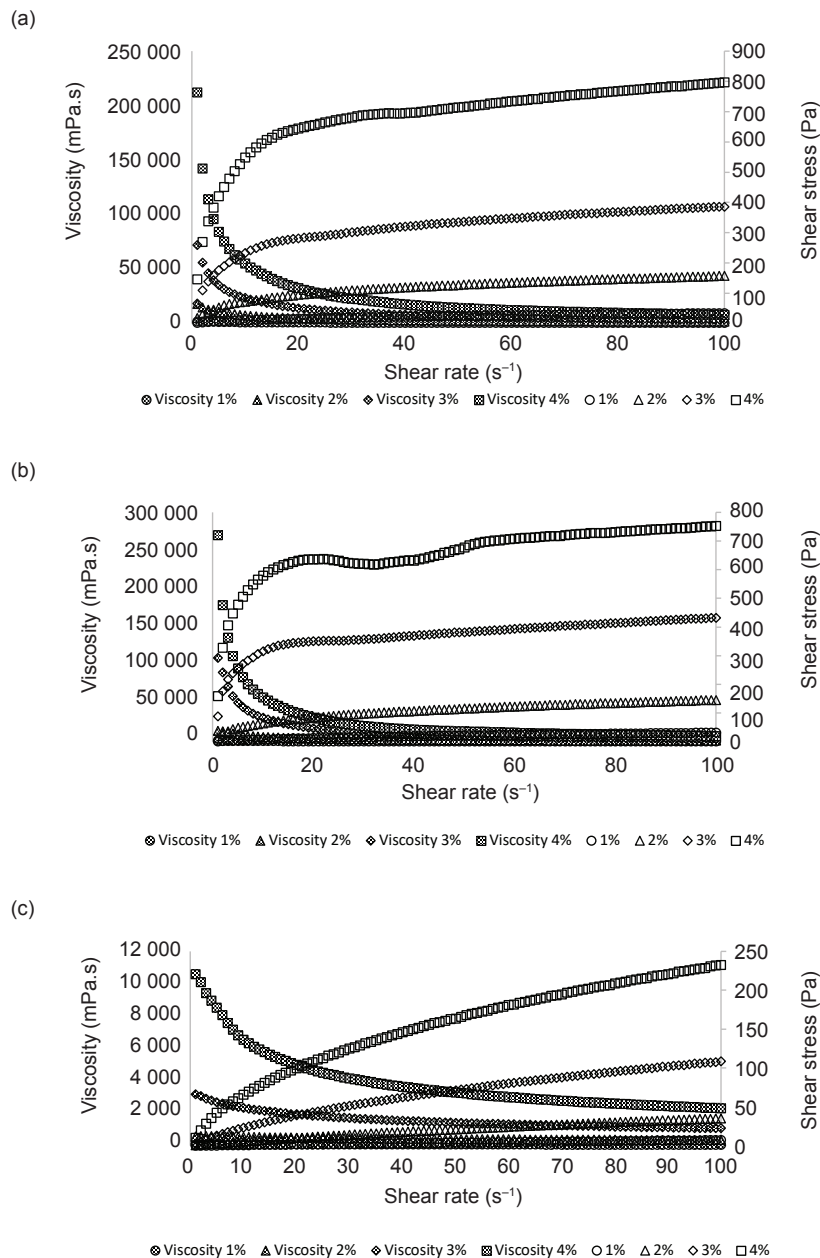
based CMC solutions were all less than 1, indicating the pseudoplastic or shear-thinning properties. Upon increasing the concentration, the value of n decreased, revealing more-obvious pseudoplastic or shear-thinning behaviour. The degree of shear-thinning properties of palm-based CMC and cotton-based CMC solutions were comparable and greater as compared to wood-based CMC solution at 1%, 2%, 3% and 4% (w/v) in water, respectively as listed in Table 3. Figure 4 shows the flow curves of palm-based CMC, cotton-based CMC and wood-based CMC solutions, at different concentrations plotted of viscosity (mPa.s) and shear stress (Pa) over shear rate (s^{-1}). At higher concentration (4%) and shear rate $1 s^{-1}$, cotton-based CMC solution recorded a highest viscosity (270 000 mPa.s) (Figure 4a), followed by palm-based CMC (212 000 mPa.s) (Figure 4b) and wood-based CMC (10 600 mPa.s) (Figure 4c). According to Newton's Law, shear stress is viscosity times shear rate. Therefore, the viscosity is shear stress divided by shear rate. This explained why wood-based CMC solutions have lower shear stress (Pa) (Figure 4c) value as compared to palm-based and cotton-based CMC solutions (Figures 4a and b). The flow curves in Figure 4 clearly show that all CMC solutions exhibited pseudoplastic or shear-thinning behaviour with reference to Figure 3.

The results of amplitude sweeps are presented as a diagram with strain or shear stress plotted on the x-axis, and storage modulus (G') and loss modulus (G'') plotted on the y-axis; both axes on

TABLE 3. POSITION OF G' AND G'' AND FLOW POINT VALUES (crossover $G'=G''$) OF CMC SOLUTIONS

CMC solutions	G' and G''	Flow point (Pa)
Palm-based		
1%	$G'' > G'$	No crossover
2%	$G' > G''$	39.6
3%	$G' > G''$	241.0
4%	$G' > G''$	514.0
Cotton-based		
1%	$G'' > G'$	No crossover
2%	$G'' > G'$	No crossover
3%	$G' > G''$	247.0
4%	$G' > G''$	691.0
Wood-based		
1%	$G'' > G'$	No crossover
2%	$G'' > G'$	No crossover
3%	$G'' > G'$	No crossover
4%	$G'' > G'$	No crossover

Note: G' - storage modulus; G'' - loss modulus; CMC - carboxymethyl cellulose.



Note: CMC - carboxymethyl cellulose.

Figure 4. Flow behaviour curves of (a) palm-based CMC solutions, (b) cotton-based CMC solutions, and (c) wood-based CMC solutions at varying concentrations: 1%, 2%, 3% and 4%.

a logarithmic scale as depicted in Figure 5. The limit of the linear viscoelastic (LVE) region is first determined. The LVE region indicates the range in which the test can be carried out without destroying the structure of the sample. The LVE region will give an information on the structure and firmness of the sample. The longer the LVE, the more firm or structured the test sample, while the shorter the LVE, the less firm it appears (Ho and Dodou, 2007). The LVE region analysed by the software is 5% strain and the region was depicted on the left side of the diagram in Figure 5.

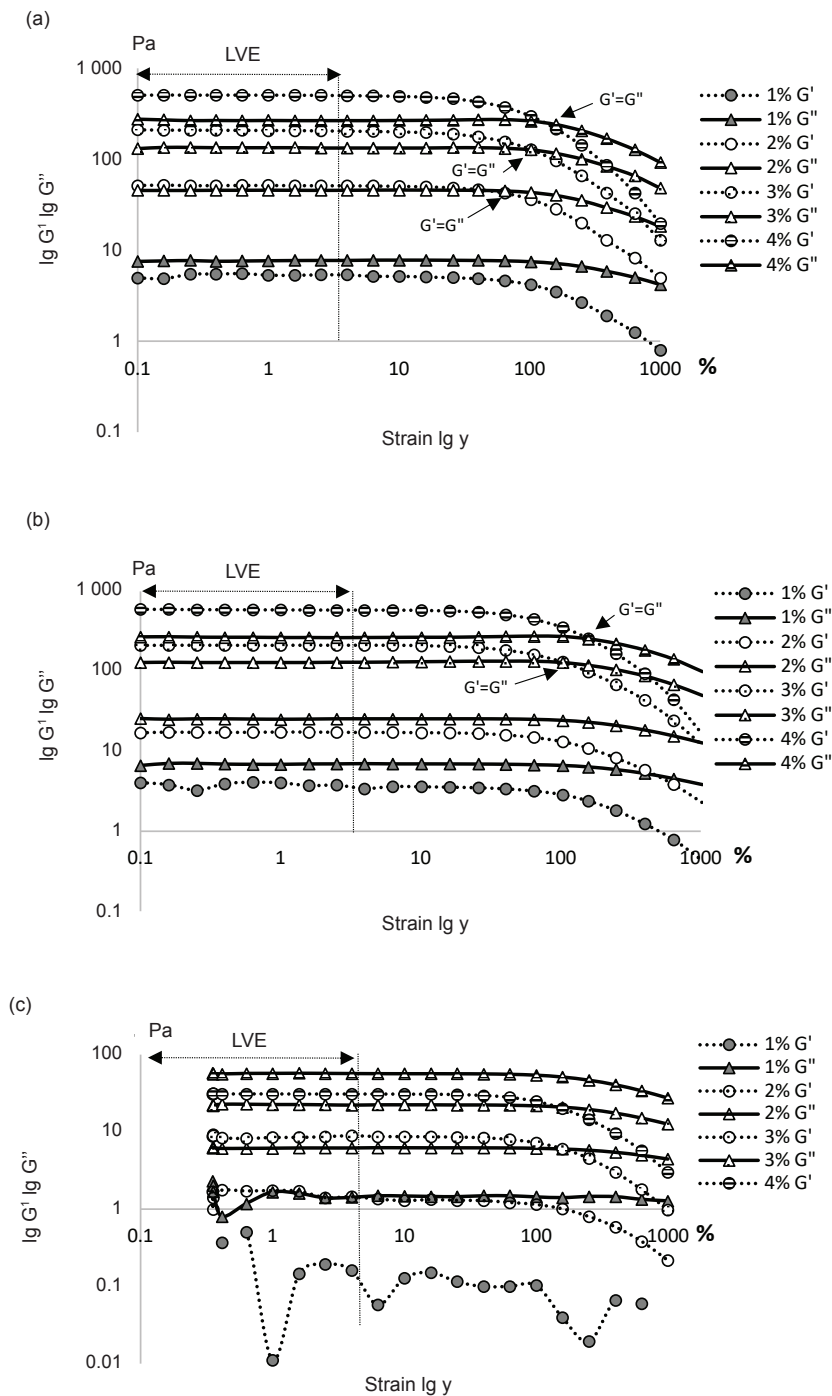
Figure 5a shows the amplitude sweeps of palm-based CMC solutions at varying concentrations: 1%,

2%, 3% and 4%. The results showed that palm-based CMC at 1% solution exhibited viscoelastic liquid properties where the loss modulus (G'') is larger than the storage modulus (G') in the LVE region, thus, making the sample fluid. At 2% palm-based CMC solutions, first, it can be seen that at small strains, G' is close and little bit higher than G'' in the LVE region, implying that the polymer fluids are more solid like or viscoelastic solid. As the strain increase, G' falls faster than G'' and crossover of $G'=G''$ or flow point occurred at strain 39.6 Pa. When the CMC concentration increased, viscoelastic properties become stronger where the distance between G' and G'' is more obvious and larger ($G'>G''$) for 3% and

4% palm-based CMC solutions. The flow point was also increased to 241.0 Pa and 514.0 Pa, respectively. The amplitude sweeps results for cotton-based CMC solutions at 1%, 2%, 3% and 4% are depicted in Figure 5b. Cotton-based CMC solutions showed viscoelastic liquid properties at 1% and 2% solutions where the G'' is larger than G' in the LVE region (Figure 5b). However, at 3% and 4%, it behaved as a viscoelastic solid material ($G' > G''$) with flow points

that occurred at 247.0 Pa and 691.0 Pa, respectively. Wood-based CMC at 1%, 2%, 3% and 4% solutions showed viscoelastic liquid properties over the entire range of strain where $G'' > G'$ in the LVE region (Figure 5c).

The LVE region determined in the amplitude sweeps test helps to further characterise the CMC solutions structure using a frequency sweep at a strain below the critical strain. In a frequency sweep,



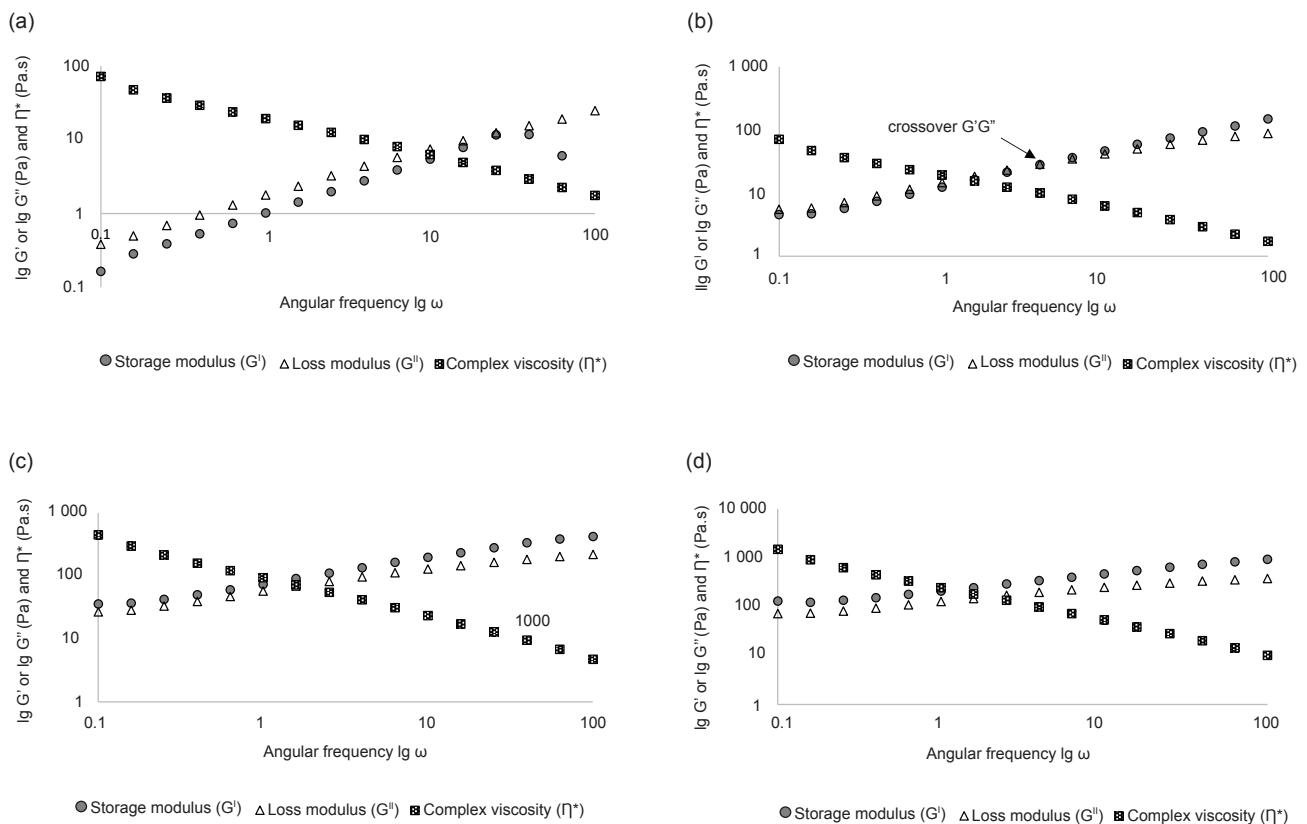
Note: CMC - carboxymethyl cellulose; LVE - linear viscoelastic; G' - storage modulus; G'' - loss modulus.

Figure 5. Amplitude sweeps of (a) palm-based CMC solutions, (b) cotton-based CMC solutions, and (c) wood-based CMC solutions at varying concentrations: 1%, 2%, 3% and 4%.

measurements are made over a range of oscillation frequencies at a constant oscillation amplitude. Since frequency is inverse of time, low frequencies allow the samples time to relax and respond, and thus, the flow properties dominate, and as the frequency increases, the sample behaves more and more in elastic fashion; hence, the G' increases with the increase in the frequency (Menard, 2008). The change in G' (a function of frequency) increases with the viscoelasticity of the materials studied and in case of gels, the weaker the gel strength, the greater is the dependence of G' on frequency (Osada and Khokhlov, 2001).

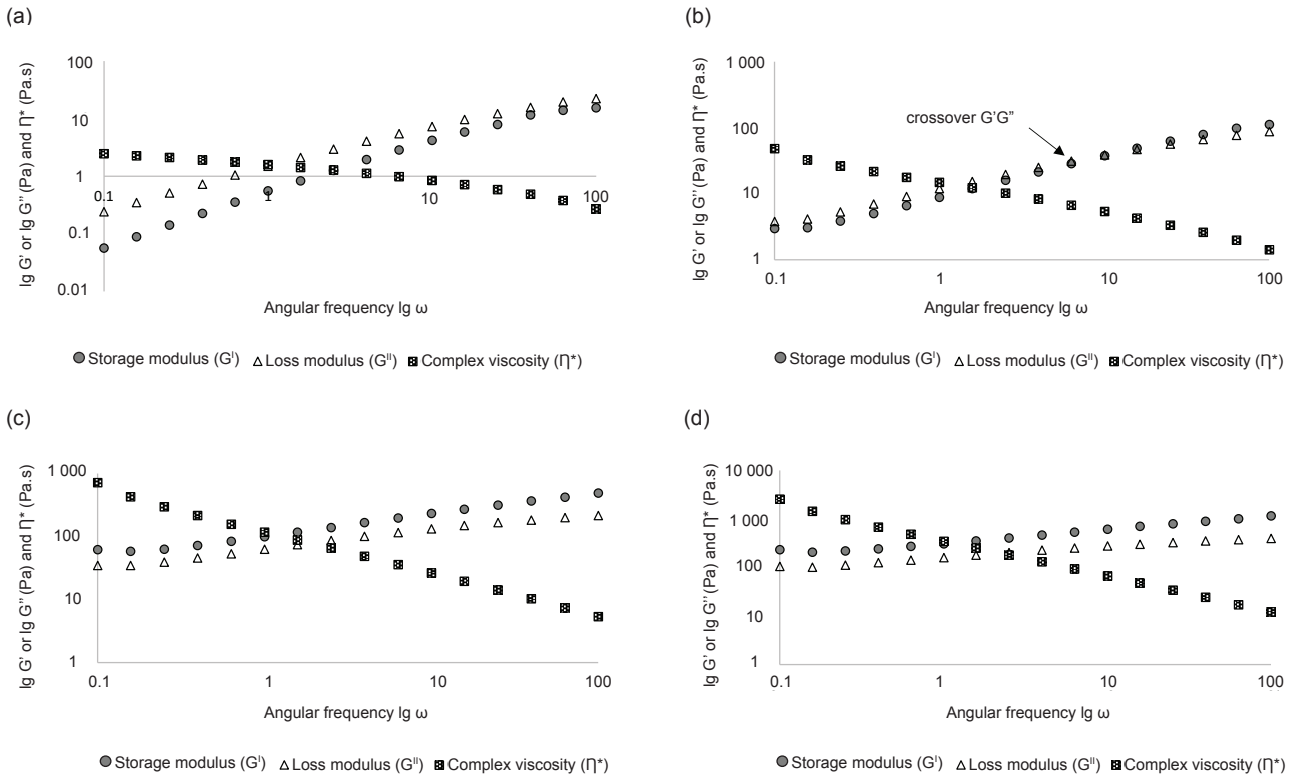
The frequency sweep performed within the linear viscoelastic (strain=5%) in the range of 0.1-100 rads^{-1} for palm-based CMC at 1%, 2%, 3% and 4% are shown in Figure 6. The results showed that a 1% palm-based CMC solution exhibited fluid-structure within the frequency regime where G'' is higher than G' (Figure 6a). While 2% palm-based CMC solution exhibited fluid-structure at low frequencies and behaved more elastic at the crossover frequency ($G'=G''$) of 3.98 rads^{-1} . At 3% and 4%, the solutions exhibited a stable gel-like or elastic solid structure with no crossover between G' and G'' within the frequency regime

(Figures 6c and 6d). The frequency sweep result for cotton-based CMC at 1% exhibited fluid-structure properties where G'' is higher than G' (Figure 7a). At 2%, fluid-structure or liquid-like properties were observed at low frequencies and the transition solid-like or elastic behaviour occurred at the crossover frequency ($G'=G''$) of 10.0 rads^{-1} (Figure 7b). The transition from liquid-like to solid-like for 2% cotton-based CMC solution occurred at a higher angular frequency (10.0 rads^{-1}) as compared to 2% palm-based CMC (3.98 rads^{-1}). This explained that palm-based CMC has higher gel strength as compared to cotton-based CMC at 2% concentration and it is consistent with the result of amplitude sweep where palm-based CMC at 2% showed a viscoelastic solid properties while cotton-based CMC at 2% showed viscoelastic liquid properties (Figure 5). At 3% and 4%, the solutions exhibited a stable gel-like or elastic solid structure with no crossover between G' and G'' within the frequency regime (Figures 7c-d). Wood-based CMC at 1%, 2%, 3% and 4% solutions showed fluid structure within the frequency regime where G'' is higher than G' (Figure 8).



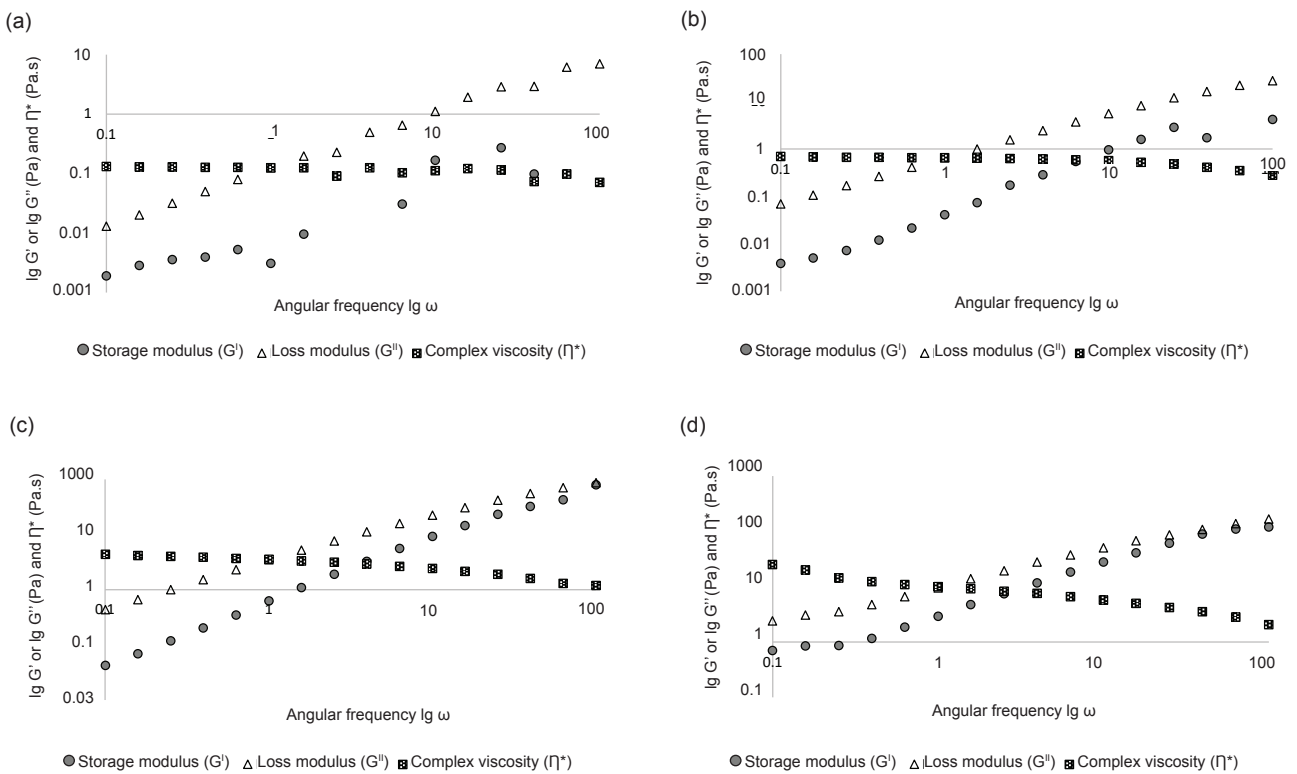
Note: CMC - carboxymethyl cellulose.

Figure 6. Angular frequency sweeps of palm-based CMC solutions at varying concentrations of (a) 1%, (b) 2%, (c) 3%, and (d) 4%.



Note: CMC - carboxymethyl cellulose.

Figure 7. Angular frequency sweeps of cotton-based CMC solutions at varying concentrations of (a) 1%, (b) 2%, (c) 3%, and (d) 4%.



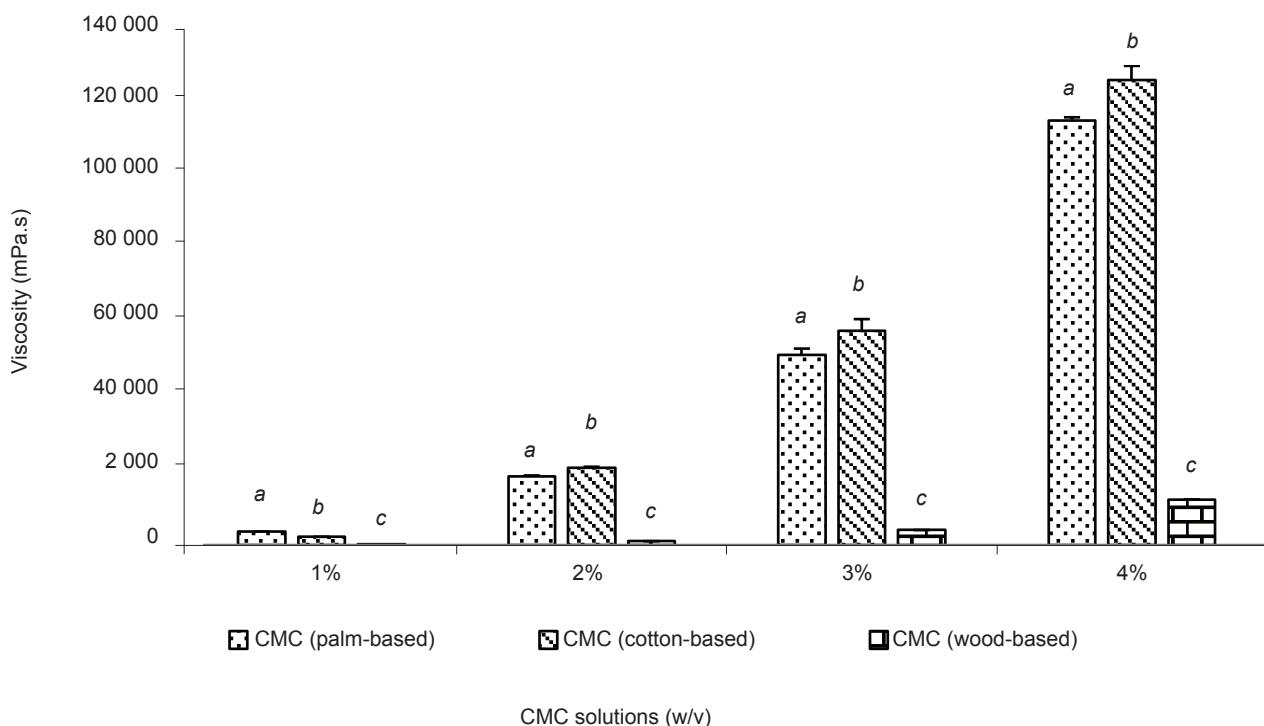
Note: CMC - carboxymethyl cellulose.

Figure 8. Angular frequency sweeps of wood-based CMC solutions at varying concentrations of (a) 1%, (b) 2%, (c) 3%, and (d) 4%.

The viscosity of CMC solutions can also be measured through Brookfield DV-III Ultra Rheometer. The measurement was conducted at room temperature and speed of 30 rpm, with more than 10% torque. The result shows that at 1% solution, palm-based CMC recorded the highest viscosity (3563 ± 122 mPa.s) as compared to cotton-based CMC (2210 ± 35 mPa.s) and wood-based CMC (140 ± 0 mPa.s). However, at varying concentrations, cotton-based CMC solutions recorded the highest viscosity as compared to palm-based and wood-based CMCs; 2% solution ($21\ 033 \pm 232$ mPa.s), 3% solution ($58\ 266 \pm 3104$ mPa.s) and 4% solution ($126\ 311 \pm 3855$ mPa.s) as shown in Figure 9. These results may be due to a higher DS value of cotton-based CMC (DS=1.69), followed by palm-based CMC and wood-based CMC that explained why the flow point of cotton-based CMC solution was higher than palm-based CMC solutions at 3% and 4%. The viscosities recorded were significantly different with $p < 0.05$.

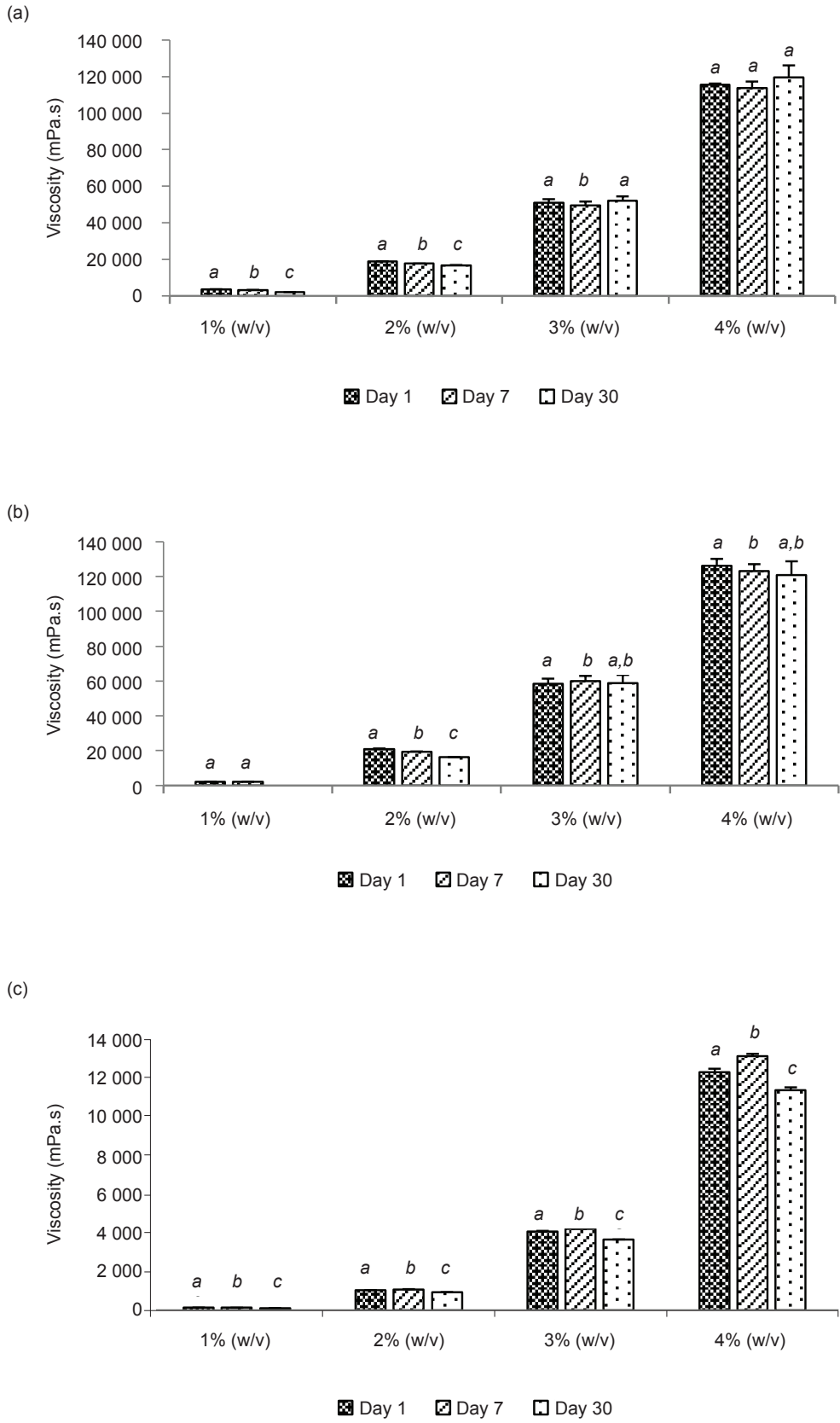
The viscosity was further measured after Day 7 and Day 30 of storage at room temperature as depicted in Figure 10. The viscosity of wood-based CMC solutions was significantly different ($p < 0.05$)

at all concentrations throughout the storage. Wood-based CMC solutions are liquid-like and recorded the lowest viscosity as compared to palm-based and cotton-based CMC solutions. Therefore, the changes in viscosity over time are more affected. Meanwhile, the viscosity of palm-based CMC solutions was significantly different ($p < 0.05$) at 1% and 2% throughout the measurement at Day 1, Day 7 and Day 30 of storage. Cotton-based CMC solution at 1% recorded insignificant difference ($p > 0.05$) in viscosity measurement at Day 1 and Day 7 of storage. However, the viscosity measurement could not be performed after Day 30 of storage due to the instability of the test sample. Cotton-based CMC solution at 2% recorded a significant difference ($p < 0.05$) in viscosity throughout the 30 days of storage. At 3%, both palm-based and cotton-based CMC solutions recorded insignificant difference ($p > 0.05$) in viscosity measurement after 30 days of storage. At higher concentration of 4%, palm-based CMC solutions could be considered stable where the viscosity was not significantly different ($p > 0.05$) at Day 1, after Day 7 and Day 30 of storage (Figure 10a) as compared to cotton-based (Figure 10b) and wood-based (Figure 10c) CMC solutions.



Note: CMC - carboxymethyl cellulose.

Figure 9. Viscosity of palm-based, cotton-based and wood-based CMC at varying concentrations (1%, 2%, 3% and 4%), measurement at room temperature, speed 30 rpm and more than 10% torque; values with different superscript letters within the same concentration are statistically different ($p < 0.05$).



Note: CMC - carboxymethyl cellulose.

Figure 10. Viscosity of (a) palm-based, (b) cotton-based and (c) wood-based CMC at varying concentrations (1%, 2%, 3% and 4%) at Day 1, after Day 7 and Day 30 of storage at room temperature; values with different superscript letters within the same concentration are statistically different ($p < 0.05$).

CONCLUSION

The values of flow behaviour for all CMC solutions were less than 1, indicating the pseudoplastic or shear thinning properties. At a minimum of 2%, palm-based CMC solution exhibited viscoelastic solid properties where transition from liquid-like to solid-like occurred at lower frequency. While, cotton-based CMC exhibited viscoelastic solid properties at 3% solution and transition from liquid-like to solid-like occurred at higher frequency. At 2% solution, palm-based CMC provide better gel strength compared to cotton-based CMC. Wood-based CMC exhibited viscoelastic fluid properties with no gelling behaviour at all concentrations. Palm-based CMC may potentially replace CMC from other sources as rheological modifier for the development of sustainable cosmetic and personal care products.

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REFERENCES

- Amin, M C I; Soom, R M; Ahmad, I and Lian, H H (2007). Carboxymethyl cellulose from palm oil empty fruit bunch-their properties and use as a film coating agent. *Jurnal Sains Kesihatan Malaysia*, 4(2): 53-62.
- Ariffin, H; Hassan, M; Kalsom, M U; Abdullah, N and Shirai, Y (2008). Effect of physical, chemical and thermal pre-treatments on the enzymatic hydrolysis of oil palm empty fruit bunch. *J. Trop. Agric. Food. Sci.*, 36(2): 259-268.
- ASTM (1995). Designation: D 1439-97. Standard test methods for sodium carboxymethylcellulose. Annual Book of ASTM Standards. American Society of Testing and Materials (ASTM).
- Astimar, A A; Husin, M and Anis, M (2002). Preparation of cellulose from oil palm empty fruit bunches via ethanol digestion: Effect of acid and alkali catalyts. *J. Oil Palm Res.*, 14(1): 9-14.
- Barba, C; Montane, D; Farriol, X; Desbrieres, J and Rinaudo, M (2002). Synthesis and characterization of carboxymethylcelluloses from non-wood pulps II: Rheological behaviour of CMC in aqueous solution. *Cellulose*, 9(3): 327-335.
- Benchabane, A and Bekkour, K (2008). Rheological properties of carboxymethyl cellulose (CMC) solutions. *Colloid Polym. Sci.*, 286: 1173-1180.
- Borsa, J and Racz, I (1995). Carboxymethyl cellulose of fibrous character, a survey. *Cellul. Chem. Technol.*, 29: 657-663.
- Ching, Y C and Ng, T S (2014). Effect of preparation conditions on cellulose from oil palm empty fruit bunch fibre. *BioRes.*, 9(4): 6373-6385.
- Eliza, M Y; Shahrudin, M and Wan Rosli, W D (2015). Carboxymethyl cellulose (CMC) from oil palm empty fruit bunch (OPEFB) in the new solvent dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF). *J. Phys.: Conf. Ser.*, 622: 012026.
- Ghannam, M T and Esmail, M N (1997). Rheological properties of carboxymethyl cellulose. *J. Appl. Polym. Sci.*, 64(2): 289-301.
- Heinze, T and Koschella, A (2005). Carboxymethyl ethers of cellulose and starch: A review. *Macromol. Symp.*, 223(1): 13-40.
- Ho, K Y and Dodou, K (2007). Rheological studies on pressure-sensitive silicone adhesives and drug-in-adhesive layers as a means to characterise adhesive performance. *Int. J. Pharm.*, 333(1-2): 24-33.
- Holdsworth, S D (1971). Applicability of rheological models to the interpretation of flow and processing behaviour of fluid food products. *J. Texture Stud.*, 2(4): 393-418.
- Hutomo, G S; Marseno, D W; Anggrahini, S and Supriyanto, (2012). Synthesis and characterization of sodium carboxymethylcellulose from pod husk of cacao (*Theobroma cacao* L.). *Aust. J. Fr. Stud.*, 6(6): 180-185.
- Menard, K P (2008). *Dynamic Mechanical Analysis: A Practical Introduction*. CRC Press, Boca Raton. 240 pp.
- Nazir, M S; Wahjoedi, B A; Yussof, A W and Abdullah, M A (2013). Eco-friendly extraction and characterization of cellulose from oil palm empty fruit bunches. *BioRes.*, 8(2): 2161-2172.
- Nguyen, QH and Nguyen, ND (2012). Incompressible non-newtonian fluid flows. *Continuum Mechanics - Progress in Fundamentals and Engineering Applications*. (Yong Gan eds.). IntechOpen, London. p. 1-27.

- Niraula, B; King, T C and Misran, M (2004). Evaluation of rheology property of dodecyl maltoside, sucrose dodecanoate, Brij 35p and SDS stabilized o/w emulsion: Effect of head group structure on rheology property and emulsion stability. *Colloids Surf. A Physicochem. Eng. Asp.*, 251(1-3): 59-74.
- Osada, Y and Khokhlov, A (2001). *Polymer Gels and Networks*. Taylor and Francis, Boca Raton. 400 pp.
- Padzil, F N M; Lee, S H; Ainun, Z M A; Lee, C H and Abdullah, L C (2020). Potential of oil palm empty fruit bunch resources in nanocellulose hydrogel production for versatile application: A review. *Materials (Basel)*, 13(5): 1245.
- Parid, D M; Abd Rahman, N A; Baharuddin, A S; Mohammed, M A P; Mat Johari, A and Abdul Razak, S Z (2018). Synthesis and characterization of carboxymethyl cellulose from oil palm empty fruit bunch stalk fibres. *BioResources*, 13(1): 535-554.
- Ramli, S; Mohd Ja'afar, S; Abdul Sisak, M A; Zainuddin, N and Abdul Rahman, I (2015). Formulation and physical characterization of microemulsions based carboxymethyl cellulose as vitamin C carrier. *Malays. J. Anal. Sci.*, 19(1): 275-283.
- Rosnah, M S; Astimar, A A; Wan Hasamudin, W H and Gapor, M T (2012). Conversion of lignocellulose from oil palm biomass into water-soluble cellulose ether. *J. Oil Palm Res.*, 24: 1412-1420.
- Rosnah, M S; Abd Gapor, M T and Wan Hasamudin, W H (2004). Production of carboxymethylcellulose (CMC) from oil palm empty fruit bunch. *MPOB Information Series No. 228*.
- Rosnah, M S; Ku Halim, K H and Wan Hasamudin, W H (2002). The potential of oil palm lignocellulosic fibres for the cellulose derivatives production. *Proc. of the Research and Consultancy Seminar*. Faculty of Mechanical Engineering, UiTM Shah Alam, Malaysia. p. 140-145.
- Rowe, R C; Sheskey, P J and Quinn, M E (2013). *Handbooks of Pharmaceutical Excipients*. Seventh edition. Pharmaceutical Press, London. 1033 pp.
- Singh, R K and Khatri, O P (2012). A scanning electron microscope based new method for determining degree of substitution of sodium carboxymethyl cellulose. *J. Microsc.*, 246(1): 43-52.
- Sisak, M A A; Daik, R and Ramli, S (2015). Characterization of cellulose extracted from oil palm empty fruit bunch. *AIP Conf. Proc.* 1678: 050016. DOI: 10.1063/1.4931295.
- Stigsson, V; Kloow, G and Germgard, U (2001). An historic overview of carboxymethyl cellulose (CMC) production on an industrial scale. *Pap. Asia*, 17(10): 16-21.
- Varshney, V K and Naithani, S (2011). Chapter 2: Chemical functionalization of cellulose derived from nonconventional sources. *Cellulose Fibres: Bio- and Nano-Polymer Composites: Green Chemistry and Technology* (Kalia, S; Kaith, B S and Kaur, I eds.). Springer-Verlag, Berlin. p. 43-60.
- Wan Rosli, W D; Rohaizu, R and Ghazali, A (2011). Synthesis and characterization of cellulose phosphate from oil palm empty fruit bunches microcrystalline cellulose. *Carbohydr. Polym.*, 84(1): 262-267.