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MICRORHEOLOGICAL MEASUREMENT OF MICROCRYSTALLINE CELLULOSE SOLUTION USING SINGLE PARTICLE TRACKING

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ABSTRACT

The aim of the research was to develop micro rheological measurement system to determine the alpha apparent and the complex shear modulus of microcrystalline cellulose (MCC) solutions based on a single particle tracking technique (SPT) using video microscopy (VM). The temporal displacement of a micro particle, acted as a probe in MCC solution was recorded, trackedand analyzed using custom-made MATLAB program. Videos were recorded at 30 fps resulted in the output of radial frequency range from 0.4 rad/s to 10 rad/s. The results from the local measurement in MCC solutions were compared with the bulk measurement using rheometer. The measurements were dependent on the local position of the probe in the solution. The results from the developed SPT-based measurement system were comparable to the common measurement using rheometer.

Keywords: MCC solution; microrheology; single particle tracking; rheometer.

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1. INTRODUCTION

Rheology is the study on how a material deforms and flowsunder applied forces [1]. We can extract rheological property which contains information about storage and dissipation of energy in the material [2]. There are two types of rheology. The first is passive rheology, which internal system is explored by studying Brownian motion. The second is active rheology which the response of a material to external driving forces is explored [3].

Rheology study at micron-scale is called microrheology. The study reported in this paper employs the first where Brownian motion of a micron sized particle as a probe is observed to measure the microrheological properties of the surrounding medium. The relation between the motion of the probe in a viscous medium and the microrheological properties of the vicinity has been established [4]. The random motion is due to thermal energy and related to the diffusivity of the material [5].

With the rapid development in computer processing and programming, it is possible to capture the video of the micron sized particle using video microscopy. A robust programming is able to track the temporal displacement of the particle and a program can be written to calculate the required physical quantity [6].

The sample of interest is microcrystalline cellulose (MCC) in water solution. The solution is nonhomogeneous fiber solution. The local measurement of the solution is challenging since the complex shear modulus (G^*) is expected to vary from one location to others. However, this research will open wide possibility of local measurement for other type of viscoelastic material.MCC can be found as a good dry binder in medication tablet [7]. It shows non-Newtonian behaviour when diluted with water at low concentrations, independent to angular frequency. Furthermore, magnitude of its dynamic storage reaches plateau condition in relative high concentrations with storage moduli bigger than ten times than the loss moduli [8-9]. As reported in other research, the treatment using sonication process can altered the morphology structure and tensile modulus of these cellulose solutions. That treatment can change the size from microfiber to nanofibre scale, while the tensile modulus will increase with the increase of the concentrations [10].

MCC is an important raw material used in cosmetics and foods manufacturing such as

toothbrush, gel, and mayonnaise [11-12]. The excellent quality and grade of various products are largely depending on its rheological properties. The rheological properties of the products have to be distinguished in order to enhance the strength, and optimize its stability and the consistency. These products have limited shapes in definite temperatures and pressures. Yet, manufactures have to identify the rheological properties using standard methods and efficient instruments [13].

The aim of this research was to measure microrheological properties of MCC using Single Particle Tracking (SPT). Obtained results were compared to common method using rheometer. Rheometer has been commonly used to get rheological properties of viscoelastic material. However, substantial amount of minimum 1 ml of sample is required for each measurement. The measured physical quantities using rheometer exhibit the response of the material in bulk, but do not show the properties in microscopic level especially at the local position of interest in the material. Therefore, one of the alternative tests is to introduce microrheological measurement, which employs the use a single microparticle as probe in the material. The Brownian motion of the particle in the material shows the microrheological properties at its vicinity. The probe trajectory is tracked and analyzed.

The mean square displacement (MSD) of a particle undergoing Brownian motion in two dimensions is described by

$$\mathrm{MSD} = \left\langle \Delta r^2(n\Delta t) \right\rangle = \frac{1}{N-n} \sum_{i=1}^{N-n} (\vec{r}_{i+n} - \vec{r}_i)^2 \quad (1)$$

wherethe particle displacement, Δt is the lag time between displacement data, N is the number of data, and n and i are increment index of the data respectively [14].

Once the MSD is obtained, α_{app} can be calculated using the following relation

$$\alpha_{app} = \frac{\log(\mathrm{MSD})}{\log(\Delta t)} \quad (2)$$

Equation (2) is general formula to determine diffusively of materials, where the pure solid has $\alpha_{app} = 0$ and pure fluid $\alpha_{app} = 1$ [14].

Complex shear modulus (G^*) refers to an applied shear stress, which resulted from harmonic processes. G^* contains information about storage G' and loss modulus G''. For $0 < \alpha_{app} < 1$,

they are related by the following relation.

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (3)$$

This is determined from the Fourier transform of MSD from Equation (1),

$$G^*(\omega) = \frac{k_B T}{\pi a i \omega \Im(\mathrm{MSD})} \quad (4)$$

where and are Boltzmann constant and medium temperature respectively [2].

G' is a measure of a sample to store energy during applied periodic shear the stress, meanwhile the loss modulus is a measure of a sample to loss energy on internal changing such as friction, molecular reformation during periodic applied the shear stress. Storage modulus is related to the elastic behavior and loss modulus is related to the viscous behavior of a sample [15].The α_{app} will indicate the diffusivity while G^* will indicate the viscoelasticity the MCC solution.

2. METHODOLOGY

2.1. System Development

The developed system employing SPT consisted of four stages; sample preparation, observation conditioning, particle tracking and calculation program development. Observation conditioning and particle tracking involves video microscopy technique where the bead trajectory in the sample is video-recorded and undergoes post-analysis. The particle which is a single bead was tracked by Tracker freeware [16]. The data was fed into the self-developed MATLAB program to perform microrheological analysis.

Fig. 1 (left) shows measurement procedure using the developed system. Video file was obtained from a microscope camera. After the tracking process, the .txt file was obtained. The file is then feed into self-made program written in MATLAB®. The program was developed in Graphical User Interface (GUI) format for easy use in the future.

Fig. 1 (right) shows the apparatus for the developed system. The sample slide was placed on the stage of an inverted optical microscope (GX51, Olympus). The oil immersion objective lens (N.A. 1.4, 100×) was used for viewing. For video recording of the bead trajectory, CCD camera (Moticam 3.0 MP) was attached to the view port of the microscope. The camera was

connected to computer through USB port. The video sampling rate is limited by the camera capabilities. The camera setting was adjusted to record minimum 23 frames per second (maximum limit 30 fps) to obtained the most in tracking information. The video was transferred to PC for post analysis as mentioned in Fig.2. Current advance in optical microscope provides tools to control the camera such as magnification and intensity of light using built-in software bundled via computer [17].

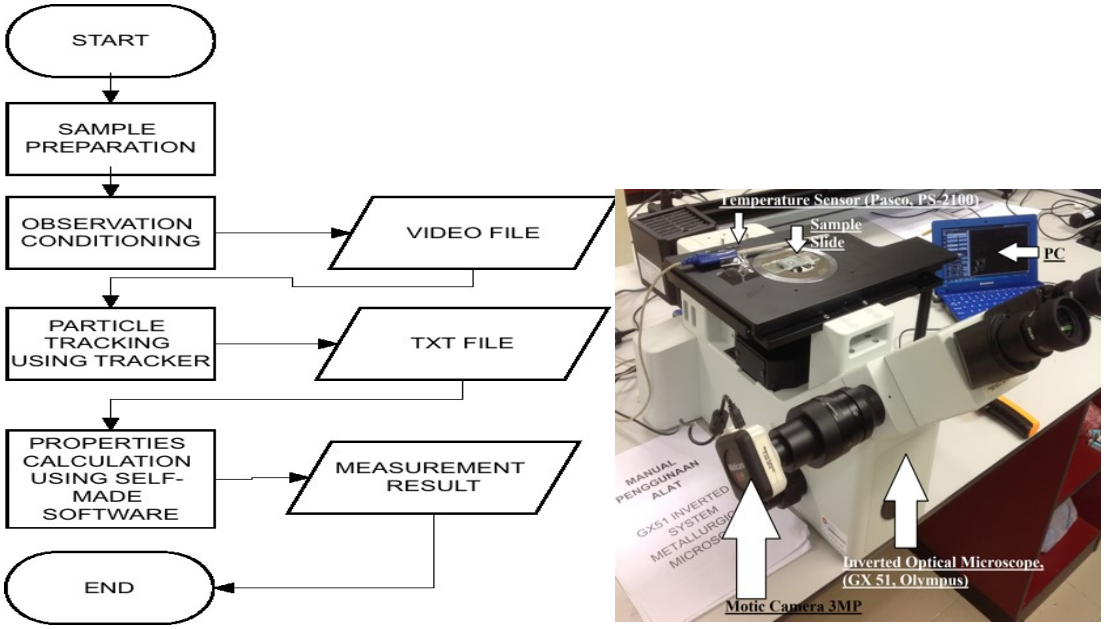

Fig.1.(left) Measurement procedures in the developed measurement system and (right)experimental work station

Several procedures were performed to get the best condition for particle tracking. The experiment was performed in the environment temperatures between 26.5 ^{o}C and 30.0 ^{o}C. Consequently, selection data was determined based on highest fps and time recording is less than one minutes. The recorded temperature was used temperature sensor (PASCO® PS-2100) which was located 5 cm from the sample slide.

2.2 Sample Preparation

The sample of interest, MCC in powder form (Sigma-Aldrich®, Product No.310697) was dissolved in deionized water. A pre-determined amount of MCC was weighted using analytical balance (ATX 224, Shimadzu). The volume of *v* mL deionized water was pipetted into a volumetric flask. The mass of *w* g MCC was put into the flask. The solution was shaken using lab dancer for 90 seconds. The concentration of the solution was identified by its

percentage of MCC mass in a volume of water (% w/v), defined as [18],

$$\text{Concentration in \%w/v} = \frac{\text{MCC mass in gram}}{\text{volume of water in mL}} \times 100\% \quad (5)$$

Above relation is commonly used in polymer studies. The MCC solution subsequently went through the sonication treatment process. This process aims to achieve the uniformity condition of the MCC solution [19].

Fig.2.MCC solutions in 10% w/v, 5% w/v, 1% w/v and 0 % w/v

Fig. 2 shows the samples prepared with MCC concentrations at 0, 1, 5 and 10% w/v respectively. Higher % w/v exhibits low transparency. The sonication process was performed using sonicator instrument (Q Sonica, Sonicator) at 20 kHz for three sonication duration: 30, 60 and 90 minutes respectively. Different sonication duration of samples was prepared to investigate its effect on the storage modulus of the MCC solutions.

2.3.Slide Preparation

For the SPT measurement, the sample is required to contain a probe. The probe trajectory is observed under video microscopy. In order to put the probe in the sample, a polystyrene bead (Polysciences, 1.68´109 bead/mL) with diameter (2.95±3%) μm) is used. The bead solution is diluted in water at ratio 1:105; bead solution to water. The bead solution concentration is too low to give noticeable effect on the microrheological properties of sample solution.

The procedure to prepare 1 mL sample + bead solution is followed. Firstly, 1 mL of sample was prepared in new vial using pipette. Secondly, the 0.01 mL bead solution was pipetted into the vial. Finally, the mixture was shaken on lab dancer for 90 seconds.

The sample must be prepared in slide form to be put on microscope stage for video microscopy. The sample slides were prepared using a piece of clean microscope slide (HmbG®, 10227101PX), then two thin strips of double-sided tape were cut and stacked on one side of the slide. The separation between strips was about 2.0 to 2.4 cm apart. Furthermore, 40 μL of sample were taken by pipette and put on the slide, between the tape

strips. A piece of cover glass was placed on top of the sample and stick on the tape strips. Finally, a small amount of nail polish is put at the open edges of the cover slip to seal the sample.

2.4.Experimental Procedure

G^* was determined using the developed system and a rheometer. Proposed system offers advantages over the later method. It requires the amount of sample only in microliter order [11-12]. Experimental setup is relatively simpler without mechanical control and contact as in the rheometer.

For measurement by the developed system, the sample is put on the focus of an optical microscope and the video of a probe (embedded microparticle) was recorded. Fig. 3 shows a snapshot of a bead as a probe in a MCC solution. Fibrous structure indicated the non-dissolved MCC. It can be expected that the measurement is highly depends on the position of theprobe in the sample. The bead exhibits random motion behaviour inside the solutions known as Brownian Motion (BM) and the positions can be tracked in a short time. The Tracker and custom-made program using GUI facilities of MATLAB® program have been used for particle tracking purpose. Algorithms were filled in the GUI so that the program is easy to use for BM analysis [16].

For measurement by the developed system, the rheometer (AR-G2®, TA Instruments) has been used as comparison technique to obtain microrheological data of the sample. The plate type used for the rheometer was geometry plate (60 mm 1^o steel cone; code: 992176) according to the followed setting; truncation gap was 30.00 μm, geometry inertia was 23.17 μN.m.s^2, normal force factor was 707.41 $1/m^2$ and bearing friction was 0.321 μN.m/(rad/s). The controlled variable oscillatory stress at 0.1768 Pa and frequency sweeps mode was between 0.5 and 60 rad/s. A drop of the sample was put between plates on the rheometer. Measurements were performed by computer control and the results were obtained immediately after each stress oscillatory of plates.

Fig.3.A snapshot of a bead (at crossline) in a solution. Crosshairs shows 2.95 micron scale

3. RESULTS AND DISCUSSION

3.1.Single Particle Trajectory Plot

The CCD camera in the developed system is able to record the video at maximum 30 fps depending on the setting such as resolution and brightness. The sampling rate is important to get more data in frequency domain. Since required G^* is in the frequency domain, the calculated data interval in G^* is limited by the sampling rate. In this study, the minimum acceptable sampling rate is 23 Hz.

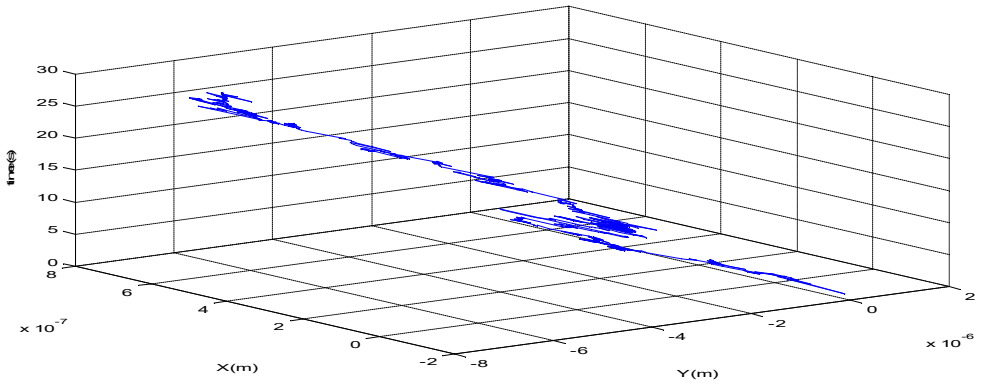

Fig. 4. The Brownian Motion (BM) of a proble in two dimensions (x-y plane)

The temporal trajectories of a particle in a sample are obtained by freeware Tracker. These data were fed into the developed program. The program is able to display the graph in one click once data from Tracker is uploaded. Fig. 4shows an example of the trajectories of the probe particle in water. Displacement in *x* and *y* directions (video recording plane) were plotted against elapsing time (vertical axis). The time interval displacements points depend on

the video sampling rate 30 fps resulted in 33 ms time interval (time interval = 1/sampling rate). The figure clearly shows the random motion of the particle in *xy*-plane. This random walk is caused by fluctuating thermal force in the sample.

3.2. Mean Square Displacement (MSD) Plot

Subsequently, the developed program calculated and plotted MSD graphs from the SPT data in the previous section. Fig. 5 shows MSD for a particle probe in water in three different temperatures. The MSD data are linearly proportional to Δt similarly as reported in other study [20]. This indicates the reliability of the developed program to calculate MSD for further analysis.

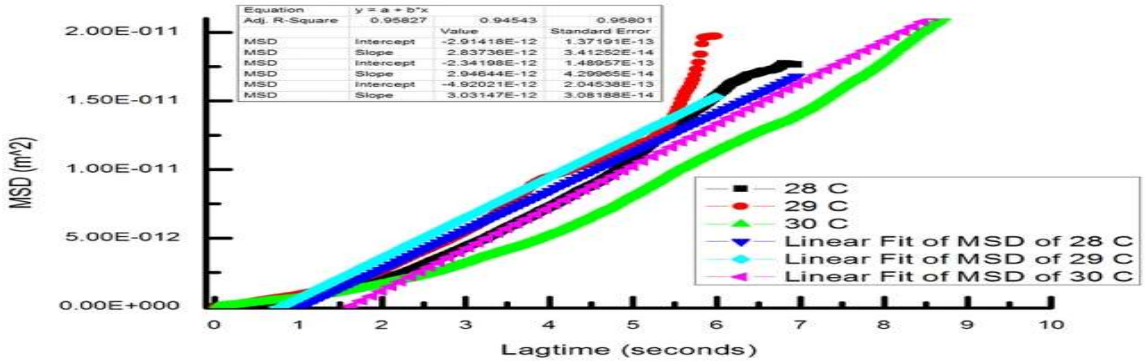

Fig.5. Linearity of MSD versus lag-time (Δt) of the water

3.3. Apparent Alpha (α_{app})

α_{app} is one of microrheological properties measured in this study. α_{app} is calculated based on Equation (2), which requires prior MSD calculation as discussed in the previous subsection. Measurements were resulted α_{app} at various values between 0 and 1. Fig. 6 shows α_{app} versus sonication treatment duration for 1% w/v, 5% w/v and 10% w/v concentrations respectively. Regardless of solution concentration and sonication treatment time, the α_{app} lies between 0 and 1.

Fig. 7 replicates Fig. 6 but it is α_{app} versus concentration. Based on these results, the MCC solutions can be categorized as sub-diffusive materials. No specific relation between α_{app}, concentrations and sonication treatment duration since the motion of the particle probe in the solution is specific to the condition of local microscopic environment which consists of

nonhomogeneous distribution of cellulose fiber and water.

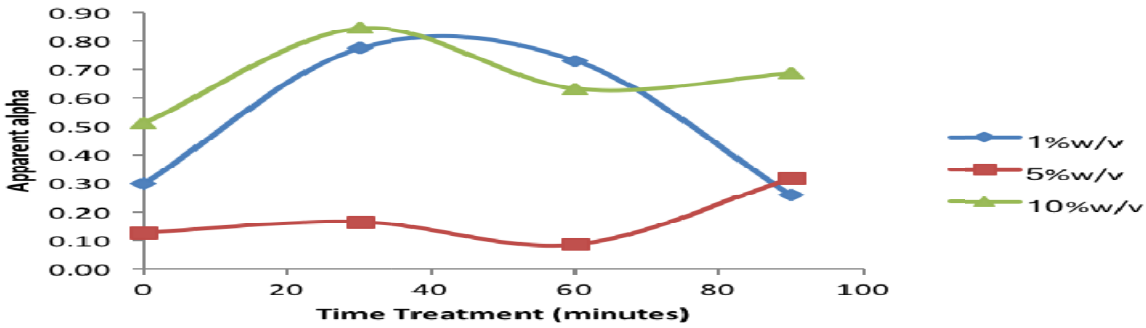

Fig.6. α_{app} at various sonication treatment duration

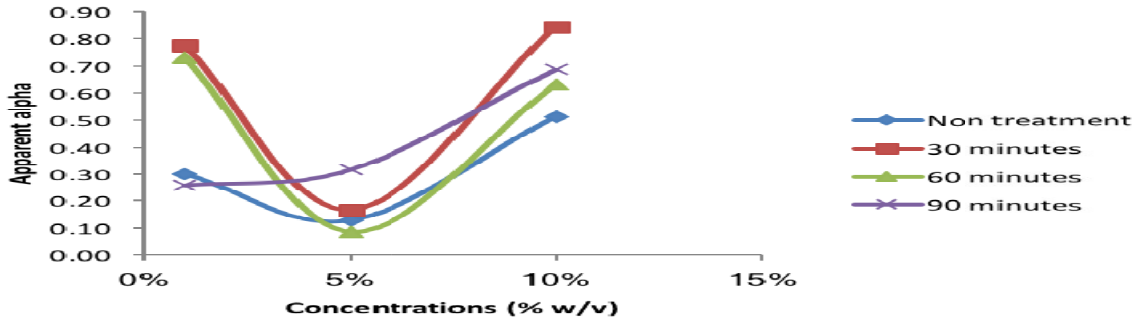

Fig.7. α_{app} at various concentrations

To prove the performance of the developed system, the best comparison is by using water sample only identified as 0% w/v. Fig. 8 shows G' and G'' in the calculated range 0.4 rad/s to 63 rad/s. Data from the developed system is measured at 28.1 ^{o}C, while the rheometer is measured at 28.0 ^{o}C. Both result from the developed system and rheometer show comparable relationship with frequency. These values are also comparable to the result from other reference study [21]. None of these results are exactly the same as the reference, but all shows the same pattern in increasing frequency. Two points can be concluded:

(1) Measurement using rheometer is validated using water with the previous study.

(2) Measurement and calculation in the developed system are validated using water with (1) above. Any discrepancies in values are expected due to thermal force in SPT from the light illumination in the microscope.

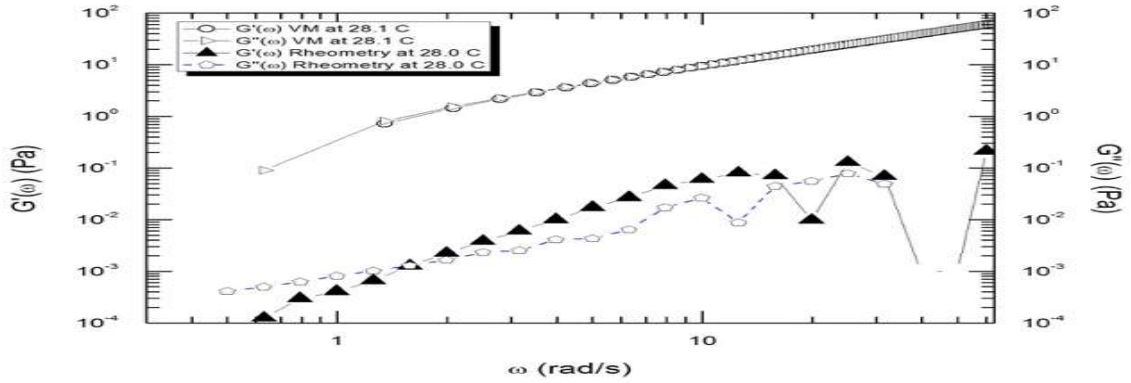

Fig.8. The G' and G'' of the water at 28.1°C

Fig. 9 shows 1% w/v storage and loss modulus at room temperatures. At this concentration, the magnitude of storage and loss modulus is inversely proportional to temperatures. Results show the storage modulus is dominant than loss modulus indicative of solid-like condition of solutions [1]. The maximum magnitude is at a range of 10^2-10^3 Pa. This frequency range gives constant magnitude exhibiting solid condition.

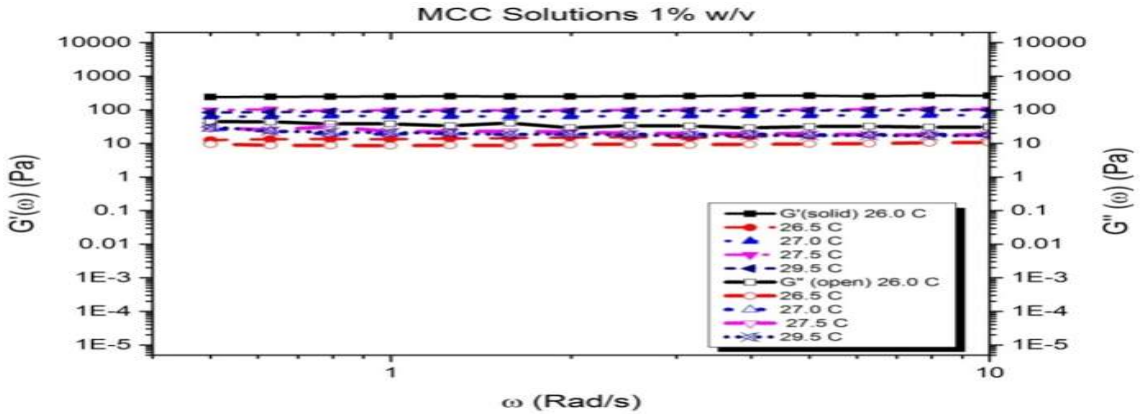

Fig.9. Storage and loss modulus of 1 %w/v at 20-30°C measured by the developed system

Fig. 10 shows result for 5% w/v indicating more dominant loss modulus at higher concentration of attributed liquid condition [11]. The temperature affects to change magnitude response which is in the range between 10-10,000 Pa. This attributes to the changing phase from liquid to solid conditions. Hence, temperature contributes to the phase change of solutions.

G' increases at higher concentration of 5 and 10% w/v. Various concentrations and temperature will change the storage and loss modulus of solutions. Fig.9 to Fig. 11 show the temperature-dependent storage modulus similar reported in previous study [22]. Even the temperature changes, the storage modulus is greater than loss modulus. At microscale, this

pattern is understood due to interaction of MCC fiber to response the external force at constant strain. The results are found dominant to flat condition for both storage and loss modulus.

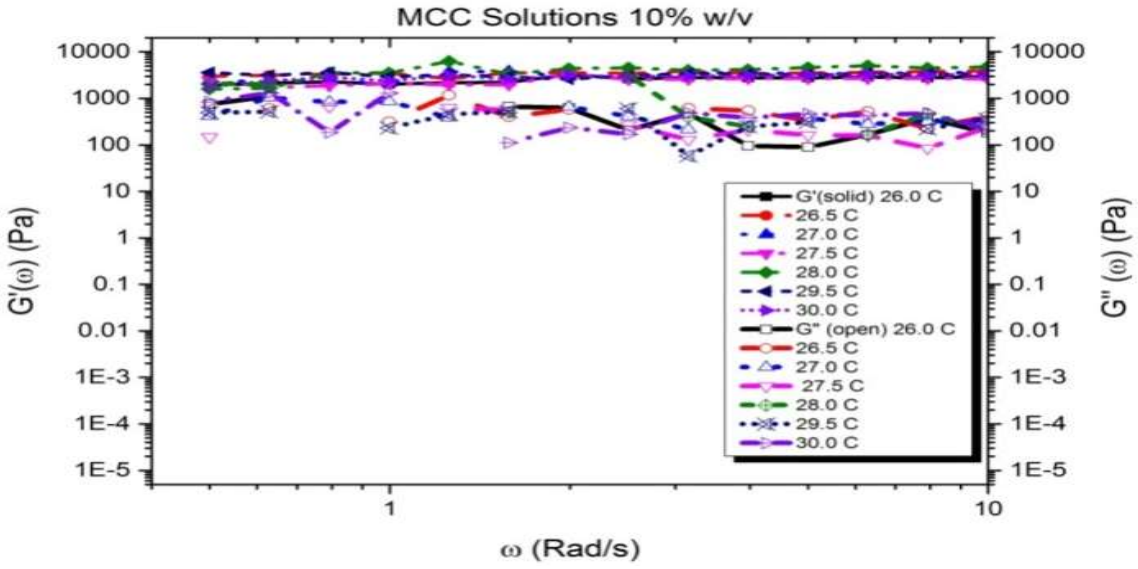

Fig.10. Storage and loss modulus of 10 % w/v at 20-30°C measured by the developed system

Table 1 summarizes the magnitude of CSM in various treatment and concentrations within the experimental range of frequencies. General relationship between variables (sonication time and solution concentration) in the measurement are difficult to deduce since the SPT measurement highly relies on the position of the bead in the sample. However, it offers potential alternative measurement at local environment which was not accessible previously based on observation of Brownian motion.

The developed program is written to calculate α_{app} and G^* from temporal displacement data from Tracker. In this study, sample of interest is MCC solution at concentration 0% w/v, 1% w/v, 5% w/v and 10% w/v. Result shows comparable result for water between the developed system and rheometer. Both measurements can complement each other depending on the purpose of research. This is because the developed system measure microrheological properties at local microscopic scale while rheometer measure at bulk macroscopic level. Finally, this research showed comparable results between the developed system and the rheometer for samples without sonication treatment.

Table 1. The CSM range using SPT and rheometry at various concentrations (% w/v)

No.	Method	Sonication Time (min)	Range of G^* Magnitude (Pa)		
			1% w/v	5% w/v	10% w/v
1	Rheometer	None	10^0 - 10^1	10^3-10^4	10^3-10^4
2	SPT	None	10^0- 10^1	10^3-10^4	10^2-10^3
3	SPT	30	10^{-2} - 10^1	10^0-10^2	10^{-1}-10^0
4	SPT	60	10^3 - 10^4	10^3-10^4	10^0-10^2
5	SPT	90	10^3 - 10^4	10^3-10^4	10^0-10^1

4. CONCLUSION

A microrheological measurement system using a single particle tracking for cellulose solution was successfully developed. The system requires only 50 µL sample compared to the rheometer, which requires minimum 1 mL. The heart of the system lies on the single particle tracking in the target sample and transform to the meaningful G^* in frequency domain.

A custom-made program was completely written in user-friendly GUI to calculate G^*. The program was written in MATLAB. The required data for the program is the temporal displacement of the probe particle. G^* on deionized water (0% w/v solution) sample obtained from the developed system were comparable with the measurement using rheometer indicating the reliability of developed the system.

Results also showed that cellulose solution exhibit different behavior at microscopic level than macroscopic measurement using rheometer a justification from graphs. The positioning of particle probe in the solution is important in the measurement using the developed system.

5. ACKNOWLEDGEMENTS

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