MICRORHEOLOGICAL MEASUREMENT OF CELLULOSE SOLUTIONS USING A SINGLE PARTICLE TRACKING

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ABSTRACT

The aim of the research was to develop microrheological measurement system to determine the alpha apparent (α_{app}) and the complex shear modulus ($G^*(\omega)$) of microcrystalline cellulose (MCC) solutions based on a single particle tracking technique using video microscopy (VM). A micron sized particle acting as a probe in cellulose solution was tracked by a freeware called Tracker. The temporal displacement of the particle was recorded and analyzed in spectrum domain using custom-made program using MATLAB. Videos were recorded at about 30 fps depending on the recording setting resulted in output of radial frequency range from 0.4 rad/s to 10 rad/s. The results from the local measurement in cellulose solutions were compared with the bulk measurement using rheometer. Since the solution is a kind of nonhomogeneous complex material, which contained long chain fiber, the measurements were dependent on the local position of the probe in the solution. To conclude, the microrheological measurement system was successfully developed using a single particle tracking technique for the cellulose solution. The results were comparable to the common measurement using rheometer. The implication of this study suggested that local measurement in complex material solution might not give the same values of the physical quantities compared to bulk material and the local measurement technique was required sample of less than 1μL only. The developed program offers user-friendly calculation of complex shear modulus from local measurements for other kind of materials; homogenous and nonhomogeneous solutions.

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PENGUKURAN MIKROREOLOGI BAGI LARUTAN SELULOSA BERASASKAN JEJAK ZARAH TUNGGAL

ABSTRAK

Kajian ini bertujuan membangunkan sistem pengukuran mikroreologi untuk menentukan alfa ketara (α_{app}) dan modulus ricih kompleks ($G^*(\omega)$) bagi larutan mikrohablur selulosa (MCC) berasaskan teknik penjejakan zarah tunggal menggunakan mikroskopi video. Satu zarah bersaiz mikro bertindak sebagai prob dalam larutan selulosa dijejaki oleh perisian percuma Tracker. Sesaran temporal zarah direkodkan dan dianalisis dalam domain spectrum menggunakan program yang ditulis sendiri dalam MATLAB. Video direkodkan pada kira-kira 30 fps bergantung kepada pengesetan rakaman menghasilkan output dalam julat frekuensi dari 0.4 rad/s hingga 10 rad/s. Dapatan daripada pengukuran setempat dibandingkan dengan pengukuran pukal menggunakan rheometer. Oleh sebab larutan tersebut adalah sejenis bahan kompleks tak homogen yang mengandungi fiber berantaian panjang, pengukuran sangat bergantung kepada kedudukan setempat prob dalam larutan. Kesimpulannya, satu sistem pengukuran mikroreologi berjaya dibangunkan untuk larutan selulosa menggunakan teknik penjejakan zarah tunggal. Hasil yang diperolehi setara dengan pengukuran biasa menggunakan reometer. Implikasi kajian ini mencadangkan bahawa teknik pengukuran setempat dalam larutan bahan kompleks tidak memberikan nilai kuantiti fizikal yang sama berbanding bahan pukal dan teknik pengukuran setempat yang hanya memerlukan sampel kurang daripada 1μL. Program yang dibangun menawarkan pengiraan mesra pengguna bagi modulus ricih kompleks daripada pengukuran setempat bahan-bahan lain; larutan homogen dan tak homogen.

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LIST OF SYMBOLS

A	Surface of the sample [m^2]
α_{app}	Apparent alpha
α	Cone angle [degrees or ^{o}]
$\alpha(\omega)$	First logarithmic of MSD in frequency domain
Δt	Two successive time or lag-time [s]
D	Diffusion constant [m^2/s]
Δx	Displacement of the sample [m]
E	Tensile modulus [Pa]
η	Viscosity [Pa.s]
ζ	drag coefficient
$\langle \Delta r^2(n\Delta t) \rangle$	MSD data [m^2]
$\left[\frac{\partial \ln \langle \Delta r^2(\Delta t) \rangle}{\partial \ln \Delta t} \right]$	Derivative of log-log MSD data to lag-time
f	Applied force [N]
GSER	Generalized Stokes-Einstein Relation
$G^*(\omega), G'(\omega), G''(\omega)$ $G(\omega)$	Complex Shear Modulus (G*), Storage Modulus, Loss Modulus, Shear Modulus [Pa], respectively
$\Gamma[1+\alpha(\omega)]$	Gamma function
h	Thickness [m]
$i = \sqrt{-1}$	Imaginary number
j	Index of positions, j=1, 2, 3, …N-1
K_α	generalized diffusion coefficient [$m^2 s^{-\alpha}$]
k_B	Boltzmann Constant [J/K]
$\Im\{\langle \Delta r^2(\Delta t) \rangle\}$	Laplace transform of MSD
n	Increment index of Mean Squared Displacement (MSD) calculation
N	Number of data recording (integer number)
ω	Radian frequency [rad/s]
$P(r,\Delta t)$	Probability to find positions of particle
π	3.1416
R_i	Internal radius [m]
r_j	Position of Brownian Motion (BM) data
R_e	External radius [m]
R	Radius of probe [m]
$S_{equilibrium}$	Power Spectral Density [m^2/Hz]
$2\sigma^2$	Intercept constant in the best fitting curve of MSD

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	[m]
sin(arg) , cos(arg)	Trigonometric functions
T	Room Temperature [K]

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CHAPTER 1

INTRODUCTION

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1.1 Background of Study

The complex shear modulus is deeply studied in the field of rheology. Rheology is the study on how a material deforms and flows under applied forces (Mezger, 2006). We can extract viscoelasticity property which contains information about storage and dissipation of energy (Thomas G. Mason, 2000; Mezger, 2006). 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 (Gardel, Valentine, & Weitz, 2005).

Rheology study at micron-scale is called microrheology. This study employs the first where Brownian motion of a micron sized particle as a probe is observed to measure the viscoelastic properties of the surrounding medium. The relation between

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the motion of the probe in a viscous medium and the rheological properties of the vicinity has been established (Squires & Mason, 2009). The random motion is due to thermal energy and related to the diffusivity of the material (Chaikin & Lubensky, 2000).

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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.

Cellulose is an advanced material from natural origins like flora and bacteria. Cellulose has been developed, explored and used in wide applications. For example, nanocellulose-embedded composite material offers alternative to high demand for woods with better material properties. Such properties are high surface area, high aspect ratio, high strength modulus and dimensional stability compared to natural materials. There are three categories of nanocellulose, namely micro/nanofibrillated cellulose (M/NFC), nanocrystalline cellulose (NCC) and bacterial nanocellulose (BC). Cellulose has intermediate properties between Hookean solids and Newtonian liquids. It is commonly known as viscoelastic material. The viscoelastic properties were determined by physical properties that is thermodynamics, chain conformations, mobility and chain diffusion (Rubinstein & Colby, 2003). Based on these properties, researchers were constructing models of cellulose. Among the constructed models are Maxwell model, Rouse model, Doi-Edwards model and des Cloizeaux and de Gennes model (Aust, Kroger, & Hess, 1999; De Gennes, 2008; Schiessel, Metzler, Blumen, & Nonnenmacher, 1995). Usually the viscoelastic properties of the cellulose solution are

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measured using rheometer. However, it would be of interest to go down at microscopic level where the rheological properties of the solution might differ with the bulk measurement using rheometer.

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1.2 Problem Statements

Currently, rheometer has been used to get rheological properties of viscoelastic material. However, substantial amount 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 rheological properties at its vicinity. The particle trajectory is tracked and analyzed.

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The sample of interest is cellulose solution. The solution is nonhomogeneous fiber solution. The local measurement of the solution is challenging since the complex shear modulus 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.

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The goal of the program is to get the apparent alpha (α_{app}) and the complex shear modulus ($G^{*}(\omega)$) of a sample. The α_{app} will indicate the diffusivity of a material while $G^{*}(\omega)$ will indicate the viscoelasticity of a material.

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Usually, the analysis of the data from the trajectory of the particle requires intensive knowledge in computer programming. No available integrative program has been developed commercially to calculate the required rheological properties. Therefore, this study attempt to developed a measurement system which covers the particle tracking and post analysis of the data in user-friendly Graphical User Interface (GUI) program.

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1.3 Research Questions

Several questions are devised to motivate this study.

1. How to track a particle undergoes Brownian motion in cellulose solution?
2. How to calculate the complex shear modulus from the trajectories data of the particle in question 1?
3. Are the calculated complex shear modules comparable to the result from measurement using rheometer?

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1.4 Research Objectives

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The objectives of the research is

1. To develop a microrheological measurement system using a single particle tracking for cellulose solution.
2. To develop a user friendly software to calculate alpha apparent (α_{app}) and the complex shear modulus ($G^*(\omega)$) in above system.
3. To compare results between local measurement using the above system and bulk measurement using rheometer.

1.5 Significance of the Study

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This study aims to develop a measurement system to measure complex shear modulus, which requires a small amount of sample. It is not limited to cellulose solution tested in this study, but can be extended to any material in liquid form or viscoelastic materials. In addition, the technique offers local measurement at specific microscopic location in a material, which might be of interest to specific applications where rheometer cannot offer.

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1.6 Limitations of the study

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This study is limited to measure the complex shear modulus cellulose solution from Microcrystalline Cellulose (MCC) in deionized water at room temperature. The solutions were prepared in 0% w/v, 1% w/v, 5% w/v and 10% w/v. The shear modulus of solution is main information to explore in this study by tracking the motion of probe bead polystyrene with diameter about 3 μm. This study is also focuses on the development of measurement system and implementation of algorithm based on passive microrheology theory.

1.7 Scope of Thesis

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This thesis consists of five main chapters. Chapter 1 introduces the brief background and the motivation toward the research. This includes the problem statements and research objectives.

Chapter 2 reviews related research in microrheology. Scientific explanation and fundamental principles relating complex shear modulus and Brownian of a single particle is described. Several measurement techniques are also discussed in term of their potentiality, performances and limitations.

Chapter 3 is divided into two main parts; measurement and software development. In the first part, procedures for sample preparation are described. In the later part, the software development is described in detail.

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Chapter 4 displays and discusses the result obtain from the developed system compared with measurement by the rheometer.

Chapter 5 highlights the drawn conclusion from the results. Several recommendations are suggested to do improve and extend the potential of the research.

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CHAPTER 2

LITERATURE REVIEW

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2.1 Introduction

Chapter 2 describes literature reviews related to concepts of rheology and its relation with Brownian Motion (BM), and measurement using Video Microscopy (VM). First of all, rheology and influence factors in testing samples using rheometer will be discussed. Secondly, the BM theory will explain both theory and it application in microrheology. Thirdly, the discussion of microrheology will be explained comprehensively. Fourthly, the VM will describe environment of video application in microrheology. Lastly, this chapter will discuss about single input and single output (SISO) in measurement system.

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2.2 Rheology

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Rheology is a branch of mechanics study to characterize materials to deform and (or) to flow in condition where the applied external force is greater than internal inertia force. This condition is applied to explore viscoelasticity of the materials using rheometry. The rheometry is a technology to get the rheology data. Rheology data contain responses of materials for a given stimulus.

Rheological properties have been important information in specify products of daily life, such as hair gels, toothpastes and papers. The products of health, foods and home materials need standardization on safety and quality (Franck, 2004; Ubbink, Burbidge, & Mezzenga, 2008). The standardization of quality of product requires ongoing research in measurement systems. Thus, applications of modern instruments and measurement research have been an important issue (Crotogino, 2012). Additionally, by research and collaborate works, standardization of product can be established.

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2.2.1 Terminology in Rheology

The Figure 2.1 shows a material, which has the thickness h (after deformation) and area A normal to the y axes. The external force f is applied on the sample resulted in horizontal deformation, Δx.

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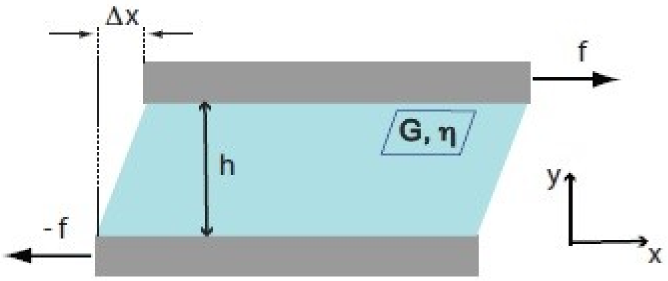

Figure 2.1. Deformation in a material

Generally, there are two measures in rheometry; stress and strain. The stress is defined ratio between applied forces (*f*) and the unit acted area (*A*) in the sample [Pa], meanwhile the strain is defined ratio between displacement (Δ*x*) and the thickness (*h*) sample [dimensionless]. By using these parameters, other information of rheological properties can be known.

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The following physical quantities are included in rheology study and related to stress and strain.

2.2.1.1 Viscosity and Elasticity

Mathematically, viscosity is defined as the ratio between the applied stress to the shear rate. Shear rate is defined rate of change in strain depending on time [1/s]. The viscosity emerges when the sample is independence to the magnitude of deformation instead of shear rate. In practical, viscosity is apparent parameter to depict behavior of a material resisting to an applied force. Material with ideal viscous condition is called Newtonian fluid.

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Another material is known elastic or solid. The force is applied to the material will be responded by a contrary force. This response is defended by the material to conserve initial conditions. By definition, elasticity is term depicted material depending on applied stress and the strain response. Ideal elastic material has linearly relation between stress and strain parameters.

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2.2.1.2 Viscoelasticity

Viscoelasticity is the properties of a material, which exhibits viscous and elastic properties. Examples of viscoelastic materials are gel, mayonnaise and toothbrush. These materials will responses dynamically toward time dependent applied force. The lag time in deformation as response toward external force is known as relaxation time of the materials. Viscoelastic material was modeled as spring and dashpot comprehensively by Voigt and Maxwell (Mezger, 2006; Rubinstein & Colby, 2003) .

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2.2.1.3 Complex Shear Modulus ($G^*(\omega)$)

Complex Shear Modulus $G^*(\omega)$ refers to applied shear stress which resulted from harmonic process. The discussion of $G^*(\omega)$ involves storage $G'(\omega)$ and loss modulus $G''(\omega)$. They are related by the following:

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