Rheological properties of film solution from cassava starch and kaffir lime oil

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Abstract. Rheology of film solution is important to determine the final characteristics of biopolymer film as packaging material. In this study, the dynamic rheological properties of cassava starch-kaffir lime oil film solution were determined. The rheology measurement was made at frequency of 0.1 to 10 Hz and 1 % strain at 25 °C. The storage modulus (G’), loss modulus (G”) and complex viscosity (η*) were determined to know the viscoelastic behavior of the film solution. The magnitude of G’ was greater than G” for all samples which indicated that the film solution was a gel-like; that is, the film solution behaves more like a solid where the deformations were elastic and recoverable. All samples show increasing trend of G’ and G” as the frequency increased. The complex viscosity decreased with increasing frequency which presented a shear thinning behavior of the film solution. The dynamic rheological properties of cassava starch-kaffir lime oil film solution was determined appropriately, thus the characterization of produced biopolymer film by casting can be correlated.

1. Introduction

Food packaging from synthetic polymers dominates the food packaging industry. Most of the synthetic polymers derived from petroleum are non-biodegradable which create a major concern related to health, safety and environmental issue such as growing of waste and pollution. The development of biopolymer film packaging serves as an alternative to reduce the use of plastic based packaging [1]. The biopolymer film is made from renewable resources obtained from natural raw materials, such as starch, cellulose, protein and pectin. The biopolymer based food packaging provides good barriers to oxygen, moisture, and external flavors [2]. Besides its biodegradability, the biopolymer film enriched with natural extracts could prevent microbial growth, hence improve quality and lengthen shelf life of food products.

The development of biopolymer film involves preparation of film forming solution which commonly consists of biopolymer, plasticizer and additive or surfactant. Starch is one of the promising materials to obtain film forming solution. The main components of starch which are amylose and amylopectin have excellent film forming ability to produce good characteristics of film [3]. The
incorporation of natural extract such as kaffir lime oil provide bioactive compound that can improve the functional properties of the produced film. Plasticizer is also required to overcome the film’s brittleness and improve its flexibility and extensibility [4].

The formulation of film forming solution may result in the formation of biopolymer film with different characteristics and properties. Thus, the formulation of film forming solution plays an essential factor to produce biopolymer film of excellent properties and functionalities. The characteristics of film forming solution is related to rheological property which is an important aspect to consider in producing biopolymer film. The rheological study describes the flow behavior and viscoelastic properties of film forming solution which could affect the spread ability, thickness, uniformity of the casting layer and mechanical properties of biopolymer film [5].

The viscoelastic properties of the film forming solution is determined from dynamic moduli that are storage or elastic modulus (G’) and loss or viscous modulus (G”). G’ represents the deformation energy stored in the sample during the shear process. G” value instead, is a measure of the energy lost from it during the shear process [6]. A viscous behavior is exhibited when G”>G’, while gel-like behavior is exhibited when G’>G”. Analysis of these moduli gives information on the structure, particularly in terms of the rigidity, elasticity and deformability [4].

Several studies have been done on rheology of film forming solution made of corn starch and sodium alginate [7], chitosan-starch enriched with murta leaf extract [8], cassava starch-konjac glucomannan [9], cassava starch [10], starch-carrageenan [11], potato starch [12], soy protein isolate [13] and tarra gum [14]. Nevertheless, rheological study on cassava starch film forming solution incorporated with kaffir lime oil has not been reported yet. Furthermore, there is limited information on the relationship between the film formulation and properties of film forming solution which will affect the properties of the obtained films. Thus, this work aimed to determine the viscoelastic behavior of cassava starch-kaffir lime oil film forming solution.

2. Materials and Methods

2.1. Materials
Cassava starch (Cap Kapal ABC, Thailand) was purchased from local supermarket in Shah Alam, Selangor. Analytical grade glycerol (Merck, Germany) was used as plasticizer purchased from local supplier. Kaffir lime (Citrus Hystrix) oil was extracted from kaffir lime peel obtained from local market in Klang, Selangor. The extraction was done by hydrodistillation method using Clavenger apparatus.

2.2. Experimental design
A three factor, five level central composite design was chosen to design the experiment using Design Expert 10.0.3. Cassava starch (3-5 %w/v), glycerol (30-50 % w/w starch) and kaffir lime oil (0.2-0.8 %v/v) were used. The formulations for 20 samples were shown in Table 1 with six replicates at the centre point.

2.3. Film solution preparation
The film solutions were prepared according to Table 1. Cassava starch was dissolved in distilled water at 75 °C using hotplate stirrer. Then, glycerol was added and the solution was continuously mixed. The film solution was cooled to room temperature before kaffir lime oil was added. Next, the film solution was stirred further to allow thorough mixing.

2.4. Rheological properties determination
Rheological properties of the film solutions were carried out by using electronic rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany) with concentric cylinder (CC27) and gap of 1.0 mm. The temperature was regulated by Paar Physica circulating bath and a controlled Peltier system (TEZ 150) with accuracy of ±0.1 °C. The data of rheological measurements were analyzed using
Rheoplus software (v3.40). Frequency sweep test was carried out at frequency of 0.1 to 10 Hz at 25 °C and 1 % strain which was determined in the linear viscoelastic region (LVR). The storage modulus (G'), loss modulus (G'') and complex viscosity (η*) were determined as a function of frequency to characterize viscoelastic properties of the film solutions.

Table 1. Film solution formulations.

| Sample | Cassava starch (%w/v) | Glycerol (%w/w) | Kaffir lime oil (%v/v) |
|--------|------------------------|-----------------|-----------------------|
| SGK 1  | 3                      | 30              | 0.2                   |
| SGK 2  | 3                      | 30              | 0.8                   |
| SGK 3  | 3                      | 50              | 0.2                   |
| SGK 4  | 3                      | 50              | 0.8                   |
| SGK 5  | 4                      | 40              | 0                     |
| SGK 6  | 4                      | 40              | 0.5                   |
| SGK 7  | 4                      | 40              | 0.5                   |
| SGK 8  | 4                      | 40              | 0.5                   |
| SGK 9  | 4                      | 40              | 0.5                   |
| SGK 10 | 4                      | 40              | 0.5                   |
| SGK 11 | 4                      | 40              | 0.5                   |
| SGK 12 | 4                      | 40              | 1.0                   |
| SGK 13 | 4                      | 23.2            | 0.5                   |
| SGK 14 | 4                      | 56.8            | 0.5                   |
| SGK 15 | 5                      | 30              | 0.2                   |
| SGK 16 | 5                      | 30              | 0.8                   |
| SGK 17 | 5                      | 50              | 0.2                   |
| SGK 18 | 5                      | 50              | 0.8                   |
| SGK 19 | 5.7                    | 40              | 0.5                   |
| SGK 20 | 2.3                    | 40              | 0.5                   |

3. Results and Discussions

Dynamic rheology measurement by frequency sweep could be used to classify dispersions of the film forming solution which are a dilute solution, an entanglement network system (or a concentrated solution), a weak gel and a strong gel [15]. The dynamic moduli, i.e. storage modulus (G’) characterized whether solid or elastic behavior and loss modulus (G'”) characterized whether viscous or liquid behavior of the film solution. If G’>G’”, the solution is more solid in nature and if G’”>G’, the liquid nature predominates [9].

Plots of storage modulus (G’) and loss modulus (G’”) versus frequency for cassava starch-kaffir lime oil film solution are shown in Figures 1 and 2. The magnitudes of G’ and G’” increased as the frequency increased for all samples. The increased concentration of starch resulted an increased of G’ and G’”, however, the trend of G’ and G’” were similar for all samples regardless of the concentration of glycerol and kaffir lime oil in the formulation. The sample with high cassava starch concentration, SGK 19 had the highest G’ and G’” which show that the solution was more elastic and viscous than the other samples. The values of G’ was higher than G’” for all samples within the frequency range from 0.1 to 10 Hz which shows that the film solution exhibited a gel-like behavior. Thus indicated that the film solution behaved much like a solid than a liquid, that is, the deformations would be essentially elastic [6]. According to Hao et al. [16], the gel-like behavior was dependent on polysaccharide concentrations, this may be due to the structure of polysaccharide at high concentrations was more stable which exhibit stronger gel-like behavior and vice versa. The film solution that shows a weak gel-like behavior might be related to reconstruction of the fixed network, where the polymer chains could no longer slip past one another. Consequently, the ability of this entangled network to temporarily store the imposed energy increased, behaving more like elastic solid [14]. The gel-like
behavior is also observed for gelatin-polyvinyl alcohol film solution [17], fish gelatin-κ-carrageenan [18] and fenugreek gum [19].

Figure 1. Storage modulus ($G'$) of cassava starch-kaffir lime oil film solution prepared at different formulations (a) 3 %w/w starch (b) 4 %w/w starch and (c) 5 %w/w starch. For detailed sample formulations, see Table 1.
Figure 2. Loss modulus ($G''$) of cassava starch-kaffir lime oil film solution prepared at different formulations (a) 3% w/w starch (b) 4% w/w starch and (c) 5% w/w starch. For detailed sample formulations, see Table 1.
Figure 3. Loss modulus (G") of cassava starch-kaffir lime oil film solution prepared at different formulations (a) 3 %w/w starch (b) 4 %w/w starch and (c) 5 %w/w starch. For detailed sample formulations, see Table 1.
The complex viscosity ($\eta^*$) of cassava starch-kaffir lime oil film solution decreased with increasing frequency and had a tendency to close to each other at the high frequency as shown in Figure 3. All samples show a similar trend regardless the formulation of cassava starch, glycerol and kaffir lime oil. The sample with high cassava starch concentration, SGK 19 had the highest $\eta^*$ which shows that the solution was more viscous and had higher resistance to flow than the other samples. The decreasing of $\eta^*$ with increasing frequency indicate that the film solution presented a shear-thinning behavior, the typical of many polymers. Such behavior is in good agreement with those found for other dispersions [15], [19], [20]. According to the views of Ma et al. [20], bond-breaking and bond-making between particles during frequency sweep may lead to structural changes in which at high frequency, the time interval is not enough to break inter and intra molecular bonds to reform. Possibly, this phenomenon led to permanent molecular alignment or disentanglement of long chain polymers, and consequently, decrease in complex viscosity.

4. Conclusion
In this study, the rheological properties of film solution from cassava starch and kaffir lime oil were reported. The storage modulus ($G'$) was higher than the loss modulus ($G''$), indicating that the film solution exhibited a gel-like behavior. The complex viscosity ($\eta^*$) show shear thinning behavior of the film solution indicated by decreasing of complex viscosity with increasing frequency. Thus, the rheological properties can be correlated to the properties of casted biopolymer film because the properties of biopolymer is affected by the processing condition.

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