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THE IMPACT OF ALOE VERA GEL TOWARDS THE RHEOLOGICAL PROPERTIES OF THERMOPLASTIC STARCH-BASED FILM

Thermoplastic starch (TPS) is a biopolymer that has gained recognition as a substitution for petroleum-based plastic. TPS combined with other material manufacturing processes through melt mixing necessitates high temperatures that can impact the product's degrading qualities. Hence, Aloe vera (AV) gel is added as a cross-linker for the process. This paper focuses on investigating the rheological properties of TPS film based on potato-soluble starch upon the addition of AV gel. Melt mixing and hot-press processes were used to create the films. The melt and dynamic rheology of the material were all measured. The result shows that the melt flow index of the TPS/AV films is reduced with the increase in the AV gel content. The formation of crosslinking between TPS and AV prevents polymer chains from sliding past each other contributing to an increase in the viscosity and reduction in shear rate. A higher value of storage modulus than loss modulus proved that the TPS/AV films behaved more like a solid than a liquid. The complex viscosity of the films decreases as the frequency increases which is caused by the shear-thinning effect. Thus, crosslinked TPS/AV films with well-understood rheological properties could be suitable for various packaging applications due to their mechanical strength, barrier properties, and potentially biodegradable nature.

Keyword: Thermoplastic starch; Biopolymer; Biodegradable plastic; Aloe vera gel; Crosslinker; Rheological properties

1. Introduction

Plastic waste accumulation is a global issue due to the growing usage of plastic-based petroleum. The superiority of petroleum-based plastics such as their variety, endurance, resilience, and toughness caused their application in daily lives to be helpful. Plus, the global market size of plastic production is increasing over time and is expected to reach more than USD 1,050 billion in 2023 [1]. In 2023, it is expected that improper handling of plastic trash will lead to the discharge of approximately 420,000 tons of chemical additives into water bodies, worsening the environmental impact of plastic pollution [2]. The poor degradation ability of petroleum-based plastic was caused by the difficulties of microbes to penetrate the plastic and take action for the disintegration process. The hydrophobic properties of the plastic led to over 100 years taken by the microbes to disintegrate the plastics [3]. Therefore, another alternative is needed to solve this issue which the development of bioplastic made from natural and renewable resources was becoming popular to replace petroleum-based plastic.

Many years ago, researchers started exploring replacing petroleum-based plastic with bio-based polymers such as cellulose, fatty acids, and starch [4-6]. Starch comprised of amylose and amylopectin is considered one of the promising materials due to its affordable price, biodegradability, wide availability, and ability to form a film plastic [7,8]. Furthermore, starch is capable of producing transparent, tasteless, and odorless films with a high oxygen barrier quality, making it ideal for food preservation [9]. Unfortunately, starch-based plastic experiences strong hydrophilic properties that lead to poor mechanical performance which limits its application. A few techniques have been invented to improve the mechanical performance of starch-based plastic such as the addition of plasticizer, combination with other types of polymers, chemical modifications, and embedment of fillers like nanoparticles, crosslinkers, and additives [10].

A crosslinker is a chemical that creates a covalent or ionic bond between two polymer chains. A cross-linking process utilizes bi-functional chemicals to combine two polymers, limiting their water-binding ability while boosting their stress-transfer qualities. Creating covalent connections between molecular

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chains makes it possible to limit polymer chain mobility and increase performance [11]. Sun et. al. used borax, adipic acid, citric acid, and boric acid as crosslinking agents in starch/polyhydroxyalkanoate and found that crosslinker improves the smoothness of the composite films as well as a higher degree of crystallinity was obtained [9]. Adipic acid and citric acid were found to be more suitable as crosslinkers for starch/PHA composite films than boric acid or borax. Dang and Yoksan found chitosan acted as a crosslinker in TPS films causing the melt flow ability to reduce as the melt flow viscosity rises [12]. Other researchers added glutaraldehyde as a crosslinker in the starch/chitosan films with increased tensile strength, Young's modulus, and toughness of thermoplastic starch [13].

AV gel is formed from AV leaf pulp, which is mostly composed of polysaccharides such as acetylated compounds, mannose derivatives, and glucomannan. AV also has cellulose, and hemicellulose and contains 99.5 percent water [14]. Franziska et. al. analyzed AV gel and found various organic acids in AV gel such as benzoic acid, sorbic acid, malic acid, citric acid, lactic acid, and acetic acid which suggested able to act as crosslinkers [15]. A previous study claimed that the cross-linking that happened upon the addition of the AV gel was caused by organic acids, which acted as chemical bridges between plantain flour starch chains [16]. The cross-linking process between AV gel and starch increases the thermal resistance of the film explains the formation of chemical bonds between molecules and raises the molecular weight. These authors also examined the contact angle of the TPS-plantain flour/AV film. Researchers found that increasing the amount of AV gel in films made from plantain flour dramatically increased the contact angle values. With increasing surface hydrophobicity, the water contact angle increases. According to Panrong et. al., the increment in the water contact angle of biopolymers proved the formation of stronger intermolecular hydrogen bonding in the polymer matrix [17].

Therefore, this study incorporated AV gel as a crosslinker in potato-soluble starch-based film. AV which was previously used as a crosslinker proved to improve the strength of TPS which is directly affected by the polymeric material structure. However, a limited report was found discussing the flow of material matter. Thus, melt flow and rheological properties of the film were further studied in this paper.

2. Experiment

2.1. Materials

The main raw materials utilized in the production of the film were AV gel acted as a crosslinker obtained from Chemmiconnex (Malaysia), potato-soluble starch brand Bendosen (Malaysia) as a biopolymer, and glycerol as a plasticizer with a molecular weight of 92.09 g/mol, from Chemiz (Malaysia).

2.2. Preparation of the films

TABLE 1 presents the film's formulation containing TPS and AV gel. TPS acted as the control film in this paper. The film was prepared using a modified procedure from a prior study, which involved three steps: melt-blended, crushing, and hot press techniques [18]. Potato starch and glycerol were first mixed to form TPS with the composition of glycerol being 30%. The TPS and AV were then manually mixed for 30 minutes in a beaker before being placed in a desiccator for 24 hours to facilitate the crosslinking process. Thermo Haake Polylab Internal Mixer, a Banbury mixer brand, was used for the melt blending process. 170°C, 60 rpm for 5-15 minutes was the operating state. Following this, the mixture (resin) was crushed into a size of less than 2 mm using a Rexmac Compact Crusher. A Cometech hot press machine was then used to press the resin for 10 minutes at 130°C and 700 psi. The resin underwent preheating at 10 minutes before hot-pressed 700 psi was applied. Tap water was used to cool the hotplate it reached 50°C. Then the film was detached from the steel plate.

TABLE 1

Film Formulation

Sample name	TPS (g)	AV (g)
TPS	50	0
TPS/10 AV	45	5
TPS/30 AV	35	15
TPS/50 AV	25	25

2.3. Characterization of the film – Melt flow index (MFI)

To determine the effects of the crosslinker on the melt flow index, a Tinius Olsen melt flow indexer (MP600, Tinius Olsen, Horsham, PA) was used based on the ASTM D1238 standard [19]. After preheating the melt indexer for 7 minutes at 190 °C, the resin was fed into the cylinder. A load (2.16 kg) was used to measure the value of the melt flow index. The sample underwent preheating and compression for two minutes before a 10-minute extrusion process. The MFI was measured for each sample at 190°C. The weighed extrudate was then analyzed as an MFI value (g/10 min) after it had sat for 10 minutes.

2.4. Characterization of the film – Rheology

A rotational rheometer (Haake RheoStress 6000, Germany) was used to conduct the rheological tests. The plates of 20 mm diameter and a special anti-slipping parallel plate geometry were utilized. A 20-mm diameter circle was cut out of each TPS/AV film and the density was calculated. The rheological measurements were performed at 190°C. Rheometers operate between 0.1 and 100 Hz in their oscillatory mode. Before performing each measurement, strain sweeps were used to set up the deformation amplitude in the linear viscoelastic area.

3. Results and discussion

3.1. Melt flow index (MFI)

The impact of AV gel content on the melt flow index (MFI) of TPS film is shown in Fig. 1. The gradual decrement of MFI for the TPS was observed upon the addition of more AV gel ratio. This finding suggests the presence of AV in TPS formed a crosslinked between the TPS polymeric structure which extends the molecule chains and decreases their mobility. The higher reduction of MFI with a higher concentration of AV gel indicates a more crosslinked formation obtained between AV gel and TPS. This is in agreement with a previous study that found MFI reduction occurred on TPS upon the addition of chitosan due to the crosslinking formation [12]. As the degree of crosslinking increases, MFI declines consistently.

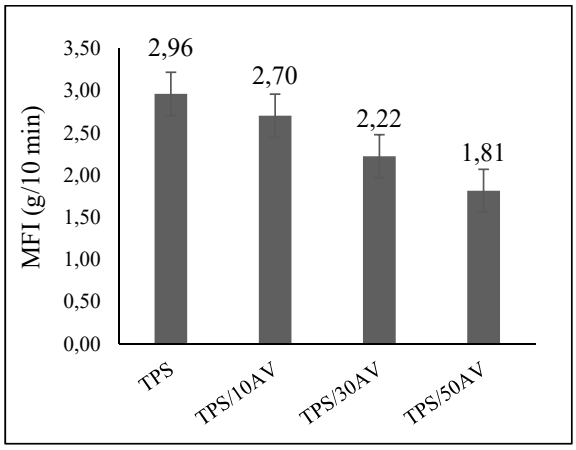

Fig. 1. Melt flow index (MFI) of TPS with different concentrations of AV gel

3.2. Viscosity and shear rate

Fig. 2 shows the viscosity and shear rate of the TPS film at different concentrations of AV gel. Viscosity represents the energy needed to make a fluid flow which is affected by the molecule's interaction in the fluid. Based on Fig. 2, the viscosity of the TPS films crosslinked with the AV gel is increased upon the addition of a higher concentration of AV gel suggesting crosslinking was happening. TPS/50AV has the highest viscosity which is 1623.47 Pa.s. The crosslink network provides resistance against shearing pressures, preventing the polymer chains from freely sliding past each other. Thus, contributes to an increased level of viscosity. This result can be supported by a similar finding that found the viscosity of the TPS film made of potato starch increased with increasing crosslinker sodium trimetaphosphate/sodium tripolyphosphate content [20]. Therefore, a simultaneous increase in the concentration of AV gel results in a very viscous blend of TPS films.

The relationship between viscosity and shear rate for the TPS with various AV concentrations is shown in Fig. 2. The viscosity of the film-forming solutions ranges from 873.067 Pa.s to 1623.47 Pa.s at shear rates of 18.26 to 25 s^{-1} showing shear rate increases with decreasing TPS/AV film viscosity. This indicates strong entanglement networks in the TPS polymeric matrix upon the addition of AV gel and displaying non-Newtonian fluid behaviour that could be due to molecules getting rearranged under a high shear rate. The TPS/AV exhibits pseudoplastic non-Newtonian fluid behaviour as the viscosity is inversely proportional to the shear rate. Chipon et. al. stated that shear rate was associated with changes in viscosity due to the gelatinization suspensions in solid-liquid properties that cause the increment in synergy between fibrils and starch particles [21]. A previous paper discussed that the reduction in viscosity may be explained by changes in the macromolecular structure of the blended compound caused by high shear rates [22].

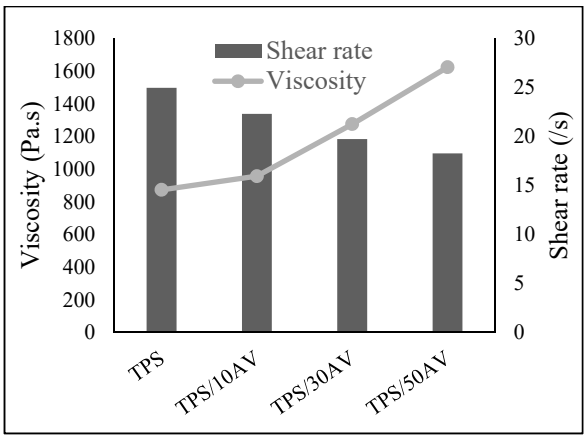

Fig. 2. Viscosity and shear rate of TPS with different concentrations of AV gel

3.3. Modulus

Storage modulus, G' represents energy stored in the material and recovered from it per cycle while loss modulus, G" is the dissipated energy per cycle [23]. Figs. 3 and 4 illustrate the storage modulus, G' and loss modulus, G" of TPS films at different AV gel concentrations. The increment in G' and G" was observed upon increment in the angular frequency. This is common behaviour faced by TPS when energy supplied to it at once improves the polymeric chain mobility [24]. The storage modulus has a higher range of values than the loss modulus. This indicates that the film solution exhibits dominant elastic behaviour rather than viscous behaviour. As a result, polymers with a storage modulus greater than their loss modulus are preferred, as they are capable of maintaining their shape while still being extruded. Therefore, it might be concluded that the TPS with AV exhibited solid-like behavior rather than liquid-like behavior, with deformations mostly being elastic. This is in agreement with Li et. al., proving that the high concentration of crosslinking solution resulted in a higher storage modulus value [25]. This is also supported by Preetha et.al. who found the storage modulus of TPS increased with the addition of crosslinker, oxidized sucrose due to crosslinked density increase [26].

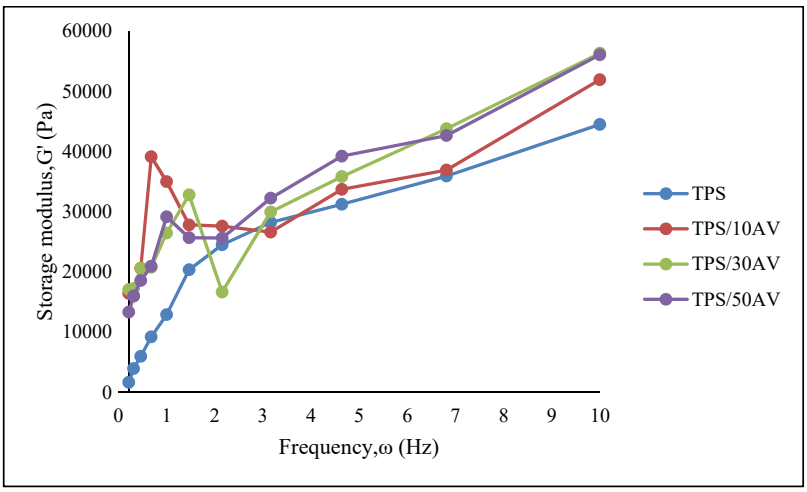

Fig. 3. Storage modulus, G' of TPS with different concentrations of AV gel

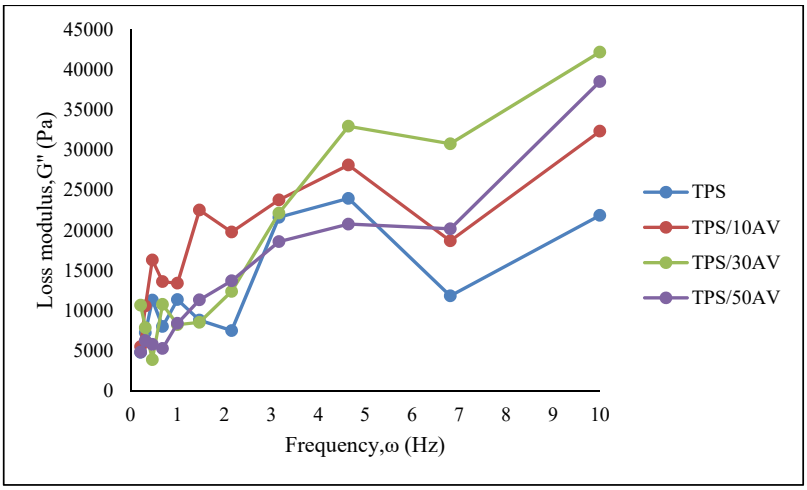

Fig. 4. Loss modulus, G'' of TPS with different concentrations of AV gel

3.4. Complex viscosity

Fig. 5 displays the complex viscosity, η* concerning the angular frequency for TPS film upon the addition of different percentages of AV gel. The shear-thinning effect of the fluids in the film caused the η* of all films to decrease with increasing frequency. Such behaviour is consistent with that discovered by Ma et. al., who stated that during frequency sweeps, molecular bonds may break and reform, changing the structure of the molecules and potentially affecting their rheological proper-

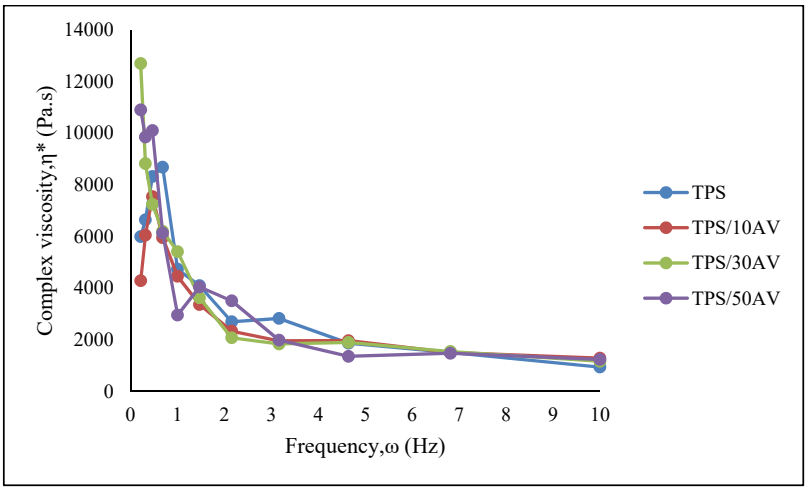

Fig. 5. Complex viscosity, η* of TPS with different concentrations of AV gel

ties [27]. This effect might have caused long-chain polymers to permanently align or detangle their molecules, which would have reduced the viscosity of complex mixtures. Complex viscosity is an essential attribute for assessing the processing flow behavior of composite materials and serves as an indirect indicator of product quality during processing [28].

4. Conclusions

The TPS/AV film with various AV gel concentrations was successfully fabricated using melt-blending and hotpress technique and the melt flow and rheological characteristics were analyzed. The rheological characteristics of the film produced are influenced by the crosslinking of TPS with AV gel. TPS/AV films had better rheological characteristics than neat TPS films, and the effect was shown to be closely connected to the concentrations of the AV gel. The storage modulus, loss modulus, and complex viscosity of the TPS varied as the concentration of AV gel increased. According to the rheological properties analysis, increment in AV gel concentration contributed to the variation value of storage modulus, loss modulus, and complex viscosity of the TPS. The viscosity of the TPS/AV films exhibits a shear-thinning characteristic, which is accompanied by a reduction in shear rate. Therefore, additional research into the rheological behaviour of TPS is crucial for defining the best conditions for processing and better managing the product made from starch.

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