

## The Influence of Glycerol on Mechanical, Thermal and Morphological Properties of Thermoplastic Tapioca Starch Film

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**Abstract:** Thermoplastic tapioca starch (TPTS) film was made by tape casting. The viscoelastic behaviour, thermal degradation and surface morphology were investigated using Dynamic mechanical analysis (DMA), Thermogravimetric analysis (TGA) and Scanning electron microscope (SEM) respectively. The DMA result shows that the storage modulus as well as loss modulus of the TPTS films with 0, 5, 10, 15 and 20% glycerol appears to reduce with increase in glycerol content due to phase relaxation as a result of molecular interaction of the starch molecules with glycerol molecules. Whereas,  $\tan \delta$  shows the effect of temperature is higher on the TPTS film with low glycerol content. The thermal degradation of the TPTS is more susceptible to heat as shown by curve 2(e) for film sample with 20% glycerol, showing that higher glycerol content reduces thermal stability of the film. Even though, lowering of glass transition temperature of the TPTS films took effect with the higher concentration of glycerol which proves ease of processibility and workability of the film. The SEM micrographs of fracture surfaces indicate intermolecular miscibility and surface adhesion increases with higher fraction of glycerol content.

**Keywords:** Tapioca starch; DMA; SEM; TGA; Biodegradable

### 1. Introduction

Non-biodegradable polymers dominate in range of applications such as food packaging as a result of their ease of processing. Conversely, there is a recent upsurge in the research trend towards sustainable biodegradable polymers. The evaluations of renewable materials placed a prime concern on starchy materials due to their abundance, low cost as well as ease of processing. The deeming factor is on improving the properties of polymer products from starch because of its base properties of hydrophilicity, inelasticity, and brittleness [1].

Starch is a polysaccharide, produced by majority of higher plants as an avenue to store energy. It is use to be kept intercellularly in the kind of granules of between 2-100  $\mu\text{m}$  in diameter. Starch granule is heterogeneous, it consists of linear (amylose) and branched (amylopectin) structures, which has both amorphous and crystalline regions. The proportions of amylose and amylopectin depend on the starch source [1].

One of the exceptional characteristics of starch-based materials is their phase transitions during processing, which includes several chemical and physical reactions among which are swelling, gelatinisation, melting, crystallisation, and decomposition. Thereby, starch processing involves disruption of molecular chains within an exact condition in the presence of a plasticizer [2].

Over the years, series of researches were conducted in order to improve the starch products to compete favourably with the petrochemical-based polymers. It can blend with biodegradable synthetic polymers to obtain improved properties and maintain the biodegradability [3]. Other researchers have postulated that starch polymer is pseudo thermoplastic when processed in the presence of excess water or plasticizer it becomes a continuous polymeric entangled material [4].

The mechanical properties of starch films are influenced by humidity and also recrystallisation as a result of retrogradation [5]. Some modifications are carried out on starch to make it suitable for other applications e.g. methylation of the OH group and starch.

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Graft copolymerisation are used to reduce the hydrophilicity of starch [6]. Furthermore, biocomposites are synthesised by blending - starch with either cellulose fiber [2], Poly(Lactic) Acid (PLA) [7], Polycaprolactone (PCL) [8], and Polyhydroxyalkanoates (PHA) [9] among many others, to improve the mechanical properties. Tapioca starch forms a transparent and rigid film without the use of a plasticizer [1]. Thus, in order to enhance its processibility and workability as a substitute to synthetic polymers in food packaging, suitable plasticiser has been evaluated against factors like strength, extensibility, water and gas barrier, and crystallinity as a yardstick for improved performance [10]. According to García *et al.* [1], glycerol plasticizer alter the interface between the adjacent molecules in the polymer chain leading to increase in extensibility of the polymer matrix. Moreover, plasticizers equally cause a shift of glass transition temperature towards lower temperature as depicted in some DSC thermograms [11], thereby reducing the rigidity in the polymer. Polyols played a vital role as plasticizers in polymer industry, most important in the class of Polyols is glycerol. The glycerol resides in the interstices within the starch molecule replacing the intra and intermolecular hydrogen bond with that of its functional group [5] as depicted in Fig. 1. The objective of this work was to evaluate the influence of glycerol on the properties of tapioca starch films by means of dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

## 2. Materials and Method

Tapioca starch was obtained from *THC Sdn Bhd* and glycerol from *R&W Chemicals*. Tape casting technique as reported by Moraes *et al.* [12] was used for the film preparation. Samples of 15 g of the final mixture were made by use of 10% w/w H<sub>2</sub>O and (0, 5, 10, 15, or 20% w/w) glycerol, the remaining part was made up by the starch powder. The total mass was thoroughly mixed using mechanical stirrer at 100 rpm. The mixture was heated at 130°C for 5 minutes at 50 rpm of agitation. The resulting mixture was spread on glass plates with the aid of doctor blade. The

product was oven dried at 35°C to 45°C for 1½ hours. Then, the samples were left at room temperature for 24 to 48 hours.

DMA measurements were carried out using *TA Instruments DMA Q800* Dynamic Mechanical Analyser. The dimensions of the samples were 20 mm × 7.5 mm × 0.68 mm (length, width, thickness). The samples were heated under ambient atmosphere from room temperature to 100°C at a heating rate of 5°C/min and a frequency of 1 Hz.

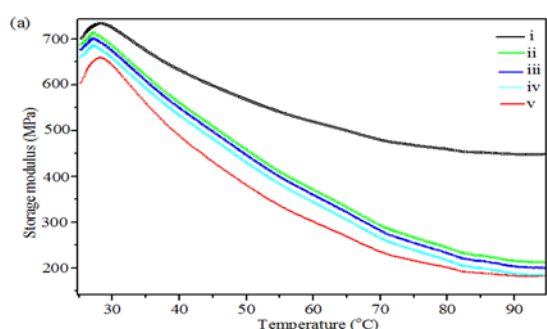
TGA measurements were conducted using *Linseis L81/1550 DTA-TGA* simultaneous thermographic analyser at a heating rate of 5°C/min. The temperature scan was run from room temperature to 800°C. The sample films were fractured by tensile machine and the cross-sections of the fractured samples were then coated with gold in a 15 Pa vacuum degree for microscopy study. SEM (*Hitachi S-4800*) was utilized to observe the morphologies of the cross-sections of all samples.

## 3. Results and Discussion

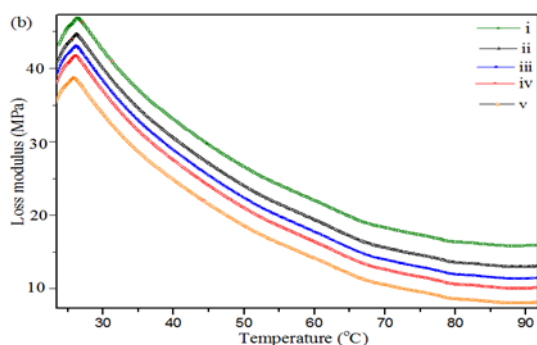
The mechanical property of polymer is often studied by DMA, a method which measures viscoelastic properties, like elastic (storage) modulus ( $E'$ ), viscous (loss) modulus ( $E''$ ) and their dependence on time, temperature or frequency. It also evaluates other material properties such as glass transition, crystallinity, crosslinking effects, fatigue and other time-dependent effects. The ratio of  $E''/E'$  is the loss tangent ( $\tan \delta$ ) [3].

The span of the temperature range limits the properties to be observed in the DMA result [13]. It could be seen from Fig. 1(a) that  $E'$  value of curve (i) with 0% glycerol has higher modulus and also lower relaxation. The curves (ii), (iii) and (iv) in Fig. 1(a) present a reduction in the value of modulus and also rapid relaxation, caused by plasticisation or rubbery elasticity from the entropy change by the applied deformation due to the effect of glycerol [8]. Curve (v) shows a deviation from the previous curves, more rapid relaxation between 35 to 80°C, and contraction afterward to the end. This could be as a result of agglomeration of glycerol molecules in the starch granules which induced nucleation process leading to formation of crystallites within the amorphous.

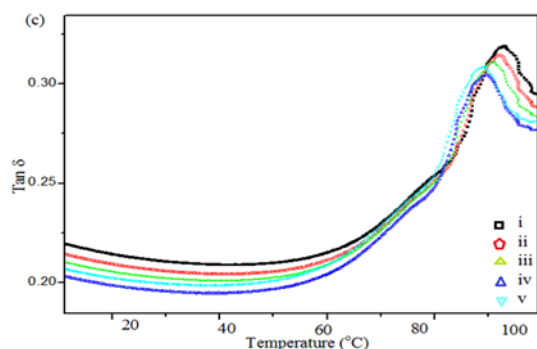
Fig. 1(b) presents loss modulus, which shows the films' response to force applied. It shows similar pattern as storage modulus [6] Similarly, Fig. 1(c), shows  $\tan \delta$ , obtained in the TPTS. The transition of the film was even in all the curves. But sudden change occur at about 40°C in curve (i) where it started to raise with increase in temperature until it attained the highest peak at 94.28°C which denotes the Tg. Likewise, curves (ii), (iii), (iv), and (v) had similar pattern, with 93.41, 92.10, 90.90 and 92.20°C as their Tg respectively.



**Fig. 1(a)** Storage modulus curves of TPTS containing (i) 0% (ii) 5% (iii) 10% (iv) 15% and (v) 20% glycerol

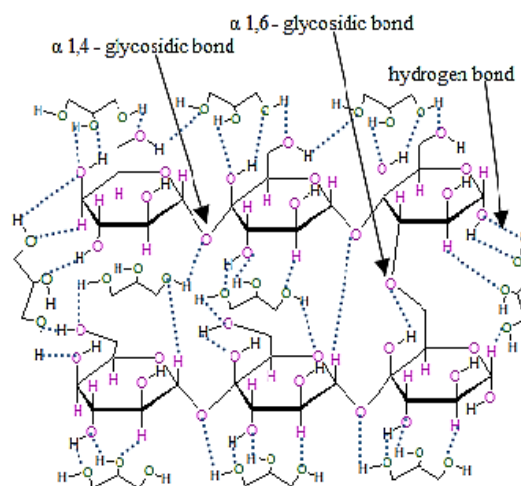


**Fig. 1(b)** Loss modulus curves of TPTS containing (i) 0% (ii) 5% (iii) 10% (iv) 15% and (v) 20% glycerol



**Fig. 1(c)**  $\tan \delta$  curves of TPTS containing (i) 0% (ii) 5% (iii) 10% (iv) 15% and (v) 20 % glycerol

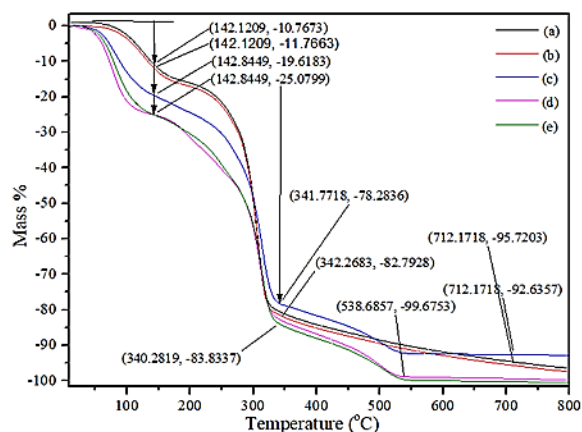
It is observed that there was downturn in the Tg value as the glycerol content increases, which was in line with the theory of plasticization, which mentioned that the efficiency of a plasticizer is measured by the Tg depression it creates in the plasticized polymer [14]. Fig. 2 shows a schematic diagram which depicts possible interactions of groups in TPTS film.



**Fig. 2** Schematic representation of hydrogen bond between starch polymer and glycerol.

Therefore, as the glycerol content changes, the Tg shifted towards lower temperature, as seen in curve (ii), (iii) and (iv). Though, curve (v) which has the highest glycerol content shows a sudden pick up in its Tg compared to the pattern of other curves, which proves a change of behaviour of the film as the glycerol increases as seen in storage modulus. This could be due to crystal growth brought about by retrogradation in higher proportion of glycerol [10].

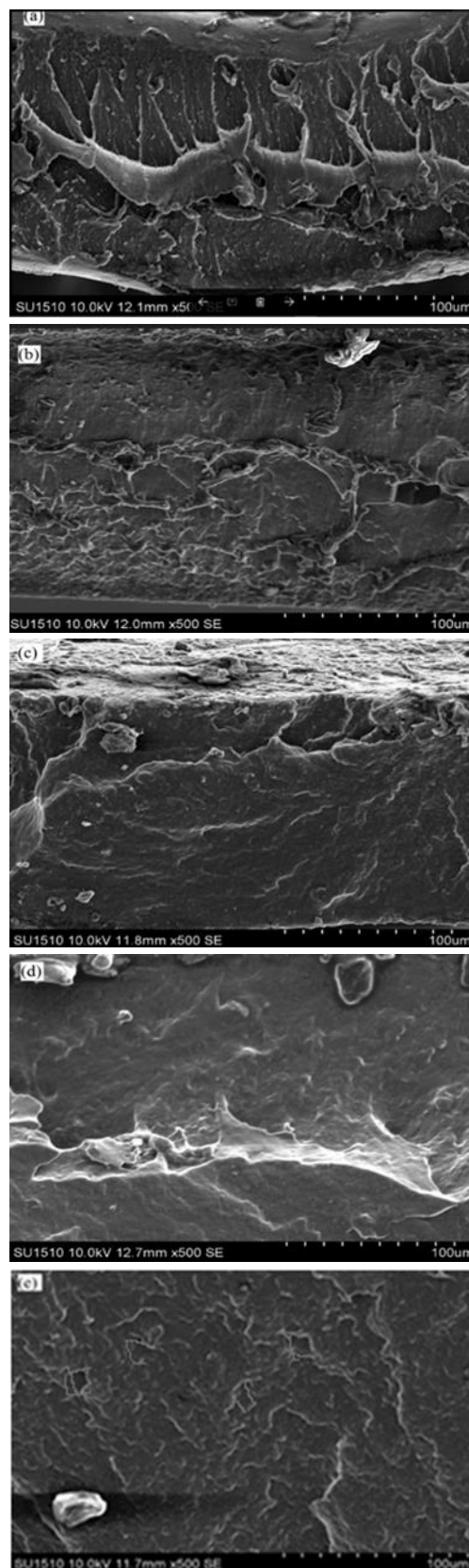
Fig. 3 shows the TGA curves of TPTS with different proportions of glycerol. Curve (a) in Fig. 3 starts to degrade in a nitrogen atmosphere at about 100°C and is fully degraded at 600°C. The incorporation of glycerol gives a drop in heat resistance of the polymer. Curve (b) in Fig. 3 yielded more to thermal degradation of about -11.77% mass at 142.12 °C compared to curve (a) which loss -10.77% at the same temperature. While curve (c), (d), and (e) gave -19.62%, -25.08% and -25.08% mass degradation at 142.81°C respectively. This shows increase in degradation rate of TPTS film with corresponding increase of glycerol content.



**Fig. 3** TGA curves of TPTS films containing (a) 0%, (b) 5%, (c) 10%, (d) 15% and (e) 20% glycerol.

All the films exhibit highest degradation from 250°C to 350°C, but there was a sign of higher thermal resistance initially in curve (e) compared to curve (d), this could be as a result of nucleation which sets in at higher proportion of glycerol, forming crystallite that pose some resistance to thermal degradation. And as most of the TPTS film is destroyed between 250°C and 350°C, together with the crystallites formed in curve (e), the resistance was reversed in favour of curve (d).

SEM images of the fractured surfaces of tapioca starch with different proportions of glycerol are shown in Fig. 4. The fractured sample exhibits smoother surface with the rise in glycerol content. This is due to the fact that the starch showed high affinity to glycerol by having a surge in miscibility. Fig. 4(a) presents a coarse surface due to the absence of glycerol. The coarse surface has reduced with the introduction of 5% glycerol as presented in Fig. 4(b). In the meantime, miscibility phenomenon grew even higher in Fig. 4(c) and (d). However, crystallites were observed in Fig. 4(e) which could be as a result of excessive amount of glycerol which lead to immiscibility within the microstructure of the film. [15, 16].



**Fig. 4** SEM micrographs of TPTS film cross-sections with (a) 0%, (b) 5%, (c) 10%, (d) 15% and (e) 20% w/w glycerol.

The major form of interaction between the two components is by hydrogen bonding between functional groups of both starch and the glycerol. Therefore, as the proportion of glycerol increases, more interactions occur between their functional groups. But, with excess glycerol against limited starch, the functional groups of the glycerol outweigh that of the starch. Thereby, repulsion occurs and phase separation starts. As a result, retrogradation of starch molecules occurs, forming back the crystal growth, which weakens the polymer strength.

#### 4. Conclusion

A detailed analysis of experimental results on TPTS film plasticised with various proportions of glycerol shows that inclusion of glycerol in TPTS film can play a vital role in increasing elasticity, ductility and workability of the polymer. But excessive amount could act negatively on the film strength. SEM results also shows that the TPTS is compatible with glycerol.

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