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THE EFFECT OF GLYCEROL CONTENT ON MECHANICAL PROPERTIES, SURFACE MORPHOLOGY AND WATER ABSORPTION OF *THERMOPLASTIC FILMS FROM TACCA LEONTOPETALOIDES STARCH*

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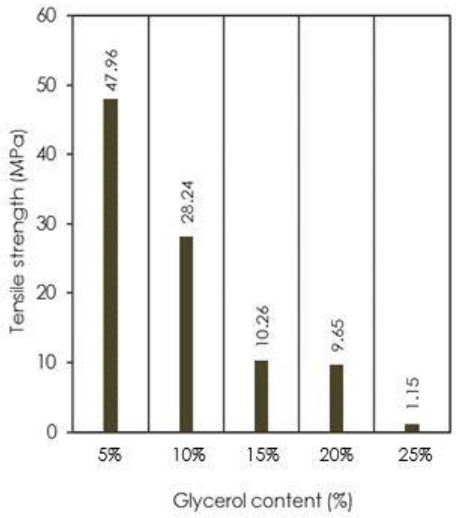
Graphical abstract



Abstract

Tacca leontopetaloides is a new plant source of starch and has high potential to produce film of thermoplastic. In this study, thermoplastic starch (TPS) derived from *T.leontopetaloides* was developed with glycerol as plasticizer through casting method at temperature range from 85 °C to 90 °C and enhanced with sulphur vulcanization method. It was found that the addition of 5%, 10%, 15%, 20% and 25% (v/v) of glycerol into *T.leontopetaloides* starch had affected the mechanical properties, surface morphology, and water absorption of the thermoplastic films. In the mechanical properties study, the TPS films have the highest tensile strength (47.96 MPa) at 5% glycerol content in the formulation. Conversely, the TPS films have increasing value of elongation at break (EAB) with increasing glycerol concentration with the higher EAB obtained at 25% glycerol content (52.90%). The morphology of thermoplastic film was examined by using Scanning Electron Microscopy (SEM). As glycerol content increased, thermoplastic films showed smoother surface, homogenous and good distribution. In water absorption test, TPS films showed lower affinity to water absorption at lower glycerol content. The weight of the TPS films increased ranging from 80.3% to 107.4% after 12 hour of immersion in water. It can be concluded that, glycerol significantly affected the properties of TPS film within the range of glycerol concentration studied.

Keywords: *Tacca leontopetaloides,* glycerol, starch, casting, thermoplastic

1.0 INTRODUCTION

Petrochemical based polymer cause serious environmental problem due to their non-biodegradability. Due to this matter, there have been significant researches in the production of biodegradable plastic such as thermoplastic starch films that made from renewable sources. According to Leejarkpai *et al*. [1], biodegradable films may help in reducing the accumulation of solid waste in terrestrial as most of the films have short service life. Besides, the compost from film degradation offers organic fertilizer to enhance the growth of crops which are possible to reduce the consumption of

chemical fertilizer [2]. In addition, when large-scale biodegradable plastics are used, the energy footprint may effectively be minimized as lesser incineration process are required [3]. Thus, biodegradable films become an important potential solution to achieve the sustainability of the environment.

Food crops such as corn, cassava, potatoes and tapioca are recently used to produce thermoplastic starch film. Starch represent the most extensively studied due to abundantly available in nature, low cost and has excellent properties that comparable with most synthetic polymers [4]. Generally, starch consists of two heterogeneous microstructures namely amylose and amylopectin which has linear bonds and highly branched bonds respectively [5]. These microstructures are notable indicator to ensure biodegradable products ultimately turn into carbon dioxide (CO_2), water vapour, and humic substances due to microorganisms activities [4].

Even though starch has a good-film forming behavior, most starches used are staple food. Therefore, to overcome the shortcomings of staple food consumption, *T.leontopetaloides* or also known as Polynesian arrowroot is one of the promising substituent material [6][7]. According to Makhtar *et al*. [7], *T.leontopetaloides* is belonging to the Taccaceae family and has thirty species which present as a wild perennial herb. The same finding reveals *T.leontopetaloides* has similar percentage of heterogamous microstructure with the common starch such as corn and tapioca that offer elasticity properties; containing 22.5% amylose and 77.5% amylopectin [8]. *T.leontopetaloides* mainly found in Pacific Islands that serves most population in the island for consumption and medicinal purposes [6]. In Malaysia, *T.leontopetaloides* is found in the east coast of Peninsular Malaysia and is not used as the food source among Malaysian population [7].

Plasticizer is the most significant factor to yield a potent thermoplastic film. Examples of plasticizer that commonly used are water and polyol such as glycerol and sorbitol. In thermoplastic starch film, gelatinization process is particularly essential because it is the indicator that starch is plasticized into thermoplastic only with the present of additional plasticizer. According to Mościcki *et al*. [4], addition of plasticizer influenced the onset gelatinization that induce higher glass transition temperature (T_g) while reducing the intermolecular interactions between the starch molecules. Besides, plasticizer also helps to increase the flexibility of native starch by providing the high interaction forces between native starch and plasticizer [9]. Generally, plasticizer with smaller molecular weights are easily incorporated with starch that lead more efficient effect of plasticizing compared to larger molecular weight [10].

The thermoplastic starch films can be obtained by proper blending treatment such as film-casting, melt-blending or extruding. A study by Fakhouri *et al*. [11] showed that, thermoplastic starch films produced through casting method improved the flexibility and the properties of thermoplastic starch (TPS) film and provide reasonable production cost for thermoplastic film. Furthermore, the addition of glycerol in casting method enhanced the properties and smoothen the process.

By depending on the different glycerol content, the condition of TPS films either it is glassy or rubbery under ambient temperature. Therefore, the objective of this study was to investigate the effect of glycerol content of starch-thermoplastic films derived from a new discovery of starch, *T.leontopetaloides* on the morphology, mechanical and water absorption properties of TPS films.

2.0 METHODOLOGY

2.1 Materials

Tubers of *T.leontopetalodes* were rinsed with water to remove the dirt and sand. The skin of tubers was peeled off manually. Then, the tubers were washed with water. To produce *T.leontopetalodes* starch powder, the tubers were cut into dices and grinded by using electrical blender. The paste formed was filtered by using Muslin cloth to extract out the starch solution. The starch was then allowed to sediment where the supernatant was decanted and sediment starch was dried in the oven at temperature 60 °C. Then, the granulated starch formed was grinded and sieved to form the powder.

Glycerol and sulphur were purchased from Merck (M) Sdn. Bhd.

2.2 Preparation of Thermoplastic Films

The TPS film were prepared using blends of *T.leontopetalodes* starch added with various amount of plasticizer (glycerol); 5%, 10%, 15%, 20% and 25% (v/v). *T.leontopetalodes* starch was dissolved in distilled water and heated at 85 °C on hotplate with constant stirring for 30 min until solution completely gelatinized. The mixture was then cooled to ambient temperature. The gelatinized mixture was casted onto the polyacrylic plates (16 cm x 16 cm x 3 mm) and was dried in ventilated oven at 45 °C until constant weight, or approximately for 36 hr. The dried films obtained were peeled off and each films formulation was prepared in triplicates. Finally, the films were completed with additional vulcanization process with 0.2% of sulphur using two-roll mill machine to obtain the even thickness of films (≈1mm).The thin layer of TPS films formed were stored in a desiccator containing sodium bromide (NaBr) for further analysis. TPS films (TF) with varies concentration of glycerol was denoted according to glycerol content, TF5, TF10, TF15, TF20 and TF25 respectively. Table 1 shows the formulated composition of thermoplastic films and Figure 1 is the condition of films after went through the processes involved.

Table 1 Formulation of thermoplastic starch film

Material	TF 5	TF 10	TF 15	TF 20	TF 25
Starch (g)	33	33	33	33	33
Distilled Water (mL)	100	100	100	100	100
Volume of Glycerol (mL)	5	10	15	20	25

2.3 Mechanical Analysis

Tensile test for the films were carried out with a Universal Testing Machine H50KT according to ASTM D882-97. The test was performed at cross head speed of 5mm min^{-1} at room temperature, 25 °C to evaluate the tensile strength and elongation at break. Sheets of film specimen of 1mm thickness were cut into size of 100mm×25mm. Thickness of samples were measured with a vernier caliper having a sensitivity of 1 mm.

2.4 Morphological Analysis

The morphology of film was examined by using Hitachi TM 3000 scanning electron microscopy operated at 15kV. The samples were fractured to examine the samples under electron beam. Magnification used to examine *T.leontopetaloides* starch and thermoplastic films were 1000×.

2.5 Water Uptake Analysis

The casted samples (size: 50mm×30mm×1mm) were immersed in water at room temperature. Then, the samples were removed at specific intervals, excess water on the surface of the samples was gently blotted with tissue paper, and the weight for each sample was recorded. This process was repeated at several time intervals. The water absorption ratio was calculated by using the equation (1).

$$X = \frac{Mx - Mo \times 100\%}{Mo} \qquad \text{Equation (1)}$$

Mx indicates the weight of the samples in the X hour; Mo indicates the initial weight of the samples; X indicates the water absorption ratio.

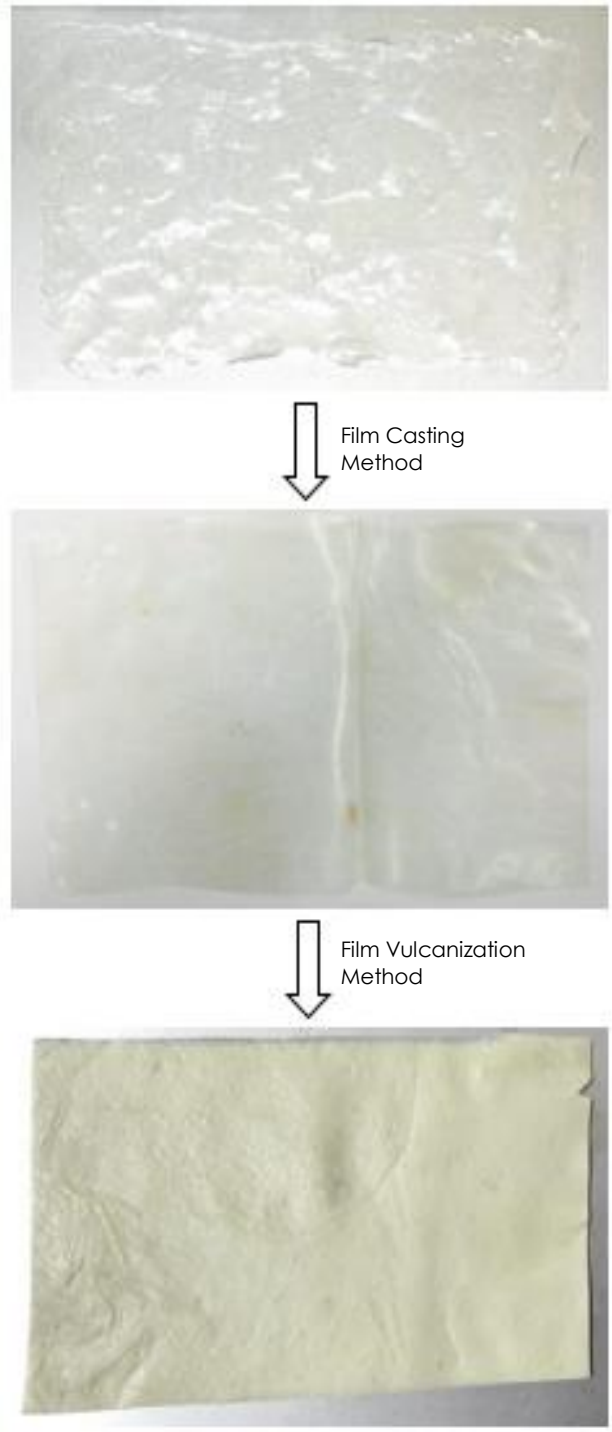


Figure 1 Condition of films after the process of casting and vulcanization

3.0 RESULTS AND DISCUSSION

3.1 Mechanical Analysis

The mechanical properties of starch films were conducted to evaluate the strength of thermoplastic films with varies amount of plasticizer. The results of tensile strength and elongation at break are illustrated in Figure 2 and Figure 3.

As shown in Figure 2, the TPS films' tensile strength value decreased as the glycerol content was increased. According to Detyohin [12], glycerol acted as lubricant that allowing the granules of starch colliding with each other under agitation stress that cause the glycerol to disrupt the molecules. The same author also stated that, as excessive lubricant present, it forces the crystallographic structure of starch became amorphous that lead the films weaken. Thus film with 5% of glycerol content indicated good mechanical properties which had 47.96 MPa compared to other films that contained with 10%, 15%, 20% and 25% glycerol which had 28.24MPa, 10.26MPa, 9.65MPa and 1.15MPa of tensile strength respectively.

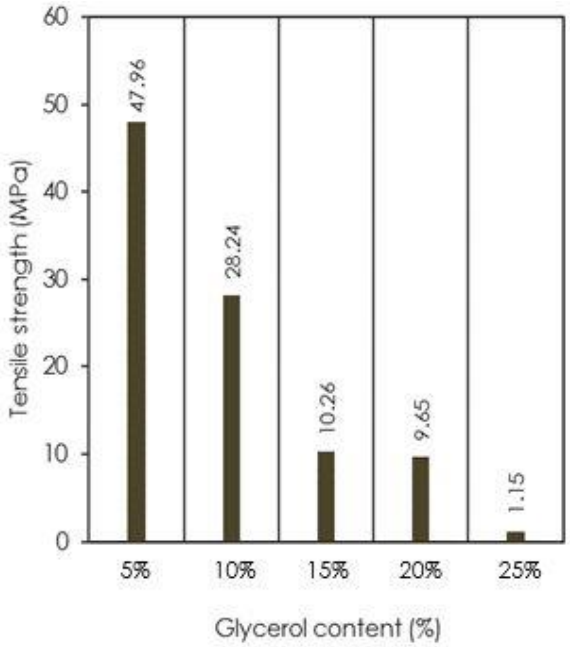


Figure 2 Tensile strength of thermoplastic films varies by different of glycerol content

From Figure 3, the effect of glycerol on the elongation at break (EAB) can be observed. TPS film contained with the lowest amount of glycerol showed very low value of EAB percentage (11.32%) while TPS film with the highest amount of glycerol has highest percentage of EAB (52.90%). It was revealed that the elongation at break is significantly influenced by the factor of plasticizer content. These findings are in agreement Al-Hassan & Norziah [13] as according to these authors, glycerol has been used to overcome the brittleness of films from high intermolecular forced into mobility that induced the films flexible and stretchable. The results of EAB obtained in the current study were in agreement with the results obtained by Hanani *et al*. [14].

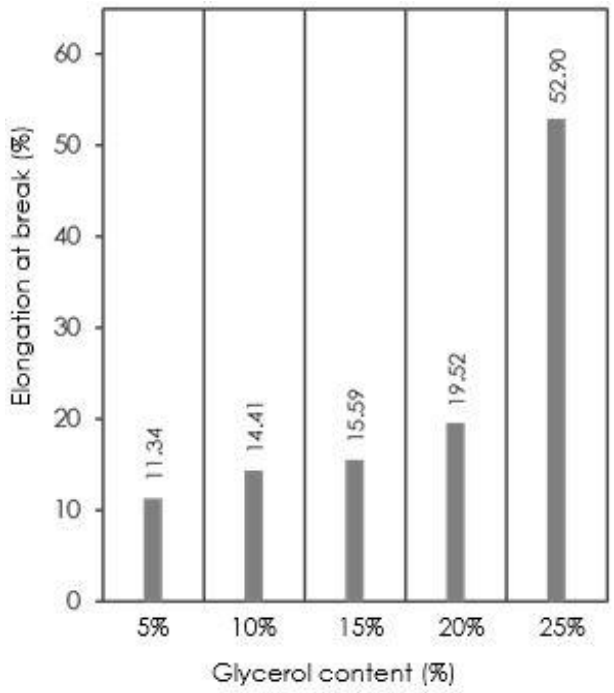


Figure 3 Elongation at break of thermoplastic films varies by different of glycerol content

3.2 Morphological Analysis

The micrographic surface of thermoplastic films produced by casting method were obtained by Scanning Electron Microscopy (SEM) at magnification of 1000×. The films image obtained by SEM as in Figure 4 shows homogenous surface and have cohesive blending matrix. According to Fakhouri *et al*. [15], casting method yield homogenous surface over other techniques which provide no phase separation. In the neat TPS films showed in Figure 4(c) and Figure 4(d), almost no agglomeration of starch granule can be observed which indicating the gelatinization process with sufficient glycerol content at 10% and 15% effectively destroyed the native starch structure. Besides, the films also showed almost no granules starch could be identified on the surface of both films. Liu *et al*. [16] reported that; the addition of glycerol could lead to the homogeneity of thermoplastic starch through casting method. The granule of starch matrix can be clearly seen in the Figure 4(a). Whilst, Figure 4(b) showed rougher surface with the presence of pores and cavities which could be due to less amount of glycerol disrupted the starch. Meanwhile, as glycerol content was further increased, the surface of film showed good dispersion but visible agglomerates that defected the surface of films can be observed in Figure 4(e) and Figure 4(f).

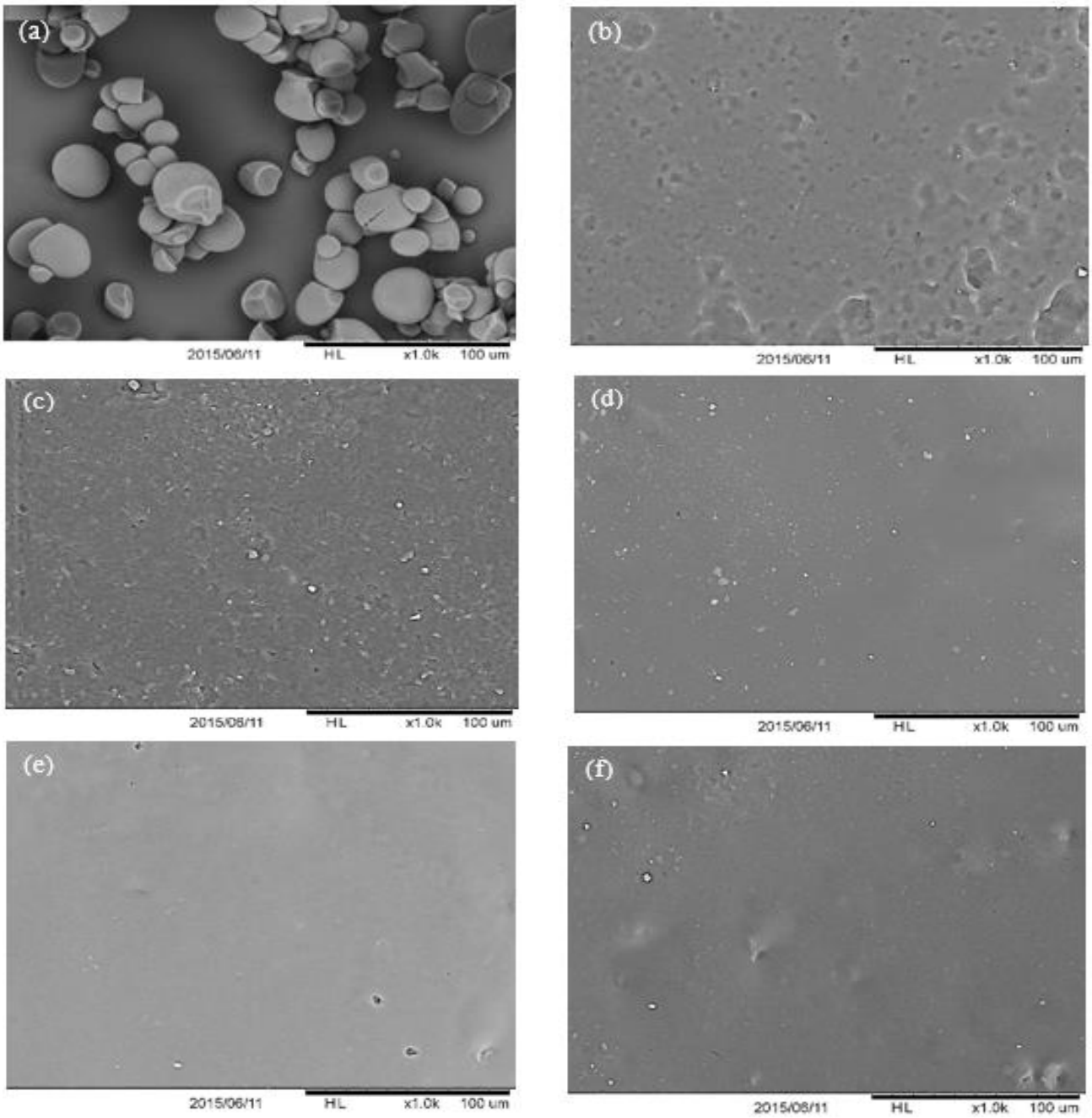


Figure 4 Scanning electron microscopy of thermoplastic films obtained by casting and vulcanization methods (magnification of 1000×): (a) pure starch (b) TF5, (c) TF10, (d) TF15, (e) TF20, and (f) TF25

3.3 Water Uptake Analysis

Figure 5 shows water absorption curve for thermoplastic films versus immersion time. The thermoplastic films immersion in water were characterized by rapid increase water uptake zone and slow absorption at extended time zone. As stated by Pang *et al*. [17], the rate of absorption on water has been influenced by the interaction between hydroxyl groups of starch and glycerol with molecules of water. From these figure, results show that the water absorption of TPS films increased proportionally with the increased glycerol content.

At rapid water absorption zone, the increased in weight in average for all TPS were 12%. TF25 shows remarkable affinity in gaining water as it absorbed 89% water compared to other films. TF5, TF10, TF15 and TF20 had lower water absorption which only 68%, 60%, 73% and 75% respectively. The affinity in gaining water absorption is due to the hydrophilic characteristic as it contains high hydroxyl group of glycerol [18]. Therefore, it is consistent with TF25 which had the highest tendency to attract more water molecules due to highest amount of glycerol content compared other films.

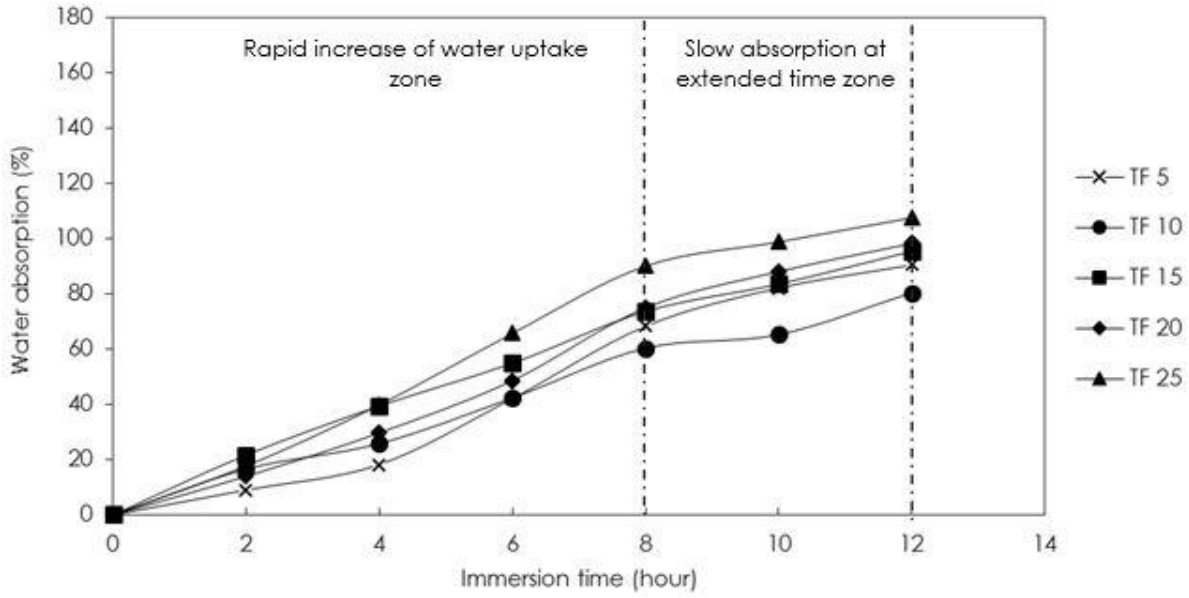


Figure 5 Water absorption of thermoplastic films by varying the glycerol content

However, at the second zone of water absorption test, all TPS films showed slow affinity in water absorption as the average increase in weight were only 6%. The final weight of all TPS at the 12 hour resultant the TF5, TF10, TF15, TF20 and TF 25 to gain 90.3%, 80.3%, 95.3%, 98.1% and 107.4% water absorption respectively.

4.0 CONCLUSION

Varying amount of glycerol content significantly affect the behaviour of thermoplastic films produced by casting film and sulphur vulcanization methods. Through this study, the properties of films with different amount of glycerol successfully revealed the morphology of films, the mechanical properties and the water absorption affinity. From the findings, as the amount of glycerol was increased, it induced better dispersion and homogeneity of films. Furthermore, it gave significant effect to mechanical properties; where TPS films contributed to high value of elongation at break as the glycerol content was further increased but decreased its tensile strength. In water absorption test, the films with higher glycerol content promoted higher affinity of water uptake.

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