



Effect of Water Loading on The Chemical Structure and Mechanical Properties of Thermoplastic Tapioca Starch Film

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Abstract: The effect of water (as a primary plasticiser) content on the chemical structure and mechanical properties of thermoplastic tapioca starch (TPTS) film was evaluated. The TPTS films were produced by tape casting technique through mixtures of fixed amount of glycerol and varied contents of tapioca starch and water. The water content used in the films formulation were 30, 45, and 60 wt %. There was observed increase in hydrogen bonding interaction between starch and water molecules depicted by the downward shift between 3303-3281 cm^{-1} . The excessive amount of water loading portrayed increase in crystallinity due to free volume movement of the starch particles. The changes in water loading also showed variation in the tensile strength and elongation at break of the TPTS films. This observation is because of the dependence of mobility of polysaccharide plastics on the water content in the premix. Therefore, starch forms entanglements with the plasticisers to form a flexible film.

Keywords: Tapioca, water, glycerol, thermoplastic tapioca starch, FTIR, XRD

1. Introduction

The increase in significance of non-food application of starch particularly in thermoplastic starch (TPS) films received attention among researchers. The plastic material presents an edge against its rivals such as glass and tin in food packaging. Nonetheless, the non-biodegradability and depleting sources of the synthetic plastics generate concern among researchers and industries [1] [2]. Starch films present benefit of environmental safety and economic viability among farmers when used as a substitute to the synthetic plastics [3]. The starch is produced globally in large scale, and

the processing methods use less energy. Therefore, films produced using starch could be cheaper compared to petroleum based films [4].

Starch, is considered wholly biodegradable polysaccharide which is biologically produced by various plants such as potatoes, yam and tapioca (tubers) and rice, maize sorghum and millets (grains) [5]. The granular starch is commonly comprised of linear amylose and highly branched amylopectin, and it is considered a crystalline material [6]. The type of crystal structure is generally supposed to be as result of systematic organisation of the amylopectin, that produce double helices after which its packed into either A, B, or C polymorphs as characterised by X-ray diffraction. Different plant sources provide one of the A, B, or C type diffraction patterns. Mostly, cereal starches produce the A-type, root and tuber starches give rise to B-type. While the C-type originate from legume starches. Though, distinctive nature of the C-type polymorph was contested among scientist and some are of the view that it is a mixture of A and B polymorphs with intermediate features and characteristics [7]. The distinction between A and B polymorphs is the packing of helices within the crystal. In the less compressed B type, six double helices produce a hexagonal arrangement around a central core which encloses water molecules, whereas in the A type the central core is filled with another double helix, producing a more closely packed structure [8]. Destructured starch is formed when a mixture of the starch with adequate volume of water is exposed to heat and shear, consequently a homogeneous melt termed as thermoplastic is obtained [9]. The polymer chemistry of TPS depicts the possible interaction of starch and water molecules. At room temperature, the starch in water changed into an ice-like structure with hydrogen bonding between polymer and water molecules resulting in gelation. The gelatinisation could occur faster with increase temperature and shear, which is as a result of the formation of inter- and intra-molecular associations, where hemiacetal oxygen, hydroxyl or methyl groups of the sugar residues of the polysaccharides contribute to hydrogen bonding or van der Waals forces of attraction [10].

The formation of mechanically enhanced polymer required high entanglement and strong intermolecular interactive matrix. The starch film is particularly rigid, water served as an agent for the films flexibility aiding the formation of polymer chain-chain interactions and entanglements. The interaction of the polymer-water molecules is partially replaced by a non-volatile plasticisers such as glycerol after curing of the TPS films [11]. Halley *et al.*, [12] states that water plays vital role in starch destructure which involves series of stages in the film processing: (i) the loss of inherent crystallinity, (ii) endothermic reaction, (iii) starch granules hydration associated with swelling, (iv) decrease in water molecules relaxation time. (v) loss of molecular (double helical) order, and (vi) leaching of the linear (amylose) molecules from the ruptured granules [12][11][10]. The importance of water in gelatinisation and mobility of polysaccharide polymers was reported by Stephen, et al. [13]. The effect of water loading on the chemical structure and mechanical properties of the TPTS films was investigated at constant glycerol content.

2. Experimental

2.1 Materials

The tapioca starch was obtained from Bio starch Industries Worldwide PLC, glycerol was sourced from Sigma Aldrich, while the distilled water was obtained from the chemistry lab.

2.2 Preparation and nomenclature of TPTS films

The films were made via tape casting method based on de Moraes, et al. [14]. A mixture of 15 wt % glycerol with varying concentrations of starch with respect to required water loading as shown in Table 1 was made. The films were termed as TPTS_{W30}, TPTS_{W45} and TPTS_{W60} for film formulation that contain 30, 45 and 60 wt % water loading.

Table 1: Symbols and sample formulations of TPTS film

Name	Glycerol (Wt %)	Water (Wt %)	Starch (Wt %)
TPTS _{W30}	15	30	55
TPTS _{W45}	15	45	40
TPTS _{W60}	15	60	25

The chemical structure changes of the bioplastics were investigated using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). While, the mechanical property was monitored by tensile tests.

The FTIR spectra of raw materials, TPTS films were recorded using a FTIR Spectrometer (Perkin-Elmer: Model 1000 Series) instrument equipped with a universal attenuated total reflectance (UATR) accessory. The spectra were recorded between 4000 cm⁻¹ and 500 cm⁻¹ frequency ranges. The data was analysed using the program of FTIR Spectrum Software (Perkin Elmer) [15].

The crystallinity of the TPTS films were examined empirically with an XRD (Bruker D8 Advance) machine. It was operated at 40 kV and 40 mA. Nickel-filtered Cu K α radiation was used in the incident beam. The square (2 mm x 2 mm) samples were analysed between $2\theta = 10^\circ - 30^\circ$ with a step size of $2\theta = 4^\circ$ [16].

The tensile properties of TPTS films were measured with an Instron 4302 series IX (Buckinghamshire, UK) as per [17] standard method. Five samples, 2.54 cm x 5 cm, were cut from each film. Initial grip separation and crosshead speed were set at 50 mm and 500 mm/min, respectively. The force deformation was recorded during the extension at 0.8 mm s^{-1} [18].

3 Results and discussion

3.1 Fourier transform infrared (FTIR) spectroscopy

The FTIR bands of TPTS films as a function of different water loading is shown in Figure 1. Curves (a) TPTS_{W30}, (b) TPTS_{W45} and (c) TPTS_{W60} present spectra of films with 30, 45, and 60 wt % of water loading. Different behaviour of the functional groups of starch and water molecules was evaluated. It is observed that the curves showed a slight downward shift with increasing water content. The broad absorption at 3302 cm^{-1} in curve TPTS_{W30} shifts to 3296 cm^{-1} and 3281 cm^{-1} in curves TPTS_{W45} and TPTS_{W60} respectively. This observation indicates intensification in hydrogen bonding stretch as the water loading increases. The frequency of absorption of CH stretch at 2921 cm^{-1} in curve (a) shifted upward to 2925 cm^{-1} and 2931 cm^{-1} as the content of water increases, because there was reduction in CH-stretch interactions as the water content increases. The scissors vibration of OH was equally observed in curve (a) at 1642 cm^{-1} which shifted downward to 1640 and 1633 cm^{-1} as the water content rises [19]. In curve (a), C-O-C and C-O-H asymmetric stretch was equally seen to have distinct intensities in all the curves and a downward shift was equally noticed from 1021 cm^{-1} in curve (a) to 1019 and 1007 cm^{-1} in curve (b) and (c) respectively. These changes signify the intermolecular hydrogen bond interactions between the starch ether group and OH group of the water molecules[20]. There is a CH₂ and CH₃ bending vibrations seen between 1465 and 1355 cm^{-1} on the starch films. This absorption was broader in TPTS_{W30} and least in TPTS_{W60} which could indicate reduction in CH₂, CH₃ vibrations as result of excessive presence of plasticizer. More so, a distinct absorption was observed at 1147 cm^{-1} and 1081 cm^{-1} in all the films which indicates the presence of -CH and -COC vibrations. And a down ward shift of C-O was observed 931 cm^{-1} in TPTS_{W30} to 919 cm^{-1} in TPTS_{W60} which could be due the effect plasticisation by water. Furthermore, a peak of -C-C vibration was observed at 842 cm^{-1} [21].

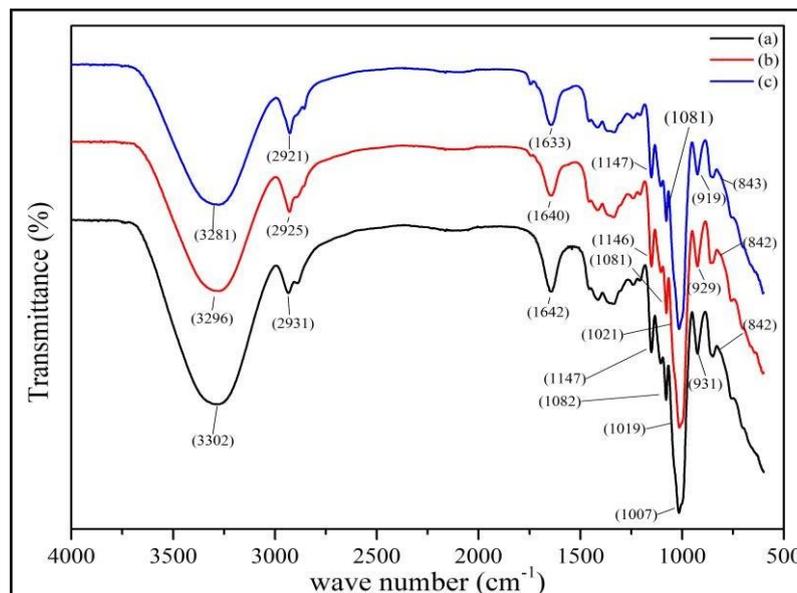


Figure 1: FTIR spectra of TPTS films with curves a) TPTS_{W30}, (b) TPTS_{W45} and (c) TPTS_{W60}

The XRD patterns of TPTS films under the influence of water molecules are shown in Figure 2. The behaviour of the diffractograms shows a complex structure such as that of B type of crystals in curve (a), (b) and (c) [22]. Curve (a) show peaks at 2θ of 17.03° and 20.98° , the detected crystalline shape at low water content depicts a B-type crystals, which shows the presence of residual crystallinity of the unconverted starch [13]. Whereas, curve (c) with peaks at 2θ

of 17.26° and 20.99° also comprise predominantly a B-type structure which depend on the hydrophilicity of the system. The crystals present in curve (a) could be due to the incomplete melting of native starch crystals, though it shows less crystal peak. While curve (c) was as a result of excessive hydrolysis of the starch particles which lead to recrystallization of the B-type of starch crystals [23]. Furthermore, an intermediate behaviour is presented by curve (b) with crystal peaks at 2θ of 17.22° , the essence of plasticization in bioplastic development is to convert the semi-crystalline granules into a homogeneous structure, instead of a complete amorphous material (Schmitt *et al.*, [24]. Therefore, the presence of insignificant amount of crystals could be obtained once the uniformity of the end product is established. With aforementioned behaviour of TPTS_{W30}, TPTS_{W45} and TPTS_{W60} samples, the TPTS_{W45} indicates better characteristic for optimum formulation of the TPTS film.

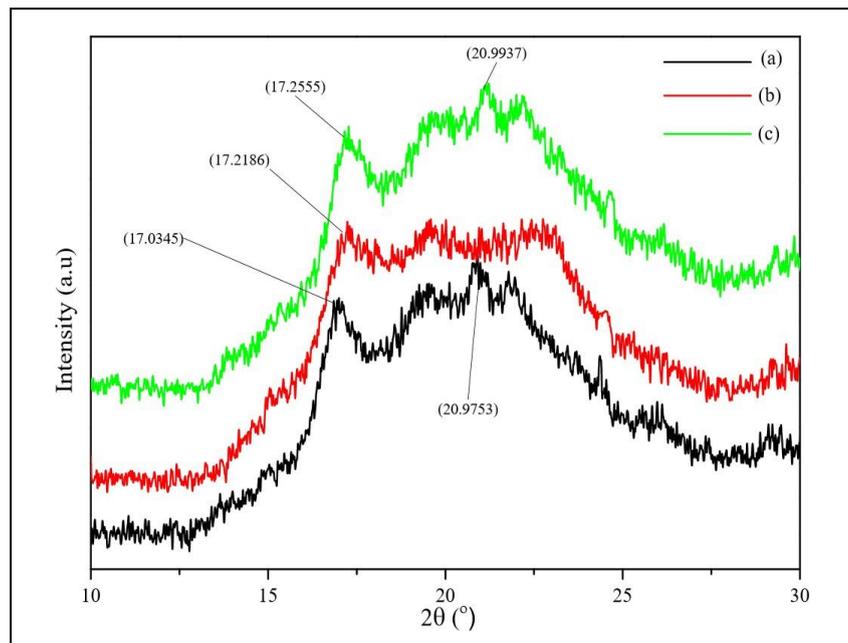


Figure 2: XRD diffractograms of TPTS films with curves (a) TPTS_{W30}, (b) TPTS_{W45} and (c) TPTS_{W60}

The mechanical properties of a polymer involve its behaviour under stress. It is a property that distinguishes polymers from other materials. It conveys property of one particular polymer either it is strong, stiff, hard, brittle, soft or flexible. The results of tensile strength (TS) and elongation at break (EB) of TPTS films with various water loadings are presented in Figure 3. The increase in wt% of water in TPTS films shows significant variations in the mechanical behaviour of the film. The tensile strength of TPTS_{W30}, TPTS_{W45}, and TPTS_{W60} were found to be 2.54 ± 0.29 MPa, 3.84 ± 0.21 MPa and 2.55 ± 0.2 MPa respectively. The highest tensile strength was shown by TPTS_{W45} which indicate strength of fully homogenised film due to greater entanglement of the molecules and completely formed hydrogen bonded material [25]. In TPTS_{W60} sample, a decline in tensile strength to 2.55 MPa was observed, which could be as a result of B-type polymorphs recrystallisation in the presence of excess water content. The behaviour of elongation at break against water loading shows an increase in ascending order at 18.66 ± 3.98 %, 34.43 ± 1.45 % and 42.3 ± 2.45 % for TPTS_{W30}, TPTS_{W45} and TPTS_{W60} respectively. The relationship of TS and EB values for TPTS_{W30} portray a rigid and brittle material. While, in TPTS_{W45} there was a continuous increase in TS with EB which connotes a plastic behaviour. Whereas, the behaviour in TPTS_{W60} appeared to be high in elasticity if compared to that of TPTS_{W30} and TPTS_{W45}. However, having high EB and low TS cannot give the quality required for packaging. Therefore the formulation of TPTS_{W45} is considered as optimum in respect to water content (Schmitt *et al.*, [24].

4. Conclusion

The TPTS film showed interaction of the functional groups of starch and water content. As the water loading increases, the hydrogen bonding increased. The film with low water content yields a B-type crystals, while TPTS₄₅ showed drop in the crystallinity. TPTS₆₀ was characterised with increased B-type of crystal induced by free movement of starch molecules. The optimal starch-water formulation was found in TPTS₄₅, it showed highest tensile strength and intermediate elongation at break. It is concluded that increased water content lead to formation of entangled water mediated film, though excessive amount of water decreases the film's tensile strength. Generally, water served as diluent, melting the innate crystals of the starch to form a well entangled amorphous starch film, though excessive water loading reduces the film's tensile strength as a result induced crystallinity.

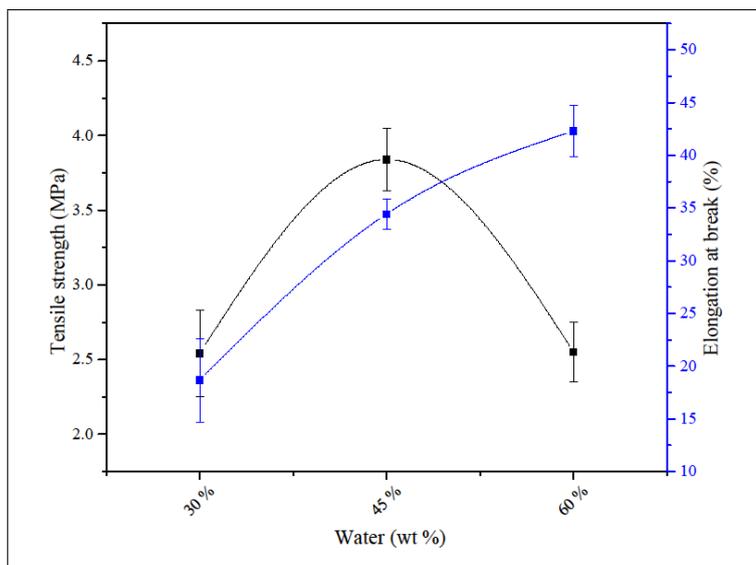


Figure 3: Tensile strength and elongation at break of TPTS films for TPTS_{W30}, TPTS_{W45} and TPTS_{W60}

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