

An investigation of the mechanical properties of starch biofilms plasticized by glycerol

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Abstract

Within the framework of sustainable growth, the use of biodegradable polymers as an alternative to synthetic polymers seems to be the best solution that could resolve waste disposal problems. The aim of this work was to prepare a biofilm based on a biodegradable polymer: starch plasticized by glycerol. Different rate of glycerol are added in order to plasticize the starch (15%, 20% and 30%). The method used for this preparation was casting, the structural and mechanical analysis was carried out to investigate the addition effect on of this plasticizer on the mechanical and structural properties.

Keywords: Starch, Glycerol, Biofilms, Plasticizer, Biopolymers, Flexibility.

I. Introduction

Numerous efforts have been made for replacement of synthetic polymers with relatively inexpensive, biodegradable, renewable and sustainable materials. These materials mainly include the chemically synthesized biopolymers such as poly (lactic acid) (PLA), poly (vinyl alcohol) (PVA), poly (caprolactone), poly (butylene succinate); the microbially produced polymers such as polyhydroxy-butyrates (PHB), polyhydroxy-valerate and the naturally derived biopolymers such as starch, cellulose, chitosan, agar, gelatin, alginate etc. and their blends [1].

Among all natural materials, starch is a potential candidate to produce biodegradable polymers since it is renewable, biodegradable and abundantly available at low cost. Among the various type of starches, corn is the most predominant material constituting 73% of the main sources of starch produced worldwide, followed by cassava (14%), wheat (8%), potato (4%), and others (1%) [2].

Corn starch has the highest amylose content (28–33%), competing with wheat starch (30–32%) followed by potato (18–20%), and cassava starch (16–19%). Starch can be thermally processed to obtain thermoplastic starch using suitable plasticizer.

Starch is one of the most abundant polysaccharides (consists of two polymeric fractions: amylose and amylopectin), used in plastics industry, as eco-friendly, biodegradable alternative for oil-based materials, for example for paper processing and packaging [3]. Biopolymer films offer several advantages over conventional packaging material due to their excellent biodegradability, biocompatibility, and wide range of potential applications [4].

For instance, these films are capable to act as carriers for functional ingredients such as antimicrobial or antioxidizing agents, thus expanding their functionalities to be active packaging. Among many biopolymers, starch is a promising

alternative due to its availability, environmentally friendly, cost-effectiveness, and ease of handling [5].

More importantly, starch is able to be formed into transparent and odorless films without any chemical treatment requirement [6]. Nevertheless, native starch films present some limitations including the brittleness and hydrophilic nature [7], which have a direct impact on mechanical and barrier properties of the films and, thus affect the packaged food product [8]. These inherent properties can be solved with addition of plasticizers such as sorbitol, polyethylene glycol, and glycerol. Among the plasticizers, glycerol has often been used as plasticizer for starch films due to its compatibility with amylose [9], which promotes better mechanical properties by interfering with amylose packing, thereby decreases the intermolecular forces between the starch molecules. In turn, plasticized-starch films are more flexible and feasible for various packaging applications. Numerous studies have proved the effectiveness of glycerol as plasticizer in a concentration of 20–40% of the weight of starch [10].

For instance, Mali, Grossmann, García, Martino, & Zaritzky, 2006 has studied the effect of glycerol concentration (0, 20, 40%) on corn, tapioca, and yam starches. They revealed that, irrespective of the starch type, the tensile strength reduced while the elongation at break increased with the increase in glycerol concentration. This largely results from the interruptions of glycerol in the starch polymeric chains, creating more free volumes and reduce the glass transition temperature, which consequently improve the film softness and extensibility. A more recent work by Zahiruddin et al [11] reported that incorporation of 25% glycerol into tapioca starch film increased the elongation of the film by 4-fold and the film exhibited higher degradation temperature indicating better thermal stability. Similarly, Santana et al.[12] reported that 30% glycerol concentration had successfully improved the mechanical properties of

jackfruit seed starch film and yield moderate barrier properties. Furthermore, blending starch films with glycerol produces films that are more prone to water. Rodriguez et al [13] demonstrated how potato starch forms manageable films without the need to add plasticisers. However, their mechanical properties could be improved by adding glycerol (Gly), which was totally compatible with potato starch.

For instance, Orsuwan & Sothornvit [14], has incorporated glycerol into carboxylated styrene-butadiene rubber/cassava starch blend films. The water solubility and moisture content of the films were improved owing to the hydroxyl groups of glycerol that has high affinity to water molecules. They also found that addition of glycerol was able to increase the storage modulus of the starch film, which is desirable for use as food packaging. Overall, the presence of glycerol plays significant role in improving workability of starch films.

Glycerol is a potential bio-based material to afford prominent biocompatible yet biodegradable polymers for a variety of applications through direct polymerization, fermentation, and chemical conversion. Besides, glycerol plays a critical role in the food packaging industry to perform a plasticizing effect; it improves the ductility of the bio-derived packaging. The native unplasticized starch film is too brittle for handling, while the glycerol-plasticized starch film has adequate flexibility and processability, but with compromised water and gaseous barrier properties. Nevertheless, more established works should be published to exploit the use of this versatile base chemical in diverse fields to good advantages, yet reducing the adverse environmental impact [15].

In the present study, glycerol (fixed at 10%,20%and 30% wt of corn starch) is dispersedCorn starch (commercial), glycerol, is supplied by VWR, PROLABO Marketing, All chemicals were used as received without further purification.

II. Materials and Methods

II.1. Materials

- **The starch** : starch (commercial, cornstarch).
- **Glycerol** : was hunted down from VWR, PROLABO. It is a viscous, transparent, water-soluble liquid. (Chemical formula C₃H₈O₃ Mn: 92.09 g/mol/ Density: 1.25 g/mL (at 25°C)/ Bp: 182°C /Mp: 20°C Flash point. 160°C).
- **Hydrochloric acid** : obtained from Sigma-Aldrich in a concentration of 37%,
- **Sodium hydroxide (NaOH)**. He was chased from Sigma-Aldrich.

II.2. Methods

Preparation of films

Films based on corn starch (commercial, cornstarch) were prepared by casting, according to the experimental protocol described by Gao et al. [15] With the variation of plasticizer rate in the different films.

Characterization of films

Fourier transform infrared (FTIR) spectroscopy

The chemical structures of the neat glycerol, neat starch and neat starch with different rate of glycerol (15%,20% ett 30%). were assessed by attenuated total reflectance-Fourier- transform infrared spectroscopy (ATR-FTIR) in an Alpha spectrometer (Bruker Optik GmbH, Ettlinger, Germany) using a germanium prism. Sixty scans were recorded and averaged at a resolution of 4 cm⁻¹ in the wavenumber range 4,000–400 cm⁻¹. Under these experimental conditions, a depth of the surface of about 1 μm was analyzed.

Mechanical properties

The tensile strength (TS); tencile strain and elongation at break (EB) of the starch-based film with different rate of glycerol are added in order to plasticize the starch (15%, 20% and 30%).

Specimens were determined by a ZWICK ROELL universal tensile machine with test control II load cell 500N. Classe extensometer 1 ; preload 1N test speed 100mm/min ; traction module speed 1mm/min ; with an initial grip separation of 72.82 mm at a speed of 100 mm/min [16]. All films were cut into strips (125 mm × 20 mm) and equilibrated at a temperature of 23 ± 2 °C and relative humidity of 53% for at least 72 h before testing

III. Results and discussion results

III.1. Chemical properties of films

Based on Figure 1, the FTIR spectrum of the TPS shows all film specimens exhibited characteristic peaks belonging to starch. The peaks at 2920 and 1640 cm⁻¹ were related to C–H stretching vibration and tightly bound water bending vibration, respectively [17]. A broad peak at approximately 3280 cm⁻¹ was attributed to complex stretching vibrations of hydroxyl groups that were associated with the formation of inter- and intramolecular hydrogen bonds [18].

Thus, the hydroxyls of glycerol are bound together or with those carried by the structure of the starch via hydrogen bridges, causing, consequently a notorious intensification of the mass due to the bound OH which confirms by the increase in the intensity the band of the C–O–H group at about 1005 cm⁻¹ from the 20% glycerol formulation. Demonstrated the effects of this percentage of glicerol in starch films that reduced interactions of hydroxyl groups in the starch matrix with creation of Intermolecular hydrogen bonding existed between glycerol and starch via hydroxyl groups of glycerol, starch.

This shift confirmed that plasticizer could disrupt the intermolecular and intramolecular hydrogen bonding between starch molecules and then facilitate the movement of starch chains, which is beneficial for the formation of

stronger hydrogen bonds between starch molecules and plasticizer [19]. The water absorbed by the starch is also detected thanks to the valence vibration of the O-H bond of the H-O-H group observed around 1640 cm⁻¹. The band

located around 1425cm⁻¹ corresponds to the deformations of the C-H groups – CH₂-. Absorptions observed between 859 and 550 cm⁻¹ are due to strain vibrations of the C–H bonds of starch.

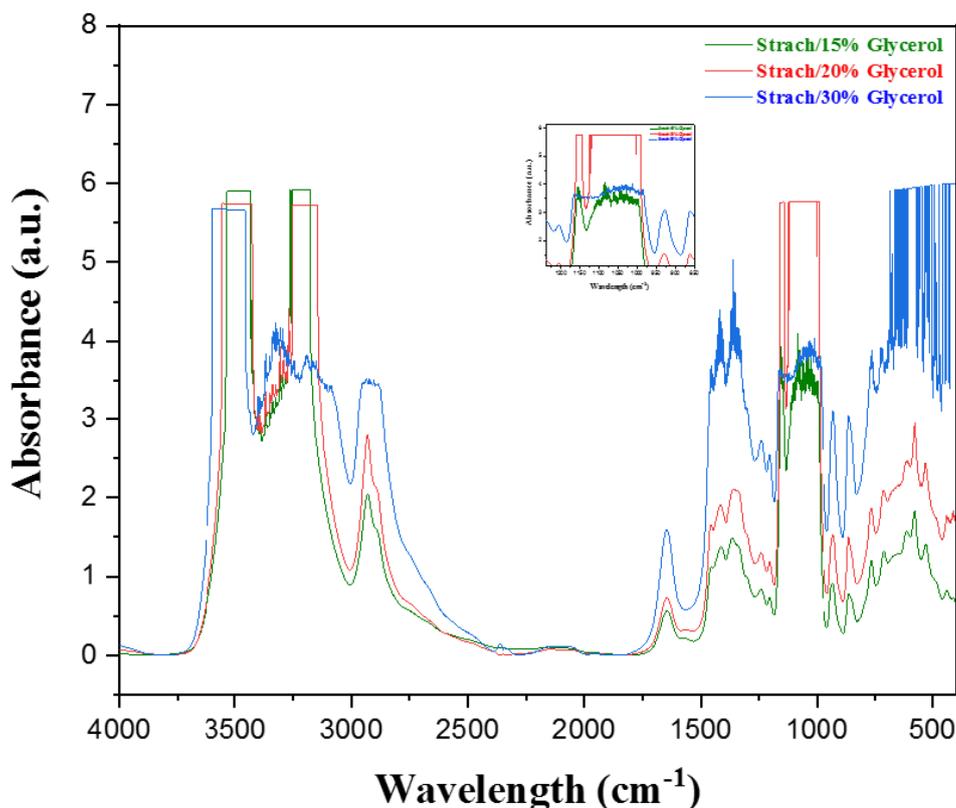


Figure 1: FT-IR spectra of starch-based films plasticized with glycerol (G) at different proportions of 30% G (a), 20% G-10%.

III.2. Mechanical properties

Mechanical properties of packaging material are crucial to evaluate the strength and durability of the material to package products and withstand extraneous forces.

Tensile strength (TS) and elongation at break (EAB) values denote the ability of food packaging film to retain its integrity under tensile stress during processing, handling, and storage [20] while Young's modulus (YM) values indicate stiffness of the material.

Figure 2. illustrates the effects of adding glycerol on the Stress, Tensile strength, Elongation at Break, Toughness and Elasticity modulus of neat starch films.

Figure 2 (a) shows the effect of glycerol on YM /TS of CS films. It can be seen that the trend of the results is similar to that of TS.

Tensile properties TS is the maximum amount of tensile stress the material can withstand before failure. On the other hand, E is an extension under tension, reflecting the elasticity of a material [20]. The results showed that the tensile properties of films starch plasticized by glycerol were in addition, films at 20% Gly showed a significantly stronger value Ts compared to films with 30% and 10 Gly. Chang et al. [22] have already pointed out the close relationship between the film the glycerol content and the mechanical

properties of the film. In other words, the presence of the 20% glycerol in the CS film formulation increased the YM more intensely compared to the effect of 10 and 30 glycerol on the other hand when we compare YM and TS between the formulation of 10% and 30% we find that the presence of glycerol significantly reduces the YM from CS movie respectively.

This finding can be associated with the hygroscopic character of the glycerol possessed by the several hydroxyl groups, which enhanced the ability of starch films to hold water. This consequently reduced the rigidity of the indicated films by drastically reducing YM while increasing softness and flexibility. This finding is similar to Mali et al. [10] who studied the effect of different concentrations of glycerol on maize starch films. They found that corn starch film reduced YM by 1188 at 551 MPa and 139 MPa, with the addition of 20% and 40% glycerol.

Figure 2 (b) shows the effect of glycerol on the EAB/Toughness of CS film. respectively. The presence of glycerol led to the mobility of the CS polymeric chain, thus under applied stress, the flexibility and elasticity of the CS film increased significantly.

For example, Lourdin et al. [23] reported that a small amount of plasticizer can easily insert between the polymer chains, which increases the free volume and mobility of the polymer chains and improves their extensibility. Similar results have been previously reported for hydroxypropil starch films by Arvanitoyannis et al [24].

If we undergo the elongation at break, we see that the value of the breaking stress at 20% glycerol increases, which is in contradiction with what is generally observed. One could conjecture that our films are quite ductile; On the other hand, the films are more ductile, resulting in easy breakage.

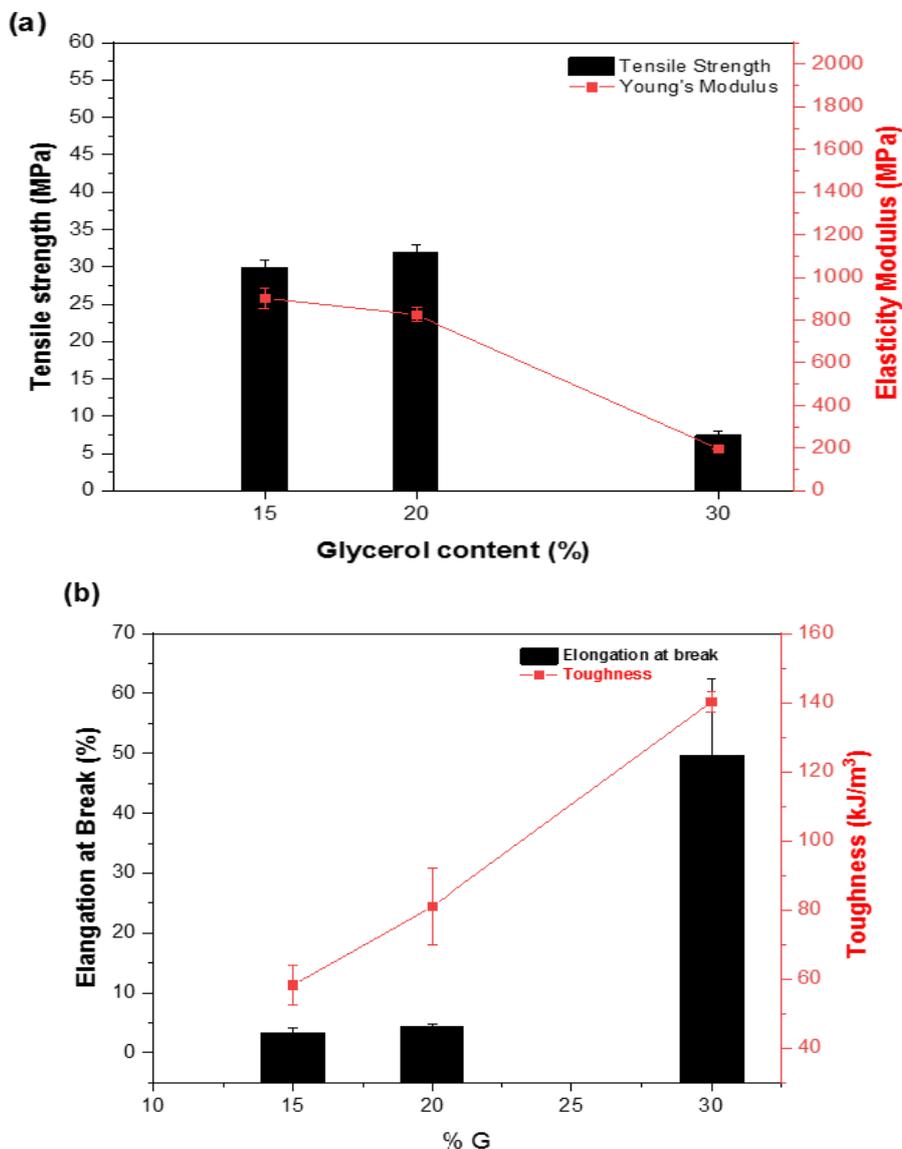


Figure 2: Mechanical properties of corn starch films containing glycerol (10%, 20% and 30%): (a) TS and YM. (b) EAB and toughness.

The study of the mechanical behavior in tension consists in following the shape of the stress-strain or force-elongation curves and in comparing the behavior in tension of the samples studied.

The force-elongation curves of our samples are represented in the Figure 3, there are two zones: We note that the behavior of the films is qualitatively almost identical in the first zone.

- Zone 1 (linear part): This zone represents the linear elastic zone, in which a release of the load results

immediately in a full recovery. According to Oudet (1986), the deformation in this zone is probably due to the deformation of the valence angles superimposed on the movements of some chains of the amorphous domain. In this zone, stress and strain are related by Hooke's law.

- Zone 2 only for the formulation of 30% glycerol: in this zone, we notice a drop in the force (stress) as a function of the elongation (deformation) due to the onset of rupture of intermolecular bonds of the hydrogen type for the essential. This zone is qualified as zone of plastic deformation, where this

one is permanent there and a relaxation of the stress does not involve any recovering.

Figure 3 shows some representative stress-strain curves for 10% and 20% starch /glycerol samples. It is clear that Figure vs exhibits typical brittle fracture behavior [25] described by

relatively high tensile strength, low percentage of elongation and no elastic limit, whereas at high glycerol content a marked increase in the percentage an elongation was observed accompanied by a very clear elastic limit Figure vs. for 30% formulation.

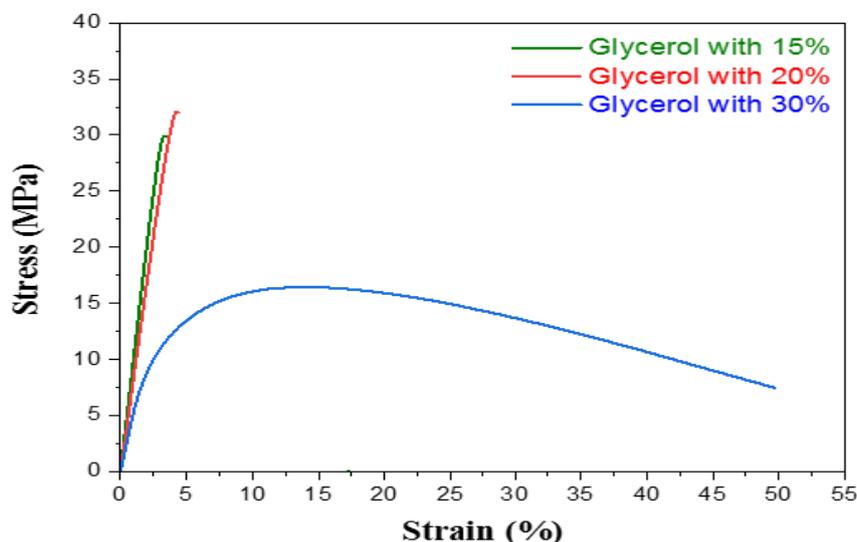


Figure 3: Effect of the price of glycerol content on the stress of starch/glycerol in terms of strain.

IV. Conclusions

Films of starch plasticized by deferent glycerol content have been prepared and their mechanical and chemical properties have been studied. FTIR spectroscopy indicated that the interactions occurred between the hydroxyl groups in the matrix of the starch/glycerol biofilms, case of the 20% glycerol formulation. The elongation at break of the biofilms increased significantly with increasing glycerol, also the tensile strength of the 20% glycerol formulation increased by a poorer 10% and 30% formulation. Therefore, we can see several changes in mechanical chemical properties when we change the level of glycerol so to make a specific application it is necessary to optimize the percentage of plasticizer.

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References

- [1] M. S. Sarwar, M. B. K. Niazi, Z. Jahan, T. Ahmad, A. Hussain. Preparation and characterization of PVA/nanocellulose/Ag nanocomposite films for antimicrobial food packaging, *Carbohydrate Polymers*. 184, 453–464, 2018.
- [2] A. Torres, S. Li, S. Roussos, M. Vert. Poly(lactic acid) degradation in soil or under controlled conditions, *Journal of Applied Polymer Science*. 62(13), 2295–2302, 1996.
- [3] A. Kraak. Industrial applications of potato starch products, *Industrial Crops and Products*. 1, 107–122, (1992).
- [4] J. W. Rhim, P. K. Ng. Natural biopolymer-based nanocomposite films for packaging applications, *Critical Reviews in Food Science and Nutrition*. 47(4), 411–433, 2007.
- [5] S. H. Othman, N. A. Majid, I. S. Tawakkal, M. A. Basha, R. K. Nordin, R. Shapi'i Ahmad. Tapioca starch films reinforced with microcrystalline cellulose for potential food packaging application. *Food Science and Technology*. 2019.
- [6] W. T. Owi, O. H. Lin, S. T. Sam, A. R. Villagrancia, G. N. C. Santos. Tapioca starch based green nanocomposites with environmentally friendly cross-linker. *56*, 463–468, 2017.
- [7] F. M. Pelissari, M. V. Grossmann, F. Yamashita, E. A. G. Pineda. Antimicrobial, mechanical, and barrier properties of cassava starch-chitosan films incorporated with oregano essential oil, *Journal of Agricultural and Food Chemistry*. 57(16), 7499–7504, 2009.
- [8] R. A. Shapii, S. H. Othman, M. N. Naim, R. Kadir Basha. Mechanical properties of tapioca starch-based film incorporated with bulk chitosan and chitosan nanoparticle: A comparative study. *Pertanika Journal of Science and Technology*, 27 (S1), 95–107, 2231–8526, 2019.
- [9] M. G. A. Vieira, M. A. da Silva, L. O. dos Santos, M. M. Beppu. Natural- based plasticizers and biopolymer

- films: A review, *European Polymer Journal*. 47(3), 254–263, 2011.
- [10] S. Mali, M. V. E. Grossmann, M. A. García, M. N. Martino, N. E. Zaritzky. Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources, *Journal of Food Engineering*. 75(4), 453–460, 2006.
- [11] S. M. M. Zahiruddin, S. H. Othman, I. S. M. A. Tawakkal, R. A. Talib. Mechanical and thermal properties of tapioca starch films plasticized with glycerol and sorbitol. *Food Research*, 3(2), 157–163, 2019.
- [12] R. F. Santana, R. C. F. Bonomo, O. R. R. Gandolfi, L. B. Rodrigues, L. S. Santos, A. C. dos Santos Pires. Characterization of starch-based bioplastics from jackfruit seed plasticized with glycerol. *Journal of Food Science & Technology*, 55 (1), 278–286, 2018.
- [13] M. Rodriguez, J. Ose's, K. Ziani, J.I. Mate. Combined effect of plasticizers and surfactants on the physical properties of starch based edible films, *Food Research International*. 39, 840–846, 2006.
- [14] A. Orsuwan, R. Sothornvit. Effect of banana and plasticizer types on mechanical, water barrier, and heat sealability of plasticized banana-based films, *Journal of Food Processing and Preservation*. 42(1), e13380, 2018.
- [15] W. Gao, P. F. Liu, X. Y. Li, L. Z. Qiu, H. X. Hou, B. Cui. The co-plasticization effects of glycerol and small molecular sugars on starch-based nanocomposite films prepared by extrusion blowing, *International Journal of Biological Macromolecules*. 133, 1175–1181, 2019.
- [16] W. Gao, H. Z. Dong, H. X. Hou, H. Zhang. Effects of clays with various hydrophilicities on properties of starch-clay nanocomposites by film blowing, *Carbohydrate Polymers*. 88, 321–328, 2012.
- [17] B. Zhang, J. Q. Mei, B. Chen, H. Q. Chen. Digestibility, physicochemical and structural properties of octenyl succinic anhydride-modified cassava starches with different degree of substitution, *Food Chemistry*. 229, 136–141, 2017.
- [18] A. Jimenez, L. Sánchez-González, S. Desobry, A. Chiralt, E. A. Tehrany. Influence of nanoliposomes incorporation on properties of film forming dispersions and films based on corn starch and sodium caseinate. *Food Hydrocolloids*, 35, 159–169, 2014.
- [19] A. A. Ahmet, V. Ilberg. Effect of different polyol-based plasticizers on thermal properties of polyvinyl alcohol: Starch blends films. *Carbohydrate Polymers*, 136, 441–448, 2016.
- [20] S. Salmieri, F. Islam, R. A. Khan, F. M. Hossain, H. M. Ibrahim, C. Miao. Antimicrobial nanocomposite films made of poly (lactic acid)–cellulose nanocrystals (PLA–CNC) in food applications-Part B: Effect of oregano essential oil release on the inactivation of *Listeria monocytogenes* in mixed vegetables. *Cellulose*, 21(6), 4271–4285, 2014.
- [21] F. E. Silva, M. C. Leal, B. D. M. Batista, K. D. A. Fernandes. PVA/ polysaccharides blended films: Mechanical properties. *Journal of Materials*. pp. 1–5, 2013.
- [22] Y.P. Chang, A.A. Karim, C.C. Seow. Interactive plasticizing- antiplasticizing effects of water and glycerol on the tensile properties of tapioca starch films. *Food Hydrocolloids*, 20, 1–8, 2006.
- [23] D. Lourdin, H. Bizot, P. Colonna. Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. *Polymer*, 38(21), 1047 – 1053, 1997.
- [24] I. Arvanitoyannis, & C.G. Biliaderis, Physical properties of polyol-plasticized edible films made from sodium caseinate and soluble starch blends. *Food Chemistry*, 62, 333–342. Arvanitoyannis, I., Nakayama, A. & Aiba, S. (1998). Edible films made from hydroxypropyl starch and gelatin and plasticized by polyols and water. *Carbohydrate Polymer*, 36, 105–119, 1998.
- [25] D.W. Van Krevelen. *Properties of Polymers*, Amsterdam: Elsevier 3rd ed, pp. 189-225, 1990.