



Original Article

Effect of starch types on properties of biodegradable polymer based on thermoplastic starch process by injection molding technique

Yossathorn Tanetrungroj¹ and Jutarat Prachayawarakorn^{1,2*}

¹ Department of Chemistry,

² Advanced Materials Research Unit, Faculty of Science,
King Mongkut's Institute of Technology Ladkrabang, Lat Krabang, Bangkok, 10520 Thailand.

Received: 28 August 2014; Accepted: 18 January 2015

Abstract

In this study effects of different starch types on the properties of biodegradable polymer based on thermoplastic starch (TPS) were investigated. Different types of starch containing different contents of amylose and amylopectin were used, i.e. cassava starch, mungbean starch, and arrowroot starch. The TPS polymers were compounded and shaped using an internal mixer and an injection molding machine, respectively. It was found that the amount of amylose and amylopectin contents on native starch influence the properties of the TPS polymer. A high amylose starch of TPMS led to higher strength, hardness, degree of crystallization than the high amylopectin starch of TPCS. In addition, function group analysis by Fourier transforms infrared spectrophotometer, water absorption, and biodegradation by soil burial test were also examined.

Keywords: arrowroot starch, biodegradable polymer, injection molding, mungbean starch, thermoplastic starch

1. Introduction

Due to environmental considerations, starch is now an attracting raw material in the production of biodegradable materials because of its abundance, low price, and availability. Starch has a granular structure, which is built by two main carbohydrate polymers, the linear amylose and the highly branched amylopectin. Both high molecular weight polymers are formed by (1,4)- α -D-glucopyranosyl repeating units. Amylose is essentially linear, whereas, amylopectin is highly branched with (1,6) glucosidic branching points occurring every 20–25 glucose units. The short chains of amylopectin are thought to be arranged as double helices, in clusters of semi-crystalline character (Leszczynski, 2004). Generally, starch sources have been shown differences in amylose and amylopectin content.

Starch can be processed under the action of both high temperature and shearing action and this is called thermoplastic starch (TPS) (Stepito, 2000). TPS from various sources has been studied, including corn and wheat starch (Naguleswaran *et al.*, 2014) potato starch (Guo *et al.*, 2001) maize starch or wheat starch (Schirmer *et al.*, 2013). Traditionally, the difference in water content and the ratio of amylose to amylopectin of various native starches have been attributed to the physical and barrier properties of thermoplastic starch (Zhou *et al.*, 2008). Many researchers have demonstrated on the influence of various starches on the mechanical properties and biodegradability characteristics of biodegradable plastics produced mainly by extrusion, compression molding, and casting techniques (Soest *et al.*, 1996; Stepito, 2003; Rosa *et al.*, 2007; Altskar *et al.*, 2008; Lopez *et al.*, 2014).

In addition, there are many investigations of the effects of starch type or amylose/amylopectin ratio on the final properties of starch-based materials. It was reported that a blend of TPS from wheat starch (0–22% w/w) with low-den-

* Corresponding author.
Email address: ksjutara@kmitl.ac.th

sity polyethylene (LDPE) exhibited a decrease in the Young's modulus (Pierre *et al.*, 1997). Moreover, high amylose maize starch and potato starch were reported to produce strong films, probably due to amylose crystallization (Soest *et al.*, 1996; Durejaa *et al.*, 2001; Cano *et al.*, 2014). The starch films prepared from the low amylose corn starches also showed low degree of crystallinity (García *et al.*, 2000).

However, the effect of starch types on properties of biopolymers based on thermoplastic starch prepared from arrowroot starch (TPAS), cassava starch (TPCS) and mungbean starch (TPMS) and processed by an injection molding technique has not yet been reported. Arrowroot is a powdery product made from the arrowroot plant, a starchy tropical root. It is white and powdery just like cornstarch. Arrowroot starch also makes an excellent substitute for talcum powder in cosmetics and it was once used in the several industries (Jyothi and Sheriff, 2009). Mungbean has been used as raw material for producing starch noodle. Mungbean starch is admired as the best starch due to its high amylose content, leading to strong gel strength. It is consumed mainly for its rich protein content (24%) but carbohydrate (62–63%) is its major component (Ohwada *et al.*, 2003). Besides, cassava starch is one of the most staple foods in the developing world. It contains significant amounts of rich in starch and poor amounts of other nutrients. It is an abundant, purity, clearness of its paste, and cheap agricultural source of starch and flour production. Moreover, it can be used to blend with other expensive synthesis polymers required to producing biodegradable polymers (Satyanarayana *et al.*, 2009).

The objective of the present study was to evaluate the effect of starch types with different amylose and amylopectin contents on properties of biodegradable polymer prepared from the different types of selected thermoplastic starch, i.e. TPAS, TPCS, and TPMS and processed by injection molding technique. The polymers were, then, characterized by function group analysis by FTIR and crystallinity tested by X-ray diffraction, as well as morphology, water absorption, tensile properties, and biodegradation properties.

2. Materials and Methods

2.1 Materials

Arrowroot starch was purchased from Chaopraya Phuchrai 1999 Co., Ltd. (Kamphaengphet Thailand) and contained 26.5 wt% amylose and 73.5 wt% amylopectin. Mungbean starch was obtained from Sittihinan Co., Ltd. (Bangkok, Thailand) containing approximately 37.9 wt% amylose and 62.1 wt% amylopectin. Cassava starch was obtained from Thaitam (Chonburi, Thailand), composed of approximately 16.4 wt% amylose and 83.6 wt% amylopectin. The chemical compositions of arrowroot, mungbean and cassava starches were shown in Table 1 (Erdman, 1986; Habibullah *et al.*, 2003; Pushpadass *et al.*, 2010). Glycerol (plasticizer) was purchased from Lab System Co., Ltd.

(Bangkok, Thailand). Low-density polyethylene (LDPE, DNDV-0405 R) with MFI of 32 g/10 min. was obtained from Global Connections Public Co., Ltd. (Samuthprakarn, Thailand). Maleic anhydride-grafted-polyethylene (MAPE, MB100D) compatibilizer was obtained from Chemical innovation Co., Ltd. (Bangkok, Thailand).

2.2 Sample preparation

Each kind of starch, i.e. arrowroot starch, cassava starch or mungbean starch was pre-mixed with glycerol (plasticizer) in a closed container at room temperature and kept overnight. The weight ratio of starch and glycerol was maintained at 70:30. The TPS polymers were firstly compounded with LDPE and MAPE compatibilizer. The weight ratio of the TPCS and LDPE was kept at 80:20 and the MAPE content was maintained at 5% by weight of the LDPE. The minor content of LDPE polymer was added in order to increase flowability during injection process. Different TPS polymers were compounded using an internal mixer (Lab-Tech Engineering, Bangkok, Thailand) at the temperature of 140°C at the screw rotation speed of 40 rpm for 12 min in order to obtain a homogeneous sample and the specimens were then shaped by the injection molding technique using injection pressure and injection flow speed at 30 bar and 50 rpm, respectively. The injection temperature was varied from 150-170°C (from feed zone to die end).

2.3 Fourier transforms infrared spectrophotometer

Fourier transforms infrared (FTIR) spectrum of each sample was recorded with a Spectrum 2000 GX spectrometer (Perkin Elmer, U.S.A.) using KBr disk technique with a resolution of 4 cm⁻¹ in a spectral range of 600-4,000 cm⁻¹ using 16 scans per sample.

2.4 X-ray diffraction

X-ray diffraction (XRD) diffraction measurements were carried out using a D8 Advance X-ray diffractometer (Bruker, Madison, U.S.A.) with CuK α radiation (wavelength 0.1542 nm) operating at 40 kV and 35 mA. The scattering

Table 1. Chemical compositions of different starches.

Chemical composition (%)	Cassava starch	Arrowroot starch	Mungbean starch
Moisture	0.5	8.6	9.3
Carbohydrate	85.0	94.4	82.3
Amylose	16.4	19.9	37.9
Amylopectin	83.6	75.4	62.1
Protein	0.3	4.2	23.3
Fat	1.1	0.2	1.9
Ash	0.2	2.4	3.0
Others	0.6	0.5	0.9

angle (2θ , with θ being the Bragg angle) covered the range from 3° to 60° with a step size of 0.02° and a sampling interval of 10 s. Percentage crystallinity of each sample was determined by following equation

$$\text{Crystallinity (\%)} = A_c / (A_c + A_a) \times 100 \quad (1)$$

where A_c and A_a were the area of crystallinity region and the area of amorphous region of a sample determined from a diffractogram, respectively.

2.5 Morphology

A JEOL-6400 scanning electron microscope (Tokyo, Japan) was employed to study the morphology of a sample. Each tested sample was sputter-coated with a thin layer of gold to prevent electrical charge during observation and a sample was immersed into liquid nitrogen before being fractured.

2.6 Mechanical property

Mechanical tests were evaluated according to ASTM D-638 at the temperature of $23 \pm 1^\circ\text{C}$ and relative humidity of $60 \pm 5\%$. The starch mixtures with different starch type as prepared above were stored in a desiccator containing a saturated solution of ammonium nitrate for one day to equilibrate the moisture content of $60 \pm 5\%$ before measurements. A mechanical measurement of each dumbbell shaped specimen was carried out using a Universal Testing Machine (Lloyd Instrument, LR 5K, West Sussex, UK) with a 100 N load and the crosshead speed was maintained at 40 mm/min. It should be noted that the mechanical property results were obtained by averaging the measurement results of ten independent specimens. Hardness test was conducted according to ASTM D-2240 using Shore A hardness durometer (Intro enterprise, Thailand). The hardness values were recorded from ten different measurements for each sample. In addition, impact test was carried out using Izod Impact tester (Yazuda 199311, Japan) and was also measured ten independent specimens according to ASTM D-256.

2.7 Water absorption

Water absorption test was carried out according to ASTM D-570. Samples were dried at 105°C for 3 hours and then immersed in distilled water. The amount of water absorbed by a sample was determined daily for 30 days. The percentage of water absorption was calculated as followed:

$$\text{Water absorption} = (W_2 - W_1) / W_1 \times 100 \quad (2)$$

where W_2 and W_1 were the wet weight and the dried weight of a sample, respectively.

2.8 Biodegradability by soil burial test

A dumbbell sample was buried at approximately 10 cm under the soil surface. The water content of the soil was maintained in the range of 30-40% and the test was carried out for 0, 4, 8, and 12 weeks. After that, a tensile test of a soil-buried sample was conducted in comparison with an original sample.

3. Results and Discussion

3.1 IR Spectroscopy

FT-IR is a powerful technique for identifying types of chemical bonds of polymers. FTIR spectra of different TPS polymers are shown in Figure 1. The broad band appeared at $3,250\text{-}3,500\text{ cm}^{-1}$ was attributed to O-H stretching. The peak in the range of $1,070\text{-}1,275\text{ cm}^{-1}$ was characteristic for C-O-C stretching. The bands in the range of $1,000\text{-}1,200\text{ cm}^{-1}$ was assigned for C-O-H stretching and $1,641\text{-}1,646\text{ cm}^{-1}$ was attributed to bounded water presented in starch. These peak positions were due to the TPS component (Shi *et al.*, 2007). Other vibrational bands from LDPE component were found in the wavenumber range of $2,800\text{-}3,000\text{ cm}^{-1}$ and were assigned from C-H asymmetric stretching of $-\text{CH}_2-$. The band in the range of $1,450\text{-}1,475\text{ cm}^{-1}$ was characteristic for $-\text{CH}_2-$ deformation. Moreover, the wavenumber in the range of $855\text{-}931\text{ cm}^{-1}$ were designed for C-H bending and the band at 718 cm^{-1} was owing to CH_2 -rocking from of LDPE and MAPE component (Bower, 1996). It was found from Figure 1 that all the TPS polymers showed the same IR peak positions and no distinct new peak position could be observed since all different TPS polymers consists of the same chemical structure of polysaccharides.

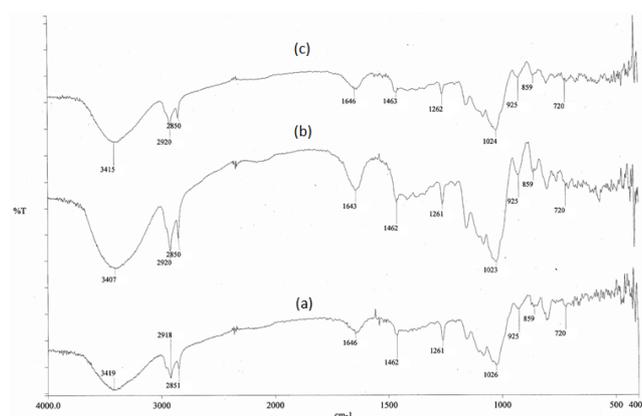


Figure 1. IR spectra of TPS polymers by different types of TPS, (a) TPAS, (b) TPCS, and (c) TPMS.

3.2 X-ray Diffraction

X-ray diffraction technique can be used to identify crystal structure and regular molecular arrangement of starch. X-ray diffraction patterns of different TPS polymers are shown in Figure 2. The peak at 2θ of 19.6° corresponded to the V_h type pattern of starch due to the amylose-lipid complex formation forming by the effective starch gelatinization (Hartel, 2001). Besides, the main peaks at 2θ of 21.4° , 23.7° , and 36.0° represented the orthorhombic crystal structure of LDPE component (Pereira *et al.*, 1997). It should be noted that the crystallinity of different TPS polymers mainly resulted from the LDPE component since the LDPE component caused the major peak intensity in the diffractograms, even though, the LDPE components was introduced into the TPS polymers in very small proportion. Moreover, it was found that no significant difference in XRD patterns could be observed for the different TPS polymers. This could be due to the similarity of the composition of the different TPS polymers which was also consisted of starch and LDPE, leading to the similar XRD peak patterns.

Nevertheless, the calculated percentage crystallinity values of different TPS polymers, obtained from the diffractograms were approximately 36.2%, 37.4%, and 38.7% for the TPCS, TPAS, and TPMS polymers, respectively. It can be seen that the highest percentage crystallinity value was found in the TPMS polymer and the percentage crystallinity value of the TPAS polymer was higher than that of the TPCS polymer. The differences in crystallinity values may also be attributed to different contents of amylose and amylopectin of native starch sources as shown by the chemical compositions of different starches in Table 1.

From Table 1, it can be seen that the mungbean starch exhibited the highest amylose content. The higher content of amylose led to the higher degree of crystallization. These can be explained that the higher content of linear amylose molecules causes the effective crystallization but amylopectin does not crystallize due to its very highly branched structure and results in the formation of a less firm gel (Marie and Imada, 2004).

3.3 Morphology

Morphology of different TPS polymers examined by SEM technique is presented in Figure 3. The TPMS polymer, Figure 3(a), showed the smoothest surface without phase separation but the TPCS, Figure 3(b), and TPAS polymers, Figure 3(c), showed clearly rough surfaces. This could be due to the highest amylose content and elasticity property of the mungbean starch. Amylose content is the most important factor for the resulting of rheological and morphology. The high amylose starch, i.e. mungbean starch, showed smooth surface and better rheological property than the low amylose starches, i.e. cassava and arrowroot starches. This might be due to a comparatively less branching chains and a less compact arrangement of linear short chains. It agrees

with the findings by Tan *et al.* (2006) that the mungbean starch showed smoother than sweet potato starch due to the higher amylose content of the mungbean starch.

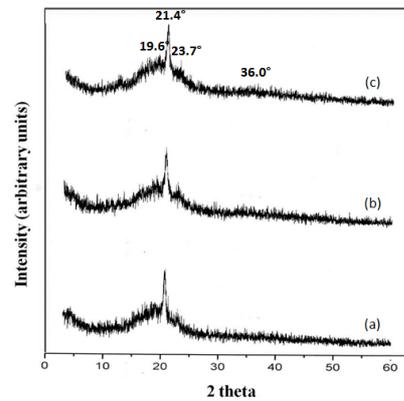


Figure 2. X-ray diffraction patterns of different TPS polymers (a) TPAS, (b) TPCS, and (c) TPMS.

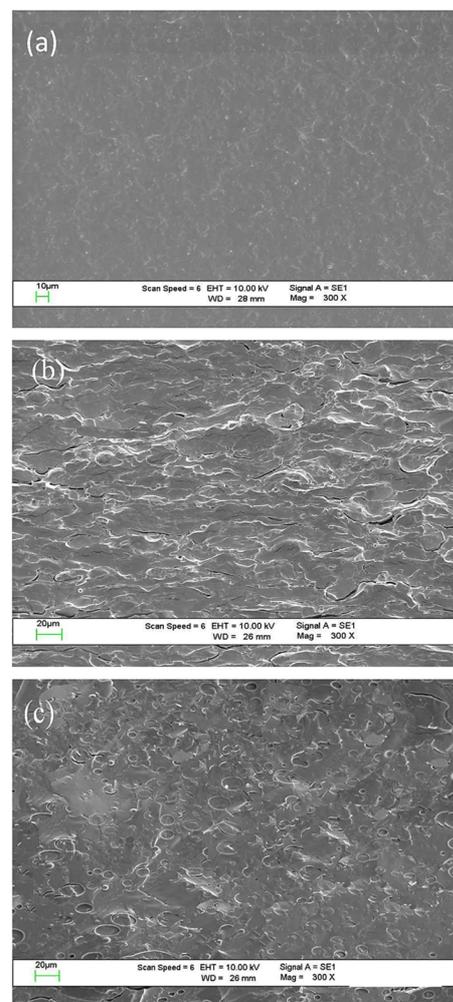


Figure 3. SEM micrographs of fracture surfaces of different TPS polymers (a) TPMS, (b) TPCS, and (c) TPAS.

3.4 Water absorption

Generally, TPS could absorb some amount of water from the environmental humidity. The water absorption behavior of different TPS polymers is represented in Figure 4. It can be seen that all TPS polymers showed the rapid increase of water absorption during the first day of testing. After that, the percentage water absorption tended to increase slowly and reached its maximum. It should be noted that the TPMS polymer showed the rapidly increase of water absorption during the three days of testing. After that, the TPMS polymer could not absorb water because the TPMS specimen degraded and cracked during the water absorption test. It could be seen from Figure 4 that the lowest percentage of absorption was found in the TPMS polymer. On the other hand, the highest percentage of water absorption was present in the TPAS polymer.

From Table 1, the mungbean starch showed the lowest amylopectin content, but the cassava starch exhibited the highest amylopectin content. The TPCS polymer did not show the highest water absorption property as expected. It could be explained by considering the carbohydrate content in Table 1. The arrowroot starch consists of higher carbohydrate content when compared with the cassava starch. Combined with the hydrophilic characteristics of carbohydrate this could lead to higher percentage of water absorption. Moreover, the lowest water absorption of the TPMS polymer could be due to lowest carbohydrate content (Table 1) and also the highest crystallization as confirmed by XRD.

3.5 Mechanical properties

The amount of amylose and amylopectin molecules of the various starch sources (Table 1) also influences the mechanical properties of TPS polymers. It can be observed from Figure 5 that the highest stress at maximal load, Young's modulus, and hardness, the lowest strain at maximal load, and impact strength were found in the TPMS polymer, result-

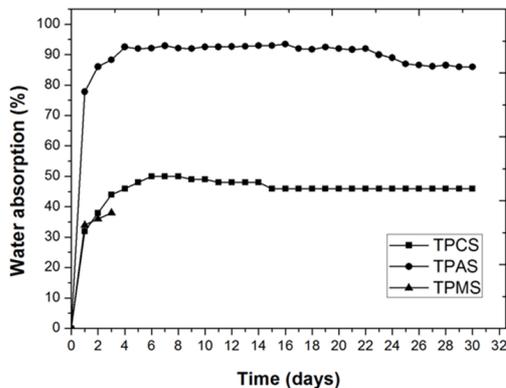


Figure 4. Relationship between water absorption and immersion time of different TPS polymers.

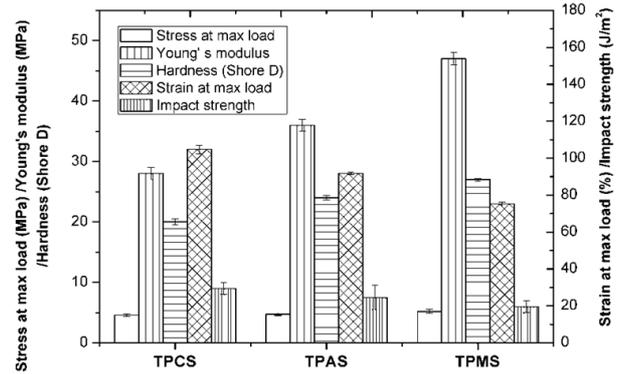
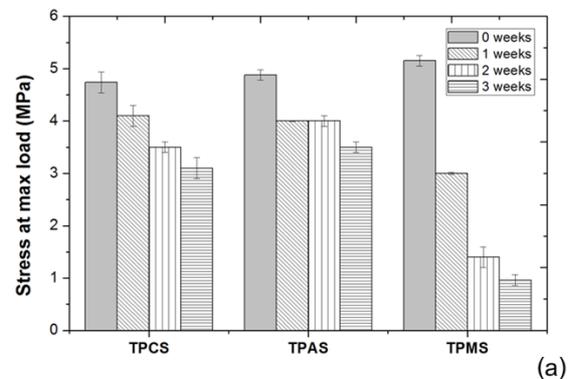
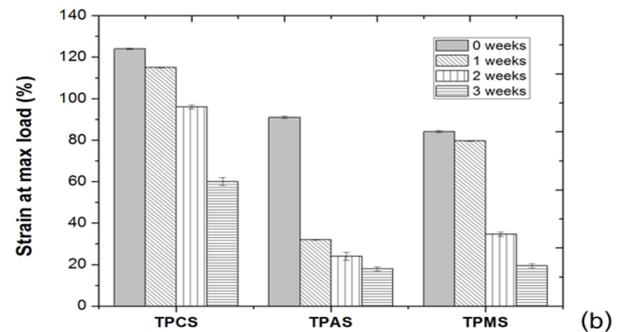


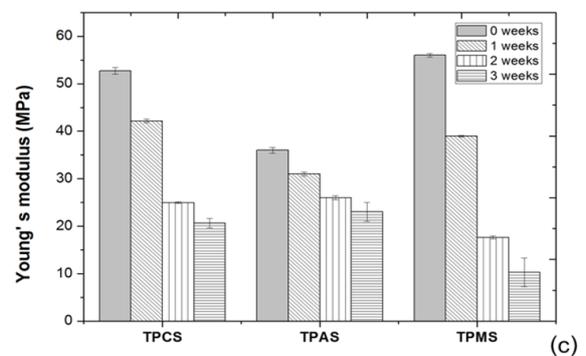
Figure 5 Mechanical properties of different TPS polymers, (a) stress at maximum load and Young's modulus, and (b) strain at maximum load and hardness.



(a)



(b)



(c)

Figure 6. Mechanical properties of the different TPS polymers after soil buried test for 0, 4, 8, and 12 weeks.

ing from the highest amylose content and lowest amylopectin content of the mungbean starch. Additionally, the TPAS polymer presented higher stress at maximal load, Young's modulus and hardness, but lower strain at maximal load and impact strength when compared to TPCS polymer. High amylose starch, generally, presents higher stiffness and hardness than high amylopectin starch due to the comparatively less branching structures (Marie and Imada, 2004). The results are also confirmed by the good phase morphology (Figure 3) and higher crystallinity (Figure 2). Similar observations were reported for high amylose rice film that was stiffer, less elastic than those of low amylose rice film, prepared from casting method (Cano *et al.*, 2014).

3.6 Biodegradable property

Biodegradable properties of different TPS polymers determined by soil buried tests for 0, 4, 8, and 12 weeks are presented in Figure 6. It was found that the stress at maximum load, Young's modulus and strain at maximum load of all TPS polymers significantly decreased after the biodegradation test. The results of water absorption properties (Figure 4) also related to the biodegradable property. The TPS polymers could absorb water from the soil TPS component, leading to the biodegradation of TPS polymer by the microorganisms existed in soil. The most rapid degradation was found in the TPMS polymer since the mungbean starch consists of high protein content (Table 1) that can be easily decomposed (Diaz, 2008).

4. Conclusion

The influence of starch types on properties of biodegradable polymers based on TPS, processed by injection molding technique was examined. It was found that properties of different TPS polymers depend on the amylose and amylopectin contents including carbohydrate contents. The high amylose polymer of the TPMS polymer presented higher degree of crystallization and mechanical properties than low amylose polymer of the TPCS polymer. Besides, the high amylose polymer of the TPMS polymer presented the lowest water absorption. The quickest biodegradation was also found in the TPMS polymer. Moreover, the TPAS polymer presented a higher degree of crystallinity and mechanical properties including faster degradable property than those of the TPCS polymer.

Acknowledgements

The authors express their sincere appreciation to the KMITL Research Fund for supporting the study financially.

References

Altskar, A., Andersson, R., Boldizar, A., Koch, K., Stading, M., Rigdahl, M. and Thunwall, M. 2008. Some effects of

processing on the molecular structure and morphology of thermoplastic starch. *Carbohydrate Polymers*. 71, 591–597.

Bower, D.I. and Maddams, W.F. 1996. *The Vibrational Spectroscopy of Polymers*. 2nd Edition, Cambridge University Press, Cambridge, U.K.

Cano, A., Jimenez, A., Chafer, M., Gonzalez, C. and Chiralt, A. 2014. Effect of amylose:amylopectin ratio and rice bran addition on starch films properties. *Carbohydrate Polymers*. 111, 543-555.

Diaz, E. 2008. *Microbial Biodegradation: Genomics and Molecular Biology*, Caister Academic Press, ISBN 1-904455-17-4.

Dureja, H., Khatak, S., Khatak, M. and Kalra, M. 2011. Amylose Rich Starch as an Aqueous Based Pharmaceutical Coating Material – Review. *International Journal of Pharmaceutical Sciences and Drug Research*. 3(1), 8-12.

Erdman, M.D. 1986. Starch from arrowroot starch Grown at Tifton. *Cereal chemistry* 63, 277-279.

García, M.A., Martino, M.N. and Zaritzky, N.Z. 2000. Microstructural characterization of plasticized starch-based films. *Starch*. 52, 118–24.

Guo, L., Liang, Q. and Du, X. 2001. Effects of molecular characteristics of tea polysaccharide in green tea on glass transitions of potato amylose, amylopectin and their mixtures. *Food Hydrocolloids*. 25, 486-494.

Habibullah, Mohammad, A. and Hamidullah, S. Proximate and mineral composition of mungbean. *Journal of Agriculture and Food chemistry*. 2007. 23, 465-466.

Hartel, R.W. 2001. *Crystallization in Foods*. Aspen Publication, Maryland, U.S.A.

Jyothi, A.N. and Sheriff, J.T. 2009. Physical and Functional Properties of Arrowroot Starch Extrudates. *Journal of Food Science*. 74, 97-104.

Leszczynski, W. 2004. Resistant starch –classification, structure, production, *Polish Journal of Food and Nutrition Sciences*. 13, 37-50.

Lopez, O., Garcia, M.A., Villar, M.A., Gentili, A., Rodriguez, M.S. and Albertengo, L. 2014. Thermo-compression of biodegradable thermoplastic corn starch films containing chitin and chitosan. *LWT - Food Science and Technology*. 57, 106-115.

Naguleswaran, S., Vasanthan, T. and Hoover, R. 2014. Amylolysis of amylopectin and amylose isolated from wheat, triticale, corn and barley starches. *Food Hydrocolloids*. 35, 686-693.

Marie, A. and Imada, F. 2004. Starch retrogradation. *Biotechnology and Genetic Engineering reviews*. 21, 215-225.

Ohwada, N., Ishibashi, K., Hironaka, K. and Yamamoto, K. 2003. Physicochemical properties of mung bean starch. *Journal Apply Glycoscience*. 50, 481–485.

Pereira, R.A., Mano, E.B., Dias, M.L. and Acordi, E.B. 1997. Comparative study on the lamellar crystalstructure of high and low density polyethylenes. *Polymer*. 38, 707-714.

- Pierre, N., Favis, B.D., Ramsay, B.A., Ramsay, J.A. and Verhoogt, H. 1997. Processing and characterization of thermoplastic starch/polyethylene blends. *Polymer*. 38, 647–655.
- Pushpadass, H.A., Bhandari, P. and Hanna, M.A. 2010. Effects of LDPE and glycerol contents and compounding on the microstructure and properties of starch composite films. *Carbohydrate Polymers*. 82, 1082–1089.
- Rosa, D.S., Guedes, C.G. and Carvalho, C.L. 2007. Processing and thermal, mechanical and morphological characterization of post-consumer polyolefins/thermoplastic starch blends, *Journal of Materials Science*. 42, 551–557.
- Satyanarayana, K.G., Carbajal, A.G. and Wypych, F. 2009. Biodegradable composites based on lignocellulosic fibers. An overview. *Progress in Polymer Science*. 34 (9), 982–1021.
- Schirmer, M., Hochstotter, A., Jekle, M., Arendt, E. and Becker, T. 2013. Physicochemical and morphological characterization of different starches with variable amylose/amylopectin ratio. *Food Hydrocolloids*. 32, 52–63.
- Shi, R., Liu, Q., Ding, T., Han, Y., Zhang, L. and Tian, C.D. 2007. Ageing of soft thermoplastic starch with high glycerol content. *Journal of Applied Polymer Science*. 103, 574–86.
- Stepito, R.F.T. 2000. Thermoplastic starch. *Macromolecular Symposia*. 152, 73–82.
- Stepito, R.F.T. 2003. The processing of starch as a thermoplastic. *Macromolecular Symposia*. 201, 203–212.
- Soest, J.J.G., Benes, K. and Wit, D. 1996. The influence of starch molecular mass on the properties of extruded thermoplastic starch. *Polymer*. 37, 3543–3552.
- Soest, J.J.G., Hulleman, S.H.D., Dewit, D. and Vliegthart, J.F.G. 1996. Change in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystallinity. *Carbohydrate Polymers*. 29, 225–232.
- Tan, H.Z., Gu, W.Y., Zhou, J.P., Wu, W.G. and Xie, Y.L. 2006. Comparative Study on the Starch Noodle Structure of Sweet Potato and Mung Bean. *Journal of Food Science*. 71, 447–455.
- Zhou, Y.B., Wang, D.F., Zhang, L. and Du, X.F. 2008. Effect of polysaccharides on gelatinization and retrogradation of wheat starch. *Food Hydrocolloids*. 22, 505–512.