Effects of hectorite loading on tear properties and biodegradability of thermoplastic starch films

Ismail Ibrahim1,2, Azlin Fazlina Osman1,2, Sinar Arcuria Adnan1,2, Lai Di Sheng3 and Nazril Haq4

1Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia.
2Biomedical and Nanotechnology Research Group, Center of Excellence Geopolymer and Green Technology (CEGeoGTech), Universiti Malaysia Perlis, 01000 Kangar, Perlis, Malaysia.
3Departments of pharmacuetic, College of Pharmacy, King Saud University, Riyadh 11451, P.O. Box. 2457, Saudi Arabia.

Abstract. Development of bio-based polymers can reduce human dependence on fossil fuel and move to a sustainable material resource. In this work, thermoplastic starch (TPS) films were produced by plasticization process, in which the crystalline structure of the starch granules was destroyed and reformed by water and glycerine through mechanical stirring and heating process. Hectorite was employed as filler to reinforce the TPS films. The hectorite was subjected to ultrasonication process for reducing the size and aggregation of particles. The ultrasonicated hectorite was added into the TPS solution to produce the TPS/ Hectorite bio-composite by film casting method. The TPS films with hectorite loading in the range of 1% to 5% were prepared. The morphology, tear strength and soil biodegradability of the TPS/hectorite bio-composite films were studied by altering the loading of hectorite incorporated into the TPS films. Results showed that the TPS/hectorite bio-composite films have higher tear strength compared to the pure TPS films. The tear strength of the bio-composite films slightly increased with hectorite content 1% and 2%. However, as the filler loading increased to 3%, there was a drastic increase of the tear strength. The maximum tear strength value was achieved by the TPS film when 4% hectorite filler was employed. The TPS/4% hectorite (ultrasonicated) has the lowest rate of soil biodegradation due to its lower moisture uptake and greatest interface interaction between starch and hectorite, inhibiting diffusion of bacteria into the films.

1 Introduction

The consumption of synthetic plastics for daily uses are raising year by year. After service life, the solid wastes of plastic materials create a significant problem for the environment [1]. In order to preserve the environment, bioplastics are promising option for saving energy and reducing the plastic wastes [2]. In this context, many researchers are developing bio-composites from renewable resources such as bio-polymers and cellulosic materials [3]. Bio-plastics industry is now becoming attractive worldwide due to the fast-growing aimed toward the use of renewable resource-based plastics and sustainable production [2]. The bioplastic market currently represents about 1% of the amount of plastic produced annually [2]. Polyhydroxyalkanoate, polylactic acid and starch blends are some of the most widely used polymers for the industrial production of biodegradable plastics and bio-based plastics [4]. There are special regulations to dispose of recycling polymers and plastic wastes [5]. The outreach of biodegradable materials such as starch-based films and packaging has brought an opportunity to decrease the affiliation with petroleum-derived materials [6].

At various laboratories all over the world, the research on biodegradable plastics based on starch began in the 1970s and continues today. Technologies have been developed for injection-molded plastics and production of extrusion films containing 50% or more of starch [7]. Starch satisfies the requirements of minimum interference with melt properties, adequate thermal stability and disturbance of product quality [8]. Starch is fully biodegradable, abundant, renewable, and inexpensive natural raw material which can be utilized as a component in plastic formulations [9]. Starch can be turned into thermoplastic starch film that is fully biodegradable and can be combined with synthetic polymers to enhance its biodegradability. When starch is consumed by microorganisms, the biodegradability of synthetic polymer will increase and under a rapid enzymatic hydrolysis, starch will be degraded leading to a void containing matrix.

Consequently, this will promote the biodegradation of synthetic polymer and reduce the mechanical properties of the plastics due to the increased surface area available for interaction with microorganisms [10]. The usage of starch as bioplastic packaging in Europe has been increased drastically from 2005 to 2015 according to EuBP market data [11]. As the biocomposite properties such as: mechanical strength, biodegradability, stability, transparency, water and gases vapor barrier have been improved drastically, the application of biocomposite in food packaging has increased. For a food
packaging material, the film must be able to protect the food from the contaminations, maintain the freshness of the food so that the food is safe to be consumed by the consumer. Starch is the best option for this situation [12].

The hectorite is a type of clay/silicate filler that can be added into the polymeric matrix to improve its properties such as mechanical properties and water/vapor permeability resistance [13]. Hectorite is a trioctahedral smectite meanwhile montmorillonite is dioctahedral smectite [14]. Hectorite is formed by modification of basalts and volcanic group at low temperature and pressure (<100°C and 1bar). High surface area of particle and high thermal stability of hectorite has made it become valuable in many applications such as absorbents and nano-composites [15-16]. Hectorite usually has similar structure with montmorillonite but have more negative charges and fewer impurities. Laponite which is the trade name of hectorite are synthetic clays with composition Na0.7(Mg,5Li0.4) Si0.5O(Si0.5O4)O(OH)3]. Compare to natural clay, the impurities of hectorite is much lower and has been well applied in many applications such as polymer film, house hold, hair product etc.[17].

2 Methodology

Bio-composite films produced in this work have two main components: thermoplastic starch and clay based filler, which was hectorite. Thermoplastic starch was prepared by mixing the starch (corn) and plasticizer (glycerol and water) together. Meanwhile, the reinforcement filler was prepared by ultrasonicating the hectorite in water medium to obtain more loosely packed layered silicates or platelets. Sodium bicarbonate was added as thickener for the bio-composite. The materials above mainly were manufactured by Sigma Aldrich and HmbG Chemicals and supplied by Euroscience Sdn.Bhd.

2.1 Materials

2.1.1 Starch

The starch contains approximately 73% amylopectin and 27% amylose and it was extracted from corn, provided by Sigma-Aldrich, code number S4126 in 2 kilogram poly bottle packing.

2.1.2 Hectorite

Hectorite which is commercially known as Lucentite SWN is a unmodified nanoclay that supplied by Kobo Products Inc. (New Jersey, USA). Its individual platelet’s length is around 25nm, while its thickness is ~1nm. It is used as filler in the TPS bio-composite in pristine and ultrasonicated form.

2.1.3 Glycerol

The glycerol used as plasticizer was supplied by the HmbG Chemicals with the code, CO347-91552409, supplied in 2.5L which concentration minimum of 99.5%.

2.1.4 Sodium bicarbonate

Sodium bicarbonate contain assay, ph (5% solution), water insoluble matter, chloride (Cl), nitrogen compounds, phosphate, sulphate, iron and lead, supplied by HmbG Chemicals (C0735-2134330) in 1kg package. It acted as the thickener.

2.2 Sample Preparation

2.2.1 Plasticization of starch to thermoplastic starch

5 grams of corn starch was added with 100ml water into 250ml beaker. After that, 2grams of glycerol was added into the starch solution as the plasticizer for the starch. After that, the mixture was keep stirring in water bath at temperature 75-85°C by using magnetic stirrer (500rpm) for 45 minutes until a gel form of starch was obtained.

2.2.2 Ultrasonication of hectorite

Hectorite powder was dispersed into distilled water (part from TPS) in the ratio of 1:100, in which its concentration was 1%, 2%, 3%, 4% and 5%. The hectorite was isolated for 120 minutes, under 20% amplitude, 20 second pulse on and 10 seconds pulse off by using Branson Digital Ultrasonic Distruptor, Model 450D.
2.2.3 Preparation of thermoplastic starch/hectorite bio-composite

The suspension of Hectorite was added into the TPS solution and continuously stirred at 75-85°C. After that, 0.5 grams of sodium bicarbonate was added into 30ml water in 50ml beaker and then added into the TPS mixture and continuously stirred for about 5 minutes. Then, the mixture was poured into Teflon-coated mold and placed in the oven at 45°C for 24 hours for drying. The processes for making film samples were repeated for hectorite without ultrasonic treatment for 2% and 4% concentration. The formulation of TPS/hectorite bio-composite films is shown in Table 1.

Table 1. The formulation of thermoplastic starch and hectorite for different loading of filler concentration

| Thermoplastic starch (wt%) | Hectoreite with ultrasonic treatment for 120 minutes (wt%) | Hectoreite without ultrasonic treatment (wt%) |
|----------------------------|----------------------------------------------------------|---------------------------------------------|
| 100                        | -                                                        | -                                           |
| 99                         | 1                                                        | -                                           |
| 98                         | 2                                                        | 2                                           |
| 97                         | 3                                                        | -                                           |
| 96                         | 4                                                        | 4                                           |
| 95                         | 5                                                        | -                                           |

2.3 Testing and Characterization of Samples

2.3.1 Tear test

The tear strength of the samples was measured by using Instron Machine, according to ISO 34 – 1:1994 Method B (a). The test runs at crosshead speed of 500 mm/min and angle test specimen (type B) without a nick. The average tear strength values were determined for every sample.

2.3.2 Biodegradability test (soil burial test)

The soil burial test was carried out according to EN ISO 846: 1997. The film samples were cut into 5cm x 1.5cm size and buried into soil for duration of 1 month. The soil was sprayed with water at certain time. The degradation rate was calculated by the weight loss rate of films at regular time. The samples were collected from soil and dirt on the films was removed. Next, the samples were dried in the oven for 24 hours at 50°C, then weighed. The equation of the weight loss of films is:

\[ \text{Weight loss (\%)} = \frac{(W_i - W_d)}{100} \]

Where:
- \( W_i \) = initial weight of dry samples
- \( W_d \) = weight of sample recovered from soil

2.3.3 Scanning electron microscope (SEM)

The fractured surface of the starch/hectorite bio-composite samples were analyzed by using scanning SEM (JEOL JSM-6460LA) to analyze the morphology of the hectorite (with and without ultrasonic treatment) in the TPS matrix. Before under scanning of SEM, the samples were coated with platinum using JFC-1600 Auto Fine Coater (JEOL Ltd., Japan). The surface morphology of the fractured samples was taken at magnification of 500X and 1000X magnifications.

3 Results and Discussions

3.1 Tear test

Table 2 and Fig. 1 show the tear strength values of the TPS and TPS/hectorite bio-composites in which the films were cut into trouser shape according to ISO 34- 1:1994 Method B (a). From the obtained results, it can be realized that the TPS/hectorite films have higher tear strength compared to the pure TPS films (0.499MPa). The tear strength of the TPS/hectorite films has slightly increased with hectorite content from 1% to 2% which were 0.758 MPa and 0.970 MPa, respectively. When the hectorite loading was increased to 3%, there was a drastic increase of the tear strength from 0.970 MPa to 2.396 MPa. However, the TPS/hectorite films experienced a slight decrement of tear strength when the hectorite loading increased to 4% (2.064 MPa). The TPS/hectorite film with 5% filler showed the highest tear strength (2.987MPa) among all the films.
Apparently, hectorite is an effective filler to improve the tear strength of the TPS film when added in the appropriate amount and if the clay filler is well dispersed in the TPS matrix. Gustavo, et al. [18] showed that, when the nanoclay dispersed well (exfoliated or intercalated) in the polymer matrix, the clay will have high surface interactions with the polymer chain. Consequently, it will prevent the slippage of the polymer chain and reduce the chain mobility, thus enhance the tear strength of the polymer.

### Table 2. Tear strength of TPS and TPS/hectorite films

| Type of sample       | Tear Strength (MPa) |
|----------------------|---------------------|
| Pure TPS             | 0.449               |
| TPS+1% Hectoite      | 0.758               |
| TPS+2% Hectoite      | 0.97                |
| TPS+3% Hectoite      | 2.396               |
| TPS+4% Hectoite      | 2.064               |
| TPS+5% Hectoite      | 2.987               |

In preliminary works, the TPS biocomposites with hectorite clay loading were prepared greater than 5 wt % (6 to 9 wt %). However, no good film was observed, perhaps due to agglomeration and overcrowding of hectorite particles in the matrix. The films were brittle and cracked after being cut into dumbbell shape. Furthermore, the samples took longtime for drying; so it is not appropriate to compare them with other biocomposites (with hectorite content 0-5wt%).

![Comparison of tear strength between pure TPS and TPS/hectorite with different loading of hectorite.](image)

**Fig. 1.** Comparison of tear strength between pure TPS and TPS/hectorite with different loading of hectorite.

### 3.2 Biodegradability test

The biodegradable test was carried out to determine the percentage of weight loss of the materials upon the measured time. The biodegradable property is the main criteria to produce an environmental friendly material. Thus, the effect of hectorite clay addition on biodegradable behavior of the TPS based film was studied. Fig. 2 shows the weight loss of TPS and TPS/hectorite films in soils for one month. As shown in Fig. 2, the TPS/4% hectorite (non-ultrasonicated) film has the fastest and highest weight loss rate which is 45% on the 4th week. The TPS/4% hectorite (ultrasonicated) film exhibits the lowest weight loss rate which is 27%. The TPS, TPS/1% hectorite with and without ultrasonication generally have the same weight loss rate which are 32%, 30% and 36% respectively. It is clear that the weight loss rate of TPS/4% hectorite with ultrasonication is slower and lower than the TPS/4% hectorite without ultrasonication.

For the first 15 days, all the films experienced very slow and almost same weight loss rate, which was in the range of 0.2% to 0.5%. The degradation rate of films has started to increase after day 15. The significant weight loss happened after the first 15 days, this was because the microorganisms in the soil was trying to adapt and grow in the new starch films environment. Thus the weight loss of the films started only after the day 15 [19]. The results clearly indicate that the biodegradability of the TPS film was decreased by increasing the amount of the ultrasonicated hectorite. On the other hand, the biodegradability of the TPS film was enhanced by increasing the amount of hectorite (without ultrasonication). The rate of degradation of film was greatly depend on the degree of crystallinity of the polymer. This is because; the microorganism most likely to attack the amorphous region of films due to its loosely packed structure [20]. The weight loss rate of the film containing 4% hectorite (without ultrasonication) is higher probably due the agglomeration of hectorite particle and weak interaction between the hectorite and starch matrix, thus leave void in the structure [21]. This will cause the moisture to be absorbed into the films, increasing the rate of hydrolysis and growth of bacteria in the void. Consequently, biodegradation of the films enhanced. Muller et al. [22] showed that the PLA/starch films had the higher disintegration rate due to the void exists in the structure. This led to high absorption of water and bacteria growth in the biopolymer structure.
The TPS/4% hectorite (ultrasonicated) film exhibits lower biodegradability than the pure TPS. This is because the hectorite that underwent ultrasonication may result in better dispersion of silicate layer and have maximum filler-matrix surface area contact, leading to strong interfacial bonding between starch and hectorite. This strong interfacial bonding will reduce the diffusivity of water into the starch film and decrease the water absorption of films. Besides that, this larger surface interaction between starch and hectorite will increase the difficulty of bacteria diffusing into the bulk of the film and forcing the bacteria to diffuse into the films by paths that are more tortuous. Therefore, the time for water and bacteria for diffusion were increased and the biodegradation of film decreased. Furthermore, the higher the surface interaction between film and starch, the higher the tortuosity of the system [23]. Therefore, the biodegradability of TPS/1% hectorite with ultrasonication is higher than TPS/4% hectorite with ultrasonication since the former have the lower degree of silicate layer dispersed into the matrix.

![Fig. 2. Weight loss of pure TPS films and TPS/hectorite (with and without ultrasonication treatment).](image)

### 3.3 Scanning electron microscope (SEM)

#### 3.3.1 TPS/hectorite biocomposite analysis

The tensile fractured surface morphology of the TPS and TPS/hectorite films were studied by Scanning Electron Microscopy (SEM). The magnification of 500x, 1000x and 5000x were used to observe the morphology of the TPS/hectorite films and the distribution of hectorite particles in the TPS matrix. There were three types of composite outcome when incorporating the nano clay into the polymeric matrix. The first one is immiscible composite where the nanoclay does not interact with matrix and neither way. The second is intercalant structure where the polymer matrix is penetrating into the silicate layer of nanoclay and give optimum strength for the films. The last one is exfoliated structure where the silicate layers were separated and dispersed randomly into the polymer matrix. This structure give high mechanical strength to films [24]. Fig. 3(a) shows the SEM image (x1000) of TPS films and the surface of TPS films was observed. From the Fig. 3(a), the surface of TPS films was smooth and show only gelatinized starch. There was no residual for the starch granules structure indicating that starch granules were completely disrupted and broken when processing with glycerol and water at high temperature. The broken and reforming hydrogen bond between starch granule with glycerol and water made the TPS films.

SEM micrographs of the TPS/hectorite 4% films with and without ultrasonication are shown in Fig. 3(c) and Fig. 3(d), respectively. By comparing both images, it was obviously seen that the TPS/hectorite films without ultrasonication have larger hectorite particle size and tended to aggregate together forming tactoid structure. TPS/hectorite without ultrasonic showed almost no intercalation structure. This showed hectorite without ultrasonication have poor compatibility with the starch matrix. Besides that, Fig. 3(d) showed that there was phase segregation between starch and hectorite particles which further testify a poor compatibility between the non-ultrasonicated hectorite with starch. Due to poor dispersion of hectorite throughout the starch matrix, the hectorite developed inadequate bond forming with the starch structure. This was the reason for poor mechanical properties of the film containing the non-ultrasonicated hectorite compared to the ultrasonone a t [25]. Fig. 3(c) shows the exfoliated hectorite layer coexist with some hectorite agglomerates. By comparing with Fig. 6(d), the size of hectorite particles was much smaller, less tactoids and well dispersed in the starch matrix, even though both of the films had the same content of hectorite. The silicate layers appear exfoliated and intercalated in the matrix of starch. The arrow in the Fig. 3(c) shows that the hectorite particle dispersed within starch matrix. The smaller the size of hectorite, the higher the interaction between hectorite particle and starch matrix. Besides that, there were no segregation in the Fig. 3(c) which indicating that the organic phases of starch have a good compatibility with inorganic phase of hectorite. Furthermore, a homogenous surface was observed due to good dispersion of hectorite in the starch matrix. However, when the loading of hectorite (ultrasonicated) was increased to 5%, there were small
amounts of aggregated hectorite particles randomly dispersed (see Fig. 3(e)). This explains why there is a slight drop of tensile strength of TPS/5% hectorite films compared to the TPS/4% hectorite film.

All the TPS/hectorite films (ultrasoundicated) show high homogeneity and transparency, showing that there is strong interaction between the hectorite and the starch matrix. The homogenous surface shows that the starch granules were completely disrupted and the clay was dispersedly well in the matrix. 4% of hectorite with ultrasoundication have no clay aggregation even at higher magnification. This also shows that the starch and the filler interact well even at low hectorite content (4%).

**Fig. 3.** SEM images (x500 magnification) for (a) pure TPS, (b) TPS/1% hectorite with ultrasoundication, (c) TPS/4% hectorite with ultrasoundication, (d) TPS/4% hectorite without ultrasoundication, (e) TPS/5% hectorite with ultrasoundication

## 4 Conclusions

TPS bio-composite films with hectorite (pristine and ultrasoundicated) were prepared. Results show that the higher the loading of hectorite, the higher the tear strength of the TPS/hectorite film. When the loading of hectorite raised to 5%, the tear strength of the bio-composite films achieved the maximum value. SEM analysis suggests that the TPS/hectorite bio-composite with ultrasoundicated hectorite exhibits better compatibility, less aggregation and better dispersion of hectorite in matrix compared to same loading of hectorite without ultrasoundication. Besides that, the tear strength of the TPS/hectorite (ultrasoundicated) was much higher than the TPS/hectorite without ultrasoundication. Lastly, the effect of hectorite on the soil biodegradability of TPS/hectorite films was investigated. Based on the soil degradable test, the ultrasoundicated hectorite was found to reduce biodegradability of the TPS films. The TPS/hectorite (ultrasoundicated) can slow down the degradation of films due to the good interaction and well dispersed of hectorite in the starch matrix. This system provides tortuous path for water and bacteria diffusion into the film and slowed down the degradation of the film.
From this research, it was found that the TPS/hectorite (ultrasonicated) has good tear strength which can be commercialized as biodegradable and environmentally friendly material in packaging application.

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant NO: FRGS/1/2019/TK.10/UNIMAP/03/3 from The Ministry of Education Malaysia

References

1. M. Fazeli and R. A. Simão. In Macromolecular Symposia. 380, 1 (2018)
2. European Bioplastics. Bioplastic marked data 2017 (2017)
3. Y. Zhu, C. Romain, C.K. Williams, Nature. 540 (2016)
4. I.Y.R. Odegard, S. Nusselder, E. Roos Lindgreen, G. C. Bergsma and L. de Graaff. CE Delft. (2017)
5. T.A. Saleh, and G.I. DanmalikiGI Global. (2020)
6. S.T. Sam, M.A. Nuradibah, KM. Chin, N. Hani. Nat. Polym. Ind. Tech. Appl. (2015)
7. R. N. Tharanathan. Trends in Food Sci. and Tech. (2003)
8. P. B. Shah, S. Bandopadhyay, J.R. Bellure. Poly. Degrad. and Stability (1995)
9. S. Theubaud, J. Aburto, I. Aliche, E. Borredon. D. Bikiaris, J. Prinos, C. Panayiotis. J. of App. Poly. Sci. (1997)
10. R. Chandra and R. Rustagi, Prog. Polym. Sci. (1998)
11. F. Aeschelmann, F and M. Carus.Industrial Biotechnology, 11(3) (2015)
12. B. Khan, M. Bilal Khan Niazi, G. Samin, and Z. Jahan. J. Food Proc. Eng., 40 (2017)
13. X. Z. Tang, P. Kumar, S. Alavi, and K. P. Sandeep. Crit. Rev. Food Sci. Nutr. 52, 5, (2012)
14. L. Bailey, H. N. W. Lekkerkerker, and G. C. Maitland. Soft Matter. 11, 2, (2015)
15. J. T. Kloprogge, S. Komarneni, and J. E. Amonette. Clays Clay Miner. 47, 5, (1999)
16. M. Liu, Z. Jia, D. Jia, and C. Zhou. Prog. Polym. Sci. 39, 8, (2014)
17. H. H. Murray, Appl. Clay Sci. 17 (2000)
18. G. F., Perotti, J., Tronto, M. A., Bizeto, C., Izumi, M. L., Temperini, A. B., Lugao., & V. R. J. Constantino. Brazilian Chem. Soc. 25 (2014)
19. M. Nafchi, M. Moradpour, M. Saeidi, and A. K. Alias, Starch/Staerke. 65 (2013)
20. N. Ghuttora, Arcadia. (2016)
21. S. R. Lee, H. M. Park, H. Lim, T. Kang, X. Li, W. J. Cho and C. S. Ha. Polymer, 43,8 (2002)
22. J. Muller, C. González-Martinez, and A. Chiralt., Mat. (Basel). 10 (2017)
23. P. Maiti, C. A. Batt, and E. P. Giannelis, Biomacromol. 8 (2007)
24. N. Eko Wahyuningsiay and H. Suryanto, J. Metastable Nanocryst. Mater. 29, (2017)
25. P., Das, L. B., Sukla, N., Pradhan, & S. Nayak. Bioresource Technology, 102(16) (2011)