Effect of EMA and antioxidants on properties of thermoplastic starch blown films

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Abstract. The objectives of this study were to investigate the effect of poly(ethylene-co-methyl acrylate) (EMA) at 10, 30 and 50 wt% on the morphological properties, moisture sorption, water vapor permeability and biodegradability of thermoplastic starch (TPS). Urea and formamide were used as a mixed plasticizer. In addition, the effect of antioxidants namely, 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (DTBH), butylated hydroxytoluene (BHT) and bis(octadecyl)hydroxylamine (BOH) at 1 wt% on the properties of TPS/EMA film was investigated. TPS/EMA films were produced by a blown film molding machine and characterized by scanning electron microscopy, moisture sorption, water vapor permeability and biodegradability measurement. Results found that the increment of EMA content in the TPS matrix could improve the water sorption, water vapor permeability and biodegradability properties of TPS/EMA films. For biodegradation, the weight loss of the blended films was directly proportional to TPS content. Regarding the antioxidants effect, the water vapor permeability of TPS/EMA films containing DTBH was higher than the one with BOH and BHT. However, the antioxidants contributed little to the biodegradability of TPS/EMA films and had no effect on the moisture sorption of TPS/EMA films.

1. Introduction
Thermoplastic starch (TPS) is a biodegradable polymer which is a promising material due to its low cost and native biodegradability [1]. Kiatkamjornwong S. et al. is focused on modifying the structure of starch [2] and Euaphasate N, et al. improved its ability to blend with other petroleum polymers to reduce its hydrophilicity and improve its mechanical properties [3]. The disadvantage of this approach is the poor compatibility between hydrophilic starch and hydrophobic polymers [4].

One way to enhance compatibility and to incorporate starch in petroleum polymer is to use a compatibilizer containing functional groups such as poly(ethylene-co-methyl acrylate), or EMA that can form hydrogen bonds with starch. Even though numerous works have reported on TPS blended with polymers such as low density polyethylene (LDPE) [1, 3-6], poly(lactic) acid (PLA) [7] and ethylene-vinyl acetate copolymer (EVA) [4], no one has studied EMA on the properties of blown TPS films. This research focuses on the effect of EMA on the properties of TPS film. EMA was used as a
compatibilizer in order to improve processability, moisture sorption, water vapor permeation and biodegradability of blown TPS films. An extensive study of these blends with the addition of various types of antioxidants was also performed on the properties such as moisture sorption, water vapor permeation and biodegradability of TPS/EMA blown films.

2. Experimental

2.1. Materials
Native cassava starch was purchased from a local market. Poly (ethylene-co-methyl acrylate) (EMA) copolymer with 20% methyl acrylate (MA) contents was purchased from Dupont. Plasticizers (Urea and formamide) were obtained from Ajax Finechem Pty Ltd. The ratio of plasticizers (urea/formamide) was 2:1 wt/wt. Three antioxidants, namely 3, 5-di-tert-butyl-4-hydroxyl hydrocinnamate (DTBH), butylated hydroxytoluene (BHT) and bis(octade cyl)hydroxylamine (BOHA) were obtained from Behnmeyer which chemical structures were listed in table 1.

| Materials | Chemical structure |
|-----------|-------------------|
| EMA       | \[
|           | \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\) \] |
| DTBH      | ![DTBH structure](image) |
| BHT       | ![BHT structure](image) |
| BOHA      | ![BOHA structure](image) |

2.2. Compounding and preparation of films
Before blending the starch and plasticizers, urea and formamide were mixed in a high-speed mixer (100 rpm, 1 min). The ratio of plasticizers and starch was 30/70 wt/wt. EMA was blended into the plasticized starch in 10, 30 and 50 wt%. In this study, 1 wt% of antioxidants was added to the mixtures containing 10 wt% of EMA. The mixtures were mixed in a high-speed mixer (1000 rpm, 10 min). The mixtures were blended in twin screw extruder. The temperature profile along the extruder barrel was 50-125 °C. Extruded strands were cut into pellets for further processing. The plasticized starch and EMA samples were referred to by number after TPS/EMA. The sample compositions of TPS/EMA films are listed in table 2.

Films were molded by blown film extruder with a screw diameter of 25 mm and L/D ratio of 30. The temperature profile of the extruder barrel was 70-115°C to obtain film thickness of approximately 0.2 mm. The films were conditioned for 3 days in closed chambers with saturated NaCl salt solutions (75% relative humidity) prior to any measurement.
Table 2. The sample codes and compositions of blended films.

| Sample         | Dry starch (wt%) | Urea/Fomamide (2:1) (wt%) | EMA (wt%) | Antioxidants |
|----------------|------------------|----------------------------|-----------|--------------|
| TPS            | 70               | 30                         |           |              |
| TPS/EMA1       | 63               | 27                         | 10        |              |
| TPS/EMA2       | 49               | 21                         | 30        |              |
| TPS/EMA3       | 35               | 15                         | 50        |              |
| TPS/EMA11      | 63               | 27                         | 10        | 1% DTBH      |
| TPS/EMA12      | 63               | 27                         | 10        | 1% BHT       |
| TPS/EMA13      | 63               | 27                         | 10        | 1% BOHA      |

2.3. Characterization and testing

*Scanning electron microscope (SEM)* - The fracture surface of TPS/EMA film was carried out with SEM to analyze the morphological properties.

*Differential scanning calorimeter (DSC)* - Thermal analysis was conducted using Mettler Toledo DSC. Nitrogen gas was purged at a rate of 20 ml/min during experiments. Scanning was carried out in a heated-cooled-heated pattern at temperature ranging from -60 to 120°C at 10°C/min.

*Moisture sorption (MS)* - Moisture sorption measurements were performed under 75% relative humidity (saturated NaCl) at 25°C. Films were prepared in dimensions of 30×50 mm. Specimens were dried and weighted the original dry value (W₀). The percentage moisture uptake (Mᵢ) as the following equation (1):

\[ Mᵢ = \frac{W_h - W₀}{W₀} \times 100 \]  

where \( W_h \) is the weight of humid specimens. Moisture sorption data were fitted according to a Peleg model as the following equation (2):

\[ Mᵢ = M₀ + \frac{t}{k₁ + k₂t} \]  

where \( Mᵢ \) denote the moisture content at any time (%), \( M₀ \) denote the initial moisture content (%), \( k₁ \) and \( k₂ \) are the Peleg rate and capacity constant, respectively, and \( t \) is time (hr).

*Water vapor permeability (WVP)* - Water vapor permeability tests were performed according to ASTM method E96 (1996) [8].

*Biodegradability* - The biodegradation of the blends was measured by soil burial. The specimens were placed in a box of 60×45 cm wide and 10 cm deep. Films were covered with soil. Water was initially added to the site and then again after for a week. The films remained at the site through the test period time with a sample removed each time in order to track their biodegradation. Measurements were performed to track the biodegradation of the samples weight loss.

3. Results and discussion

3.1. Blends morphology

The structures of the TPS and TPS/EMA films are illustrated in figure 1. The fracture surface of the TPS film showed a smoother surface which could be related to the complete destruction [9] as shown in figure 1a. The result showed the aggregated globules of EMA in the blended films. The higher the amount of EMA, the larger the aggregation of EMA was highly dispersed in the TPS matrix as shown in figures 1b-sd. The distinct interfaces and apparent cracks between starch and EMA were sign of the lack of adhesion and the immiscibility at the interface between the two polymers [10]. When 1 wt% of different types of antioxidants were added, no visible difference could be detected on the fracture surface of the TPS/EMA films, as shown in figures 1e-1g.
3.2. Differential scanning calorimeter (DSC)

The differential scanning calorimetry thermograms of the TPS/EMA blended films are shown in figure 2. Results indicated that the glass transition temperature ($T_g$) of TPS could not be detected by the DSC technique, because starch granules were destroyed, which changed their structure from crystalline to amorphous when plasticizers were added. The melting temperature ($T_m$) of TPS was clearly

Figure 1. SEM micrographs of (a) TPS film and (b) TPS/EMA1, (c) TPS/EMA2, (d) TPS/EMA3, (e) TPS/EMA11, (f) TPS/EMA12 and (g) TPS/EMA13 films.

Figure 2. DSC thermograms of TPS and TPS/EMA films at various EMA content.

Figure 3. DSC thermograms of TPS/EMA films with various antioxidants.
unidentified. In the TPS/EMA films, T_g and T_m (-35.28°C and 92.53°C) which stand out were possibly related to the addition of EMA. The melting points and glass transition temperature of EMA had no significant differences when various EMA content were in the TPS/EMA films. Only a slight change in the blended films (1°C) compared with the one of neat EMA was observed. It could be concluded the EMA itself is least miscible with starch even with the methyl acrylate segment in the structure as its compatibilizer [6]. Figure 3 showed DSCs of TPS/EMA films containing antioxidant. The blended films had no significant difference compared with TPS/EMA1.

3.3. Moisture sorption
As TPS and TPS/EMA films with the influence of antioxidants are hydrophilic substance, the investigation of their moisture sorption is required. Figure 4 illustrates the effect of starch amount on moisture sorption of TPS/EMA films. EMA film did not demonstrate the moisture sorption. However, the moisture sorption rate and capacity of the TPS/EMA films were proportional to the starch amount, due to high water sorption capacity of the starch. As a function of time, the moisture sorption was relatively higher at the initial stages, and lesser amounts of moisture were absorbed in the later stages. Then, the moisture content of the films reached a plateau indicating that they became equilibrated with the surrounding relative humidity [3].

![Figure 4. Moisture sorption of a) TPS and b) TPS/EMA films.](image)

The moisture content data were fitted using Peleg’s model to investigate moisture sorption behavior of the films. k_1 is related to the initial moisture absorption rate; k_2 is related to maximum moisture absorption capacity. k_1 and k_2 value are inversely proportional to the initial moisture absorption rate and the maximum moisture absorption capacity, respectively [11]. As seen in table 3, both k_1 and k_2 of TPS films were the lowest values. Therefore, TPS film possessed the highest initial moisture absorption rate and the maximum moisture absorption capacity. In TPS/EMA film, incremental increase of EMA contents tended to lower the absorption rate and capacity. When various types of antioxidants were added, the result of initial absorption rate and maximum moisture absorption capacities was not significantly different, as shown in table 3.

Table 3. Peleg constant from curve fitting using Peleg Model of films.

| Blended films | 75% RH, 25°C | k_1    | k_2    | r^2   |
|---------------|-------------|--------|--------|-------|
| TPS           |             | 0.0479 | 0.0263 | 0.9996|
| TPS/EMA1      |             | 0.0697 | 0.0463 | 0.9989|
| TPS/EMA2      |             | 0.2209 | 0.0633 | 0.9991|
| TPS/EMA3      |             | 0.2448 | 0.0946 | 0.9987|
| TPS/EMA11     |             | 0.0700 | 0.0483 | 0.9985|
| TPS/EMA12     |             | 0.0723 | 0.0445 | 0.9965|
| TPS/EMA13     |             | 0.0717 | 0.0464 | 0.9990|
3.4. Water vapor permeability (WVP)

Table 4 illustrates water vapor permeability of TPS and TPS/EMA films with different types of antioxidants were investigated at 25°C. The results showed that both the EMA content and antioxidants had significant effects on the WVP of the films. The water vapor permeability decreased when the EMA content increased. These results suggested that the blended films show aggregated globules of EMA. Increasing the amount of EMA leads to larger aggregate parts of immiscible blend in the starch matrix, as shown in figures 1b-1d. These layers had acted as barrier from water penetration.

The incorporation of antioxidants into TPS/EMA film caused the films to possess difference water vapor permeability. Due to the abundance of hydroxyl groups in TPS matrix, there could be interaction, i.e. hydrogen bonding among those of starch and phenolic group from BOHA or the hydroxyl amine group from BOHA and BHT. The difference in WVP of the TPS/EMA films with different antioxidants established intermolecular interactions between the TPS network and those functional groups in antioxidants. Therefore, the availability of hydroxyl group to form hydrophilic bonding with water would be limited and subsequently lead to different degree of affinity of TPS/EMA film towards water. The hydroxyl group of BHT could likely act as hydrogen donor and thereby hydrogen bonds could be formed between antioxidants and starch molecules. This coincided with the study of Jongjareonraka, who worked on the fish skin gelatin film incorporated with BHT [12]. A large antioxidant molecule, such as DTBH, could experience the steric hindrance effect and thus make bigger holes between starch molecules. As a result, the TPS/EMA film with DTBH possessed relatively higher WVP than other antioxidants. The linear molecule with hydroxyl amine group, such as BOHA, could strongly established the interaction with the hydroxyl group of starch molecules and therefore cause relatively low WVP.

| Film samples   | WVPx10^-10 (g/(m·s·Pa)) |
|----------------|--------------------------|
| TPS            | 8.65 ± 0.10              |
| TPS/EMA1       | 7.25 ± 0.04              |
| TPS/EMA2       | 1.17 ± 0.04              |
| TPS/EMA3       | 0.69 ± 0.02              |
| TPS/EMA11      | 6.01 ± 0.04              |
| TPS/EMA12      | 5.69 ± 0.06              |
| TPS/EMA13      | 4.98 ± 0.16              |

3.5. Biodegradability

Numerous works on biodegradable polymers have indicated that microorganism did consume starch and creating pores, increasing surface area of polymers/starch blends. This provides possibility for degradation. Starch consumption by microorganisms results in blend weight loss. Figure 5 illustrates difference of TPS/EMA3 film before and after soil burial. As seen in figure 6a, in the blended films with 10 wt% of EMA, the weight loss is substantial. The biodegradation rate seemed to diminish for the blended films with 30 and 50 wt% EMA.

Figure 5. SEM micrographs of TPS/EMA3 film (a) before and (b) after soil burial.
Figure 6. Effect of (a) EMA content and (b) antioxidants on weight loss of TPS/EMA films during soil burial period.

As shown in figure 6b, for the TPS/EMA films containing antioxidants, the antioxidants had little effect on weight loss. For the first seven days, the weight loss of TPS/EMA blend film with antioxidant took place at a lesser amount than TPS/EMA films. This could be explained by the polarity effect of TPS. As mentioned above, the hydroxyl groups or hydroxyl amine group of antioxidants could interact with starch; thus, TPS/EMA films with antioxidants could provide more hydrophobic properties, which would delay the degradation of TPS/EMA films.

4. Conclusions

EMA was to improve processability, although the EMA and TPS blended films were immiscible blends as confirmed by SEM and DSC. Moisture sorption and water vapor permeability in blended films were improved with the incremental increase of EMA content. EMA could act as a barrier against water permeation. In regard to biodegradability of TPS/EMA films, the weight loss of blended films depended on TPS content, and we assumed that starch consumption caused the weight loss. Regarding the antioxidant effect, the TPS/EMA blended films with added antioxidants, for example, DTBH, BHT or BOHA, interacted well with the starch matrix. A large antioxidant molecule, as in DTBH, could experience the steric hindrance effect, thus making larger holes between starch molecules. The TPS/EMA film with DTBH possessed relatively higher water vapor permeability than BHT and BOHA. Adding antioxidants would have little effect to weight loss of blended films.

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References

[1] Rodriguez-Gonzalez F J, Ramsay B A and Favis B D 2003 Polymer 44 1517-26
[2] Kiatkamjornwong S, Thakeow P and Sonsuk M 2001 Polym. Degrad. Stabil. 73 363-75
[3] Euaphasate N, Prachayawasin P, Uasopon S and Methacanon P 2008 J. Met. Mat. Miner 18 103
[4] Da Roz A L, Ferreira A M, Yamaji F M and Carvalho A J F 2012 Carbohydr. Polym 90 34-40
[5] Bikiaris D, Prinos J, Koutsopoulos K, Vouroutzis N, Pavlidou E, Frangi N and Panayiotou C 1998 Polym. Degrad. Stabil 59 287-91
[6] Prinos J, Bikiaris D, Theologidis S and Panayiotou C 1998 Polym. Eng. Sci. 38 594
[7] Shirai M A, Grossmann M V E, Mali S, Yamashita F, Garcia P S and Muller C M O 2013 Carbohydr. Polym 92 19-22
[8] Ning W, Xingxiang Z, Na H and Shihe B 2009 Carbohydr. Polym 76 68-73
[9] Zullo R and Iannace S 2009 Carbohydr. Polym 77 376-83
[10] Pushpadass H A, Bhandari P and Hanna M A 2010 Carbohydr. Polym 82 1082-9
[11] Turhan M, Sayar S and Gunasekaran S 2002 *J. Food Eng.* **53** 153-9

[12] Jongjareonraka A, Benjakula S, Visessanguanb W and Tanaka M 2008 *Food Hydrocolloids* **22** 449-58