BIODEGRADABLE POLYMER FILM BASED ON POLYBUTYLENE ADIPATE TEREPHTHALATE (PBAT) AND CASSAVA STARCH: RESEARCH AND PREPARATION

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Abstract

Thermoplastic starch compounds were prepared from cassava starch, glycerol, and tartaric acid by the twin-screw extruder. Fourier-transform infrared spectroscopy (FTIR) analysis demonstrated the formation of ester bonds during starch modification through absorption peaks at characteristic wavelengths of C=O bonding and C–O bonding. Biodegradable polymer were fabricated from thermoplastic starch (TPS) and polybutylene adipate terephthalate (PBAT) by the twin-screw extruder and then a blown film extrusion process. Scanning electron microscopy (SEM) images showed that when using modified thermoplastic starch (MTPS), the material showed a more homogeneous structure. Besides, this study also selected the optimal content of tartaric acid as a compatibilizer, screw speed, and talc powder content used in the blend when determining the tensile properties and melt flow index (MFI) of the material.

Keywords: *PBAT, thermoplastic starch, biodegradable polymer film*

1. Introduction

Recently, petroleum-based polymers have been widely used in various applications such as in packaging and mulching films. However, these materials cause several environmental problems because of the non-degradable waste that they produce., Many efforts have been made to develop environment-friendly biodegradable materials to minimize the environmental impacts of non-degradable plastics [1].

Starch is one of the most potential natural polymers because of its biodegradability and annual renewability. Besides, starch offers a attractive ingredient for new biodegradable polymers due to their low material cost and ability to be processed with conventional plastic processing equipment. Native starches are semi-crystalline materials. Before the gelatinization, the decomposition temperature of starch is lower than its melting temperature. Hence, starch-based materials cannot be process under heat using conventional plastic equipment, particularly extruders [2]. Therefore, it's necessary to combine with plasticizers such as water, glycerol, ethylene glycol or sorbitol,… to form a meltable material called thermoplastic starch (TPS) [3]. TPS can produce fully degradable films; however, they are strongly affected by moisture, poor mechanical properties, and limited application.

Because of these limitations, TPSs are often blended with other syntheses biodegradable polymer to enhance their properties such as polylactic acid (PLA), polybutylene terephthalate (PBT), polycaprolactone (PCL), polybutylene adipate terephthalate (PBAT) [4-7]. Among those polymers, PBAT has attracted a lot of attention from researchers due to its high mechanical properties and similar processing conditions for low-density polyethylene (LDPE) and fully degradable.

The difference in the surface properties between TPS and PBAT (TPS is hydrophilic while PBAT is hydrophobic) leads to low interfacial compatibility and phase separation, which can decrease the performance of materials. Several reactive coupling agents have been used to improve the interfacial adhesion between the two phases, including maleic anhydride, citric acid, maleated TPS, maleatified PBAT, epoxy additive, maleic acid, and tartaric acid [8].

Tartaric acid (TA), produced naturally in grapes, has been reported that it could enhance the compatibility of PBAT/TPS blends through acid hydrolysis reactions and esterification/transesterification reactions, leading to better properties [1,] [9] [10].

In this study, PBAT/TPS blend films were prepared using two-step compounding and subsequent blown film extrusion. The effects of tartaric acid compatibilizer on the microstructures, melting index of the blend, and the mechanical properties of the films were investigated.

2. Materials and methods

2.1. Materials

Table 1. Materials used in the study.

No.	Materials	Properties	Source
1	Cassava starch	Moisture content: < 14% Impurities content: < 0,2% Dynamic viscosity of 6% solution at 30^{o}C: 8000 – 14000cP Particle size (Through 100µm): 96-99%	Hung Duy Co., LTD, Vietnam

No.	Materials	Properties	Source
2	Glycerol	Density: $1,26g/cm^3$ Melting point: 18ºC Boiling point: 290ºC Viscosity: 1,412Pa.s	P&G Chemicals, Malaysia
3	PEG 4000	Density: $1,20g/cm^3$ Melting point: 53 – 58ºC	China
4	PBAT	Melt flow index (MFI): 5g/10 phút Tensile stress: 24,5MPa Elongation at break: 395%	Xinfu Chemical, China
5	Tartaric acid	Density: $1,79g/cm^3$ Melting point: 171 – 174ºC	China
6	Talc	Density: $2,58g/cm^3$ Particle size: 4,5µm	China

2.2. Thermoplastic starch preparation

Modified thermoplastic starch (MTPS) was fabricated according to the scheme in Figure 1.

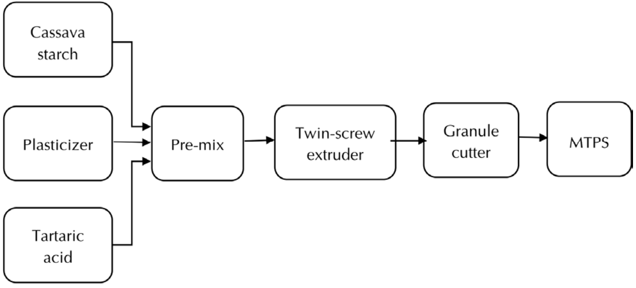


Figure 1. Preparation scheme of the thermoplastic starch.

Cassava starch, plasticizers (including glycerol, polyethylene glycol at the ratio of 80:20), and tartaric acid were mixed for 15 minutes at room temperature. The mixtures were packaged in polyethylene bags and stored for at least 24%h at room temperature to equilibrate all the components.

After that, the mixture was fed into a two-screw extruder with the barrel temperatures from the feed zone to the die zone were 120-140-160-170-170-170-170-160-150-140˚C. The screw speed was at 150%rpm.

The extruded thermoplastic starch was water-cooled, cut into pellets, and dry at 85ºC in 3-4 hours.

2.3. Preparation of the PBAT/MTPS films

PBAT, MTPS (with PBAT/MTPS weight proportions of 60/40), and the additive were pre-mix in a mixer and fed into a two-screw extruder with the barrel temperatures from the feed zone to the die zone were 120-140-160-180-180-180-180-170-160-160˚C. The screw speed was 150%rpm.

The extruded blend was water-cooled, cut into pellets, and dry at 80ºC in 4 hours.

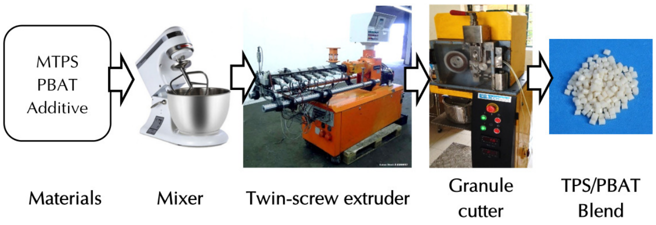


Figure 2. Preparation of the PBAT/MTPS blend.

The film samples were prepared using the Labtech blown film extrusion system. The barrels temperatures from the feed zone to the die zone 170-170-170-170-170-170-170˚C. The screw speed was 25%rpm.

Figure 3. Labtech blown film extrusion.

2.4. Characterization of the PBAT/MTPS films

2.4.1. Determination of tensile properties of PBAT/MTPS films

Tensile tests were performed using Lloyd LRX Plus (5kN) testing machine. Tensile strength and elongation at break were measured according to ISO 527-3:2012.

Tensile stress:

$$\sigma = \frac{F}{A}$$

where:

σ: is the tensile stress value, expressed in megapascals (MPa);

F: is the measured force concerned, in newtons (N);

A: is the initial cross-sectional area of the specimen, mm^2.

Elongation at break:

$$\varepsilon = \frac{\Delta L_0}{L_0}$$

where:

ε: is elongation at break, in percentage (%);

L_0: is the gauge length of the test specimen, mm;

ΔL_0: increase of the distance between grips, mm.

2.4.2. Determination of the melt flow index (MFI) of PBAT/MTPS blend

Melt flow index (MFI) of PBAT/MTPS blend was tested by MP993 Melt flow tester (Tinius Olsen, USA) according to the test method specified in ISO 1133-1: 2011 standard.

2.4.3. Scanning electron microscopy (SEM)

The samples were frozen in liquid nitrogen and then cryofractured to obtain the cross-sectional samples. The film samples were mounted on a bronze stub and sputter-coated with platinum before observation.

The surface and cross-sectional morphology of the films were observed using a JEOL JSM-6360LV scanning electron microscope.

2.4.4. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra of the films were obtained using an IRAffinity-1S spectrometer (Shimadzu, Japan) to evaluate the molecular interactions in the film matrix. The wavenumber was over the range of 4000-400cm^{-1}.

3. Results and discussion

3.1. FT-IR analysis

To increase the compatibility between TPS and PBAT, while reducing the inherent hydrophilic properties of TPS, this study using tartaric acid as a modifier for TPS.

FT-IR analysis can be used to effectively study the molecular interactions between tartaric acid and starch that occur during reactive extrusion. FT-IR spectra of the TPS and modified TPS (tartaric acid content of 3,5% by weight) was shown in Figure 4.

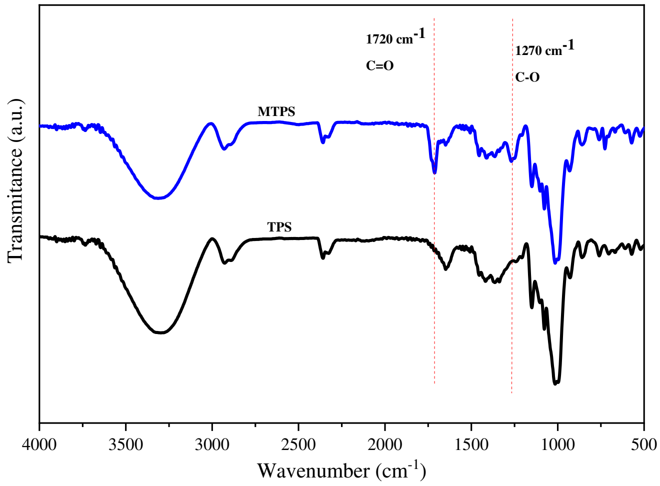


Figure 4. FT-IR spectra of the thermoplastic starch (TPS) and modified thermoplastic starch (MTPS).

Both TPS and MTPS, characteristic absorption peaks of starch molecules appeared: the absorption peaks around wave number 3310cm^{-1} occurred because of the presence of hydroxyl groups (–OH), the absorption peaks at wavenumber 2930%cm^{-1} are assigned to –CH bonds, and the absorption peaks at wavenumber 1152cm^{-1} assigned to the stretching vibration in the C–O–C bonds.

Table 2. The absorption peaks in FT-IR spectra of TPS and MTPS.

Wave numbers	TPS	MTPS	Bonds/Groups
3310cm^{-1}	✓	✓	–OH groups(stretching vibration)
2930cm^{-1}	✓	✓	–CH bonds
1720cm^{-1}	-	✓	C=O groups
1640cm^{-1}	✓	✓	–OH groups (bending vibration)
1152cm^{-1}	✓	✓	C–O–C bonds
1270cm^{-1}	-	✓	C–O bonds

We noticed that absorption peaks at wavenumber 1720cm^{-1} (assigned to C=O groups) and 1270cm^{-1} (assigned to C-O bonds) appeared on the spectra of MTPS but can not be found on those of the TPS.

Since the MTPS samples were rinsed by acetone, the excess tartaric acid was removed, so the peaks at wavenumber 1720cm^{-1} and 1270cm^{-1} were confirmed not to be tartaric acid. These peaks were evidence of the esterification between –OH groups of TPS and tartaric acid.

Similar results were reported by Olivato [11] when analyzing the FT-IR spectra of PBAT/TPS blend using tartaric acid as compatibilizer. Olivato believes that esterification reactions promoted by TA were demonstrating that TA reacts with starch, increasing its compatibility with the PBAT phase and improving the properties of the blends.

3.2. Effect of tartaric acid on properties of PBAT/MTPS blend

3.2.1. Tensile properties and melt flow index

In this section, PBAT/TPS blends were prepared using 15% by weight of the plasticizer, and the tartaric acid content changes from 2.5 to 3.8% by weight. Figure 5 was shown the effect of tartaric acid contents on melt flow index of PBAT/MTPS blend and tensile properties of PBAT/MTPS films.

The graph shows that the properties of the PBAT/MTPS blend change according to the acid content. The melt flow index and elongation tended to increase with the increasing tartaric acid content. However, these values tended to grow slowly as the acid content increased from 2.5 to 3.5%. When tartaric acid exceeding the threshold of 3.5%, these two values tend to increase significantly. When the modifier content increased from 3.5 to 3.8%, MFI increased from 5.93 to 7.71g/10min (increased by about 30%), the elongation at break increased sharply from 452% to 673%.

The tensile strength value of this material increased sharply from 10.1MPa to 18.9MPa (an increase of about 87%) when the tartaric acid content increased from 2.5% to 3.5%. However, when it exceeds 3.5%, the tensile strength value drops back to 10.9MPa.

From the data, 3.5% of tartaric acid content was selected for the subsequent studies.

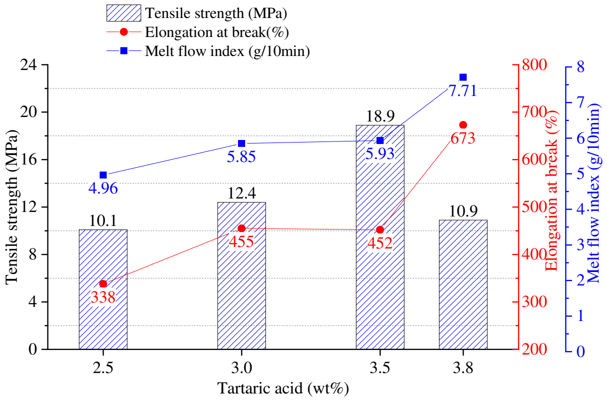
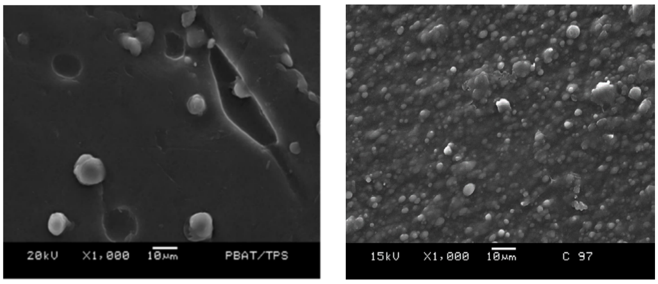


Figure 5. Effect of tartaric acid content on properties of PBAT/MTPS blend.

3.2.2. Morphology

In polymer blends, morphology is a key factor affecting the mechanical and rheological properties. To understand some of the properties of polymer blends, analyzing how the minor phase is dispersed within the continuous matrix is very important.

Cryfractured cross-section of TPS / PBAT blends with and without tartaric acid is shown in Figure 6.



(a) PBAT/TPS **(b) PBAT/MTPS**

Figure 6. SEM micrographs of PBAT/TPS and PBAT/MTPS blends.

For PBAT/TPS without tartaric acid, the blend showed a dispersed morphology in which TPS appears as dispersed particles in the PBAT matrix with a size between 5-10µm. The presence of holes in Fig. 6a after cryofracture breaking is indicative of a weak interfacial adhesion between TPS particles and the PBAT matrix, which is attributed to the different polarity between the two components. This phenomenon was also reported by Mohamed Dammak [8] when analyzing SEM images of PBAT/TPS blend without the presence of the compatibilizer.

In the presence of tartaric acid as the compatibilizer, the TPS phase was dispersed in the form of droplets with a size of about 1-5µm, and lesser particles of TPS were pulled out during the cryogenic breaking (Fig. 6b). Compared with that of PBAT/TPS, PBAT/MTPS blend presents that MTPS particles are smaller and disperse in the PBAT matrix with indistinct boundaries.

The use of tartaric acid to improve the compatibility between PBAT and TPS can be explained by the esterification reaction between tartaric acid and the hydroxyl group of TPS, reducing the hydrophilicity of TPS. On the other hand, tartaric acid acts as an acid catalyst. It reduces the viscosity of the thermoplastic starch, thus causing the denatured TPS to disperse in the PBAT in a more uniform structure. However, the excessive TA can generate higher [H+] concentration and induce the molecular weight of starch and PBAT to decline drastically and decreases the interface interaction between TPS and PBAT. This phenomenon was also reported by Shuidong Zhang when he studied to improve the compatibility between PBAT and TPS with tartaric acid [12].

3.3. Effect of screw speed on properties of PBAT/MTPS blend

The effect of screw speed on properties of PBAT/MTPS blend was shown in Table 3.

Table 3. Effect of screw speed on properties of PBAT/MTPS blend.

Screw speed (rpm)	Melt flow index (g/10 min)	Tensile strength (MPa)	Elongation at break (%)
200	5.09	17.2	380
250	5.93	18.9	452
300	6.01	18.0	495
350	8.20	**The film cannot be blown**	

The results in Table 3 show that: when the screw speed increases, the MFI of the materials tends to increase. When the screw speed increased from 200rpm to 300rpm, the MFI slightly increased from 5.09g/10min to 6.01g/10min. When increasing the screw speed from 300 to 350rpm, the MFI increased sharply from 6.01 to 8.20g/10min.

For blends made with a screw speed of 350rpm, the film cannot be blown. For blend prepared at lower speeds, the influence of the screw on the film tensile strength is insignificant. Meanwhile, elongation increases as the screw speed increases and reaches a peak of 495% at screw speed of 300rpm.

The screw speed of 300 rpm was selected in the subsequent studies.

3.4. Effect of talc content on properties of PBAT/MTPS

In this part, PBAT/MTPS blends were prepared with talc powder content changes from 0 to 6% by weight. The effect of talc content on the blend properties was shown in Figure 7.

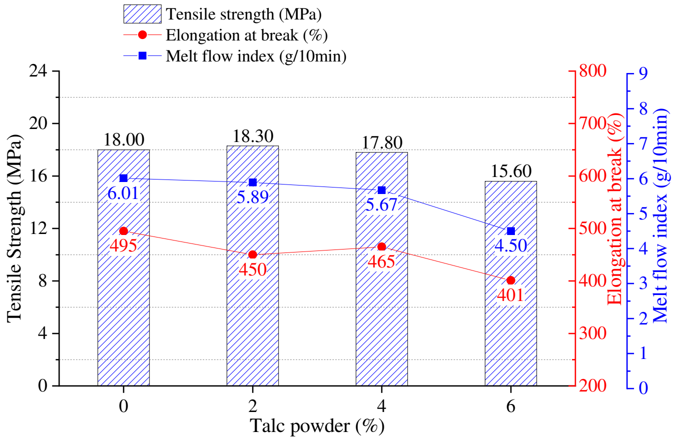


Figure 7. Effect of talc content on properties of PBAT/MTPS blends.

From the results in Figure 7, it was noticed that when the talc content in the blend increased, the MFI of the material tended to decrease. When talc powder content increased from 0 to 4%, the MFI slightly reduced from 6.01g/10min to 5.67g/10 min. Meanwhile, when the talc content increased from 4 to 6%, the MFI dropped sharply from 5.67 to 4.50g/10min. This phenomenon can be explained because talc powder interacted with the polymer matrix in the molten state and obstructed the material flow, leading to the decrease of MFI. Meanwhile, the increase in talc content from 0 to 4% did not significantly change the tensile strength and elongation of materials. When the talc content value was changed in this range, the average tensile strength ranged from 18MPa, while the elongation decreased slightly from 495% to 465%.

When the talc content value increased from 4 to 6%, the tensile properties changed drastically: tensile strength decreased from 17.8MPa to 15.6MPa, and elongation decreased from 465% to 401%.

To fabricate PBAT / MTPS film with the highest talc content without much change in properties, 4% talc powder content was chosen.

4. Conclusions

In this work, the effect of tartaric acid as a compatibilizer on the mechanical properties, morphology, and melt index of PBAT/MTPS blend has been investigated. The results of the FT-IR spectra analysis showed the formation of esterification reaction when modifying thermoplastic starch with tartaric acid with the appearance of characteristic absorption peaks of ester bonds at the wavenumber 1720cm^{-1} and 1270cm^{-1}.

The use of tartaric acid with a content of 3.5% by weight produces PBAT/MTPS blend films (60/40) with the best properties. Observing morphology through SEM images of the materials showed that the presence of tartaric acid improved the compatibility of PBAT and TPS as well as enhanced the dispersion of TPS in the blend.

The increase in screw speed and addition of talcum powder reduces the overall properties of the blend material. The research has selected the highest talc content without much change in the properties of the material at 4% by weight and 300rpm screw speed.

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