

Preparation and Characterization of PBAT/OTPS Blend Films with Epoxidized Soybean Oil (ESO) for Eco-friendly Packaging Application

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Abstract The application of starch-based films is limited by the poor water vapor barrier and mechanical properties. In this study, plasticized octenyl-succinated corn starch (OTPS) was mixed into Poly (butylene adipate-co-terephthalate) (PBAT) with various concentration (0/0.25/0.5/0.75 wt%) of epoxidized soybean oil (ESO) to enhance the mechanical properties and the hydrophobicity of blends. Tensile Strength and elongation at break of PBAT/OTPS film was slightly strengthened as the added ratio of ESO raised to 0.5 wt%, yet lessened again in 0.75 wt% sample. The yield strength and elastic modulus were highest in 0.25wt% of ESO added. In thermal properties, the melting temperature (T_m) and crystallization temperature (T_c) were highest at ESO 0.25 and the maximum degradation temperature (T_{max}) of components of the films were developed as ESO added. Also, it has been proved that the addition of hydrophobic substances reduces the hydrophilicity of the film by contact angle. This suggests the use of epoxidized oil for preparing films based on high TPS content allows obtaining enhanced interfacial adhesion. This study confirmed that ESO acts as a compatibilizer between OTPS and PBAT to improve the mechanical properties and hydrophobicity of the sample. The sample containing 0.5wt% of ESO was the most suitable for packaging application.

Keywords: biodegradable blends, OTPS/PBAT/ESO, Poly (butylene adipate-co-terephthalate), lipids

Introduction

Over the last three decades, there has been a boosted interest in reducing environmental impact of plastic waste. According to this movement, the use of environmental friendly materials in packaging materials has been a priority of packaging industry^{1,2}. Bioplastic films as alternative material to fossil-based plastics can be used to achieve sustainability. Among the various biodegradable plastics, those based on a blend of plasticized thermoplastic starch (TPS) and biodegradable polyesters are economically the most competitive³. Among them, corn starch based TPS has been steadily gained significant attentions because of its vast production. Polyesters such as PBS, PBAT, and PCL were generally used to counteract the weakness of TPS in terms of water sensitivity and poor mechanical properties⁴⁻⁶.

However, polyesters are poorly compatible with hydrophilic TPS. This limits the maximum TPS content in the blend to approximately 25-30%³. To increase the TPS content in the blends, it is necessary to use a reactive melt blending in the

presence of a compatibilizer, that covalently links the components and strongly enhances the interfacial adhesion.

Wongphan, et al.⁷ made a comparative analysis of TPS made of different modified cassava starches and PBAT blend films. Hydrophilic starch formed phase separated fibrous-like networks entangled in PBAT at higher TPS ratios, while hydrophobic octenyl-succinated starch (OS) improved compatibility and interaction with PBAT⁸. However, plasticized octenyl-succinated starch (OTPS) showed poor mechanical strength and low contact angle among the samples⁹. The source of starch influences the mechanical properties due the different amount of amylase and amylopectin. Researchers have reported strain at break of corn, cassava, and yam based starch films (28%, 46% and 25%, respectively) produced by casting with 40% of glycerol.¹⁰⁻¹¹

The addition of hydrophobic substances, such as oils and fatty acids declines the hygroscopicity due to the increase in the hydrophobic portions in the film¹⁰⁻¹². Other studies showed that the addition of lipids improves the mechanical properties and water vapor impermeability of the films due to the decrease in the size of the fat globules, resulting in the more compact structure, prevention of phase separation and advance in hydrophobicity.¹³⁻¹⁴

Epoxidized soybean oil (ESO) is an abundant and renewable raw material. Adding ESO to starch films is widely

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known as an excellent alternative to enhancing the mechanical strength and hydrophobicity of films. In this work, TPS was blended with PBAT at a weight ratio of 60/40 in the presence of different concentration of epoxidized soybean oil (ESO) by internal mixer, and the mechanical, thermal properties, FT-IR, contact angle were investigated. This study highlights the effects of ESO on the mechanical properties and hydrophilicity of OTPS/PBAT blend films.

Materials and Methods

1. Materials

Octenyl-succinated corn starch (OS) (Sunfree H, Samyang, Korea) had 7.62% of moisture, pH 6.78, DS 0.009, and 3.4 ppm of SO₂. PBG7070 grade PBAT (Ankor Bioplastics, Korea) possesses average molecular weight (M_w) 162,000 g/mol, density 1.2 g/cm³, and melting point (T_m) 125°C. Epoxidized soybean oil (ESO) was purchased at Sigma-Aldrich, which contains 4000 ppm of monomethyl ether hydroquinone as inhibitor. And the glycerol was from Daejung Chemicals, Korea.

2. Film preparation

The OS was pre-mixed with water and glycerol at a weight proportion of 60/20/20 and processed under the conditions of 150°C, 50rpm, for 8~9mins, using a kneader (TO-200, TEST ONE, Korea) for thermo-plasticization. The mixing chamber was filled with 70 g total mass for all experiments. Then the manufactured OTPS were granulated. A kneader (TO-200, TEST ONE, Korea) was used for the blending. The weight ratio of OTPS and PBAT was fixed at 60/40. OTPS/PBAT blends were prepared that contained ESO in the amounts described in **Table 1**. The kneading process was conducted under the temperature of 170°C, screw speed of 50rpm, for 8~9 mins. After kneading, films ranging 130-180 µm in thickness were produced using a hot press (QM900A, QMESYS, Korea) set at 180°C.

3. Mechanical properties

Mechanical properties including tensile strength (TS), elongation at break (EB), yield strength (YS) and elastic modulus (EM) were derived following ISO 527-3, using an universal testing machine (UTM) (GM100T, QMESYS, Korea). The 10 kN load cell was used, and the gauge length was 85 mm.

Table 1. Sample compositions with PBAT, OTPS, and ESO

	PBAT content (%)	OTPS content (%)	ESO content (phr)
ESO 0	60	40	-
ESO 0.25	60	40	0.25
ESO 0.5	60	40	0.5
ESO 0.75	60	40	0.75

4. Thermal Properties Analysis

The thermal properties of the samples were studied using differential scanning calorimetry (DSC) (Q-20, TA Instruments, USA). All specimens were heated at 20°C/min and scanned several times in the range of -50 to 200°C under nitrogen conditions. The thermal degradation properties of each blend were analyzed using thermogravimetric analysis (TGA 4000, PerkinElmer, USA). Approximately 10 ± 1 mg of each specimen was heated from 30°C to 800°C at a rate of 20°C/min under a nitrogen environment.

5. Fourier transform infrared spectroscopy (FT-IR)

The Fourier-transform infrared (FT-IR) absorption spectra of all specimens were recorded using an FT-IR spectrometer (Spectrum 65, PerkinElmer, USA) in the range of 400-4000 cm⁻¹ under ambient conditions. The spectral resolution was 2 cm⁻¹, and all specimens were scanned 64 times.

6. Contact Angle Analysis

The contact angles were determined using a contact angle tester (FEMTOFAB SDSTEZD, FEMTOFAB, KOREA). A syringe was used to place a drop of distilled water (10 µL) on the film surface, and the contact angle images were analyzed using SMARTDROP software. The effect of PEO content on the hydrophilicity of the blend films was analyzed by the change in the contact angle. Contact angles were measured at five spots on each surface to obtain average data and standard deviation values.

Result & Discussion

1. Mechanical Property Analysis

Films without ESO showed relative low mechanical property values. Also, standard deviations of the values were slightly high. This may be explained that films composed of residual

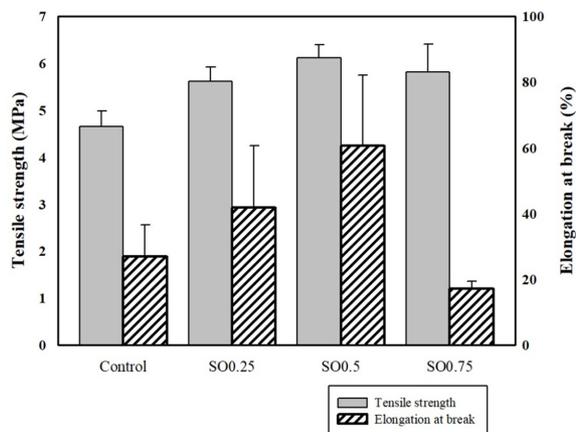


Fig. 1. Tensile strength (TS), elongation at break (EB) of PBAT (60%) and OTPS (40%) blend films with various ESO contents.

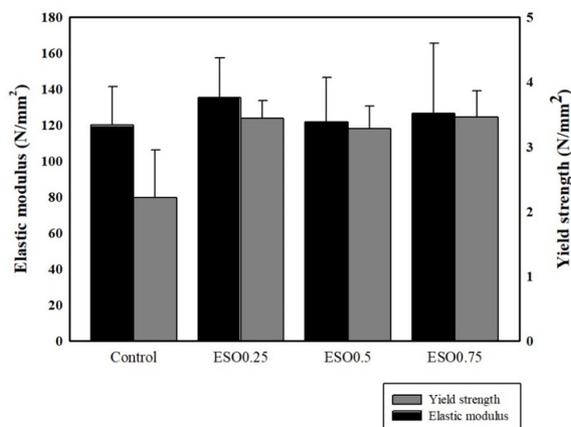


Fig. 2. Elastic modulus (EM), yield strength (YS) of PBAT (60%) and OTPS (40%) blend films with various ESO contents.

starch granules, partially melt, completely molten starch, and recrystallized starch which influenced the homogeneity of film networks and strength of the matrices¹⁵. Control sample gave the least TS (5.5 N/mm²), YS (2.2 N/mm²) and EM (119.9 N/mm²), indicating the lowest strength of the films. In the other words, films of TPS/PBAT added with ESO showed higher mechanical properties than control films. ESO 0.25 films showed slightly higher YS and EM values compared to other samples, but the differences are not statistically significant. ESO 0.5 sample presented the highest TS and EB. Flexibility of the films greatly improved up to 60% of EB values with ESO 0.5. However, ESO 0.75 gave the least EB (17.2%), even lower than control films. This tendency can be explained that the additive may facilitate the presence of glycerol between the starch chains, increasing their mobility, being the effect verified only when the minor amounts of ESO was used.¹⁶⁻¹⁸ The effect of ESO on the mechanical properties of

the films was probably caused by the transaction of the carboxylic groups of the fatty acids in the ESO with the rings of the PBAT and starch, as it was displayed in the infrared spectra (Fig. 4).⁷

2. Thermal Properties Analysis

2.1. Differential Scanning Calorimetry (DSC)

DSC analysis was carried out to investigate the thermal behaviors of the films and the results were displayed in Figure 3 and Table 2. As the ESO content elevated, the glass transition temperature (T_g) of the film slightly decreased. This attributed to the reduced cross-linking density of the epoxy network of PBAT, as the unreacted ESO acting as a plasticizer¹⁹. On the other hand, the melting temperature (T_m) and crystallization temperature (T_c) were the highest at ESO 0.25, and the values went down as the ESO content increased. This phenomenon indicates that the addition of ESO into the blends retards the crystallization because of the feature of internal epoxy groups and the low reactivity of ESO²⁰. This can be also explained by the result of FT-IR spectra. A low-intensity peak assignable to C-O stretching of the epoxide at 935 cm⁻¹ was observed to be moderately smoothed. This occurrence also correlated with the enhanced YS and EM values at ESO 0.25.

Table 2. Thermal properties of the PBAT/OTPS blends with various ESO contents

	Control	ESO 0.25	ESO 0.5	ESO 0.75
T_m (°C)	129.6	131.4	129.3	128.9
T_c	70.4	85.6	72.4	73.1
T_g	-27.2	-28.0	-28.2	-27.2
T_{max} (OTPS)	321.2	327.9	329.9	329.4
T_{max2} (PBAT)	411.7	418.5	418.0	420.5

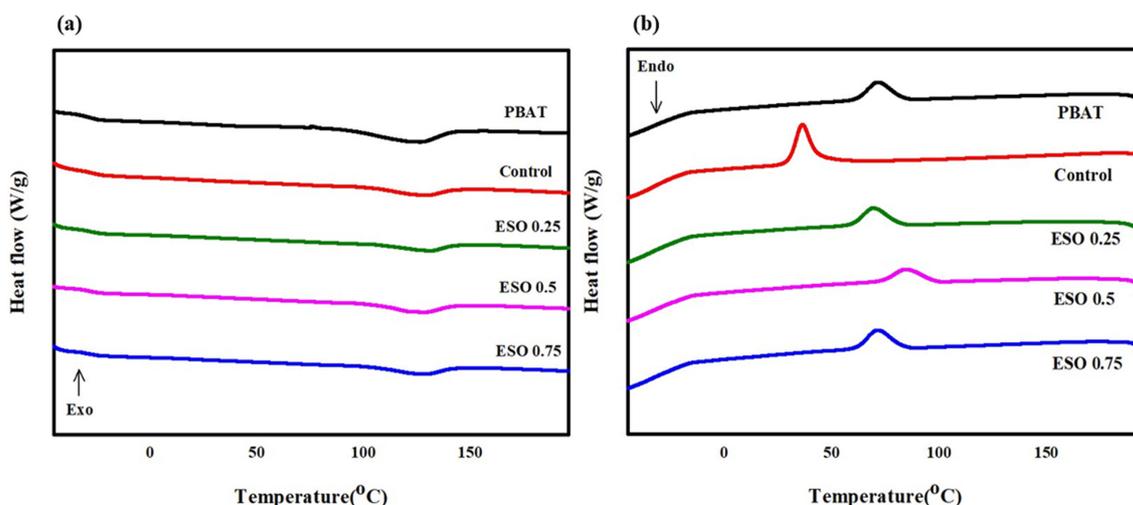


Fig. 3. DSC thermal properties of neat PBAT and blend samples prepared with various ESO contents; heating (a) and cooling (b) curves.

2.2. Thermogravimetric Analysis (TGA)

Investigated TGA results were shown in Table 2. PBAT/OTPS films had four steps of weight loss corresponding with the volatilization and degradation of water, glycerol, starch and PBAT⁷⁾. T_{max} of the samples risen compared to the control samples as ESO added. This tendency suggests an advance in thermal stability of PBAT/OTPS films through ESO addition. This also may be related to the fact that ESO provides a physical barrier that hinders the removal of volatile products produced during decomposition.²¹⁾

2. Fourier transform infrared spectroscopy (FT-IR)

The spectra of the films prepared with PBAT/OTPS blends are shown in Figure 4(a), and the detailed spectra focusing on specific regions are shown in Figure 4(b). The films with ESO displayed more intense peaks in the region of 1711 and 1264 cm^{-1} , which represents the presence of C-O and C=O groups of ester bonds, and C-O groups bonded to the starch rings, respectively^{16,22,23)}. The presence of ESO in the films was appeared as an augment in these peaks. The carbonyl group of ester bonds interacts with the hydroxyl group of starch through weak hydrogen-mediated interactions. In addition, due to the similarity of polarity, there is a hydrophobic interaction between the oil and the polyester. By these interactions, the result indicates that there was an enhancement in C-O groups bonded to the glucose ring⁷⁾. Therefore, the surface adhesion of the films is gained by the addition of the effects of various weak interactions.

Increasing ESO content weakened peaks in the region of 995 cm^{-1} , which indicates water sensitivity of matrix due to H bonds. This shows the reinforced hydrophobicity of the films with the addition of ESO²⁴⁾. Moreover, all the ESO treated specimens were displayed more intense bands and peaks in the 1730-1710 cm^{-1} and 1020 cm^{-1} regions, and the ESO 0.5 films displayed the greatest intensity of peaks and bands in

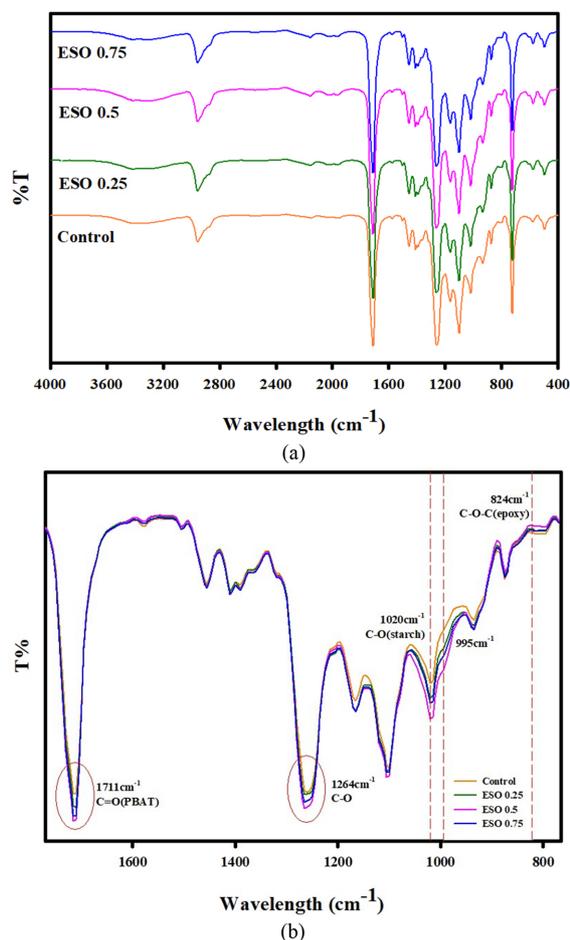


Fig. 4. (a) The infrared spectra obtained for PBAT/OTPS blend films., (b). The enlarged FT-IR spectra of PBAT/OTPS blend films.

these spectral regions. Reversely, the ESO 0.5 films exhibited the weakest bands and peaks in the 1455-1450 cm^{-1} , 1410-1338 cm^{-1} , and 824 cm^{-1} regions. The intensity ratio at 1730-

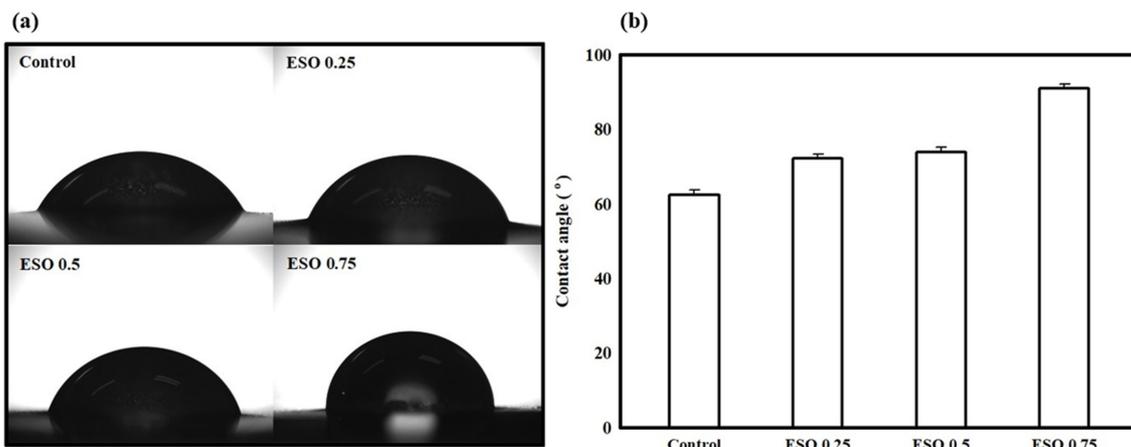


Fig. 5. Contact angle changes of PBAT (60%) and OTPS (40%) blend films at various ESO contents (a) water droplets on each specimen (b) contact angle values.

1711 cm^{-1} represents crystalline fraction of PBAT phase.⁷⁾

The intensity of the peak at 824 cm^{-1} explains the C-O-C stretching of epoxide groups and peaks at 1410-1338 cm^{-1} are attributed to O-H bending, and they suggest the reduced hydrophilicity²³⁾.

4. Contact Angle Analysis

The contact angle aggrandized as the ESO content raised (Figure 5). As shown in Figure 5a, 10 μL of distilled water droplets maintained a cohesive form as the ESO content heightened owing to an enlargement in the surface hydrophobicity. It can be seen that the contact angle (CA) is 63.8° for Control and gradual increases were observed in CA to 91° with increasing ESO contents. An increase in CA indicates an improvement in the hydrophobic properties of the surface and a lower value of the polar component of the surface energy²⁵⁾. This effect agreed with our FT-IR results²⁶⁾. Ring-opening condensation reaction between the epoxide groups of ESO and hydroxyl groups of starch and glycerol was observed in the spectra.

Conclusion

PBAT/OTPS blend films with added ESO exhibit advanced mechanical properties and hydrophobicity of the films through polymer interactions, compatibility, and crystalline fractions of film phase. YS and EM were toughest at ESO 0.25, while TS and EB were greatest at ESO 0.5 in mechanical properties. This is consistent with higher T_m and T_c of ESO 0.25 in DSC results. The infrared spectra revealed the declined characteristic peak indicating stretching C-O-C of the epoxide group and intensified crystalline fraction of PBAT phase of the films. These effects were greatest in ESO 0.5 films. Moreover, evidence of ring-opening condensation reaction between the epoxide groups of ESO and hydroxyl groups of starch and glycerol was confirmed using FT-IR. The presence of ESO improves the mechanical properties and hydrophobicity. Effects of ESO as a compatibilizer between PBAT and OTPS is related to the expansion in groups that are characteristic of ester bonds and groups that are bonded to the glucose ring. Therefore, ESO multiplies the interactions among the polymeric fractions and improving the diverse properties by enhancing the adhesion of the films. Accordingly, adding 0.5 wt% of ESO would be most desirable for packaging application of PBAT/OTPS blends.

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References

1. Krogars, K., Heinämäki, J., Karjalainen, M., Rantanen, J., Luukkonen, P., and Yliruusi, J. 2003. Development and characterization of aqueous amylose-rich maize starch dispersion for film formation. *Eur. J. Pharmaceutics & biopharmaceutics*, 56(2): 215-221.
2. Jang, H.H., and Park, S.I. 2020. Effects of PEO additions on the mechanical and thermal properties of PLA/PBAT blends. *Korean Journal of Packaging Science & Technology*, 26(2): 93-98.
3. Fourati, Y., Tarrés, Q., Mutjé, P., and Boufi, S. 2018. PBAT/thermoplastic starch blends: Effect of compatibilizers on the rheological, mechanical and morphological properties. *Carbohydrate polymers*, 199: 51-57.
4. Jang, S.H., and Park, S.I. 2010. Mechanical Properties and Degradability of Modified Starch and Polyethylene Blends. *Korean Journal of Packaging Science & Technology*, 16(2): 59-65.
5. Seligra, P.G., Moura, L.E., Famá, L. J., Druzian, I. and Goyanes, S. 2016. Influence of incorporation of starch nanoparticles in PBAT/TPS composite films. *Polymer International*, 65(8): 938-945.
6. Tavares, L.B., Ito, N.M., Salvadori, M.C., Dos Santos, D.J. and Rosa, D.S. 2018. PBAT/kraft lignin blend in flexible laminated food packaging: Peeling resistance and thermal degradability. *Polymer Testing*, 67: 169-176.
7. Wongphan, P., Panrong, T. and Harnkarnsujarit, N. 2002. Effect of different modified starches on physical, morphological, thermomechanical, barrier and bio-degradation properties of cassava starch and polybutylene adipate terephthalate blend film. *Food Packaging and Shelf Life*, 32: 100844.
8. Lauer, M.K., Tennyson, A.G. and Smith, R.C. 2022. Thermomorphological and mechanical properties of vulcanized octenyl succinate/terpenoid-derivatized corn starch composites. *Materials Advances*, 3(10): 4186-4193.
9. Liu, Z., Liu, X., Cao, Y., Xie, W., Ma, X. and Yu, X. 2013. Edible starch sodium octenyl succinate film formation and its physical properties. *Journal of applied polymer science*, 127(4): 2922-2927.
10. Mali, S., Grossmann, M.V.E., García, M.A., Martino, M. N. and Zaritzky, N.E. 2006. 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.
11. Garcia, M.A., Martino, M.N. and Zaritzky, N.E. 2000. Lipid addition to improve barrier properties of edible starch-based films and coatings. *Journal of food science*, 65(6): 941-944.
12. Kester, J.J. and Fennema, O.R. 1986. Edible films and coatings: a review. *Food Technology*, 40(12): 47-59.
13. Debeaufort, F. and Voilley, A. 1995. Effect of surfactants and drying rate on barrier properties of emulsified edible films. *International journal of food science & technology*, 30(2): 183-190.

14. Pérez-Gago, M.B. and Krochta, J.M. 2001. Lipid particle size effect on water vapor permeability and mechanical properties of whey protein/beeswax emulsion films. *Journal of agricultural and food chemistry*, 49(2): 996-1002.
15. Wadausorn, K., Panrong, T., Wongphan, P. and Harnkarnsujarit, N. 2022. Plasticized hydroxypropyl cassava starch blended PBAT for improved clarity blown films: Morphology and properties. *Industrial Crops and Products*, 176: 114311.
16. Brandelero, R.P.H., Grossmann, M.V. and Yamashita, F. 2012. Films of starch and poly (butylene adipate coterephthalate) added of soybean oil (SO) and Tween 80. *Carbohydrate Polymers*, 90(4): 1452-1460.
17. Rodrigues, M., Osés, J., Ziani, K. and Maté, J.I. 2006. Combined effect of plasticizer and surfactants on the physical properties of starch based edible film. *Food Research International*, 39(5): 840-846.
18. Liu, Z., Erhan, S. Z., and Xu, J. 2005. Preparation, characterization and mechanical properties of epoxidized soybean oil/ clay nano composites. *Polymer*, 46(23): 10119-10127.
19. Park, S.J., Jin, F.L. and Lee, J.R. 2004. Thermal and mechanical properties of tetrafunctional epoxy resin toughened with epoxidized soybean oil. *Materials Science and Engineering: A*, 374(1-2): 109-114.
20. Ratna, D., and Banthia, A.K. 2000. Epoxidized soybean oil toughened epoxy adhesive. *Journal of Adhesion Science and Technology*, 14(1): 15-25.
21. Ibáñez, A., Ferrándiz, S., & Martínez, A. 2021. The effect of different epoxidised vegetable oils on injection-moulded starch based thermoplastic polymer filled with almond shell powder. In *IOP Conference Series: Materials Science and Engineering*, 1193(1): 12015.
22. Seligra, P.G, Moura, L.E., Famá, L., Druzian, J. I. and Goyanes, S. 2016 . Influence of incorporation of starch nanoparticles in PBAT/TPS composite films. *Polymer International*, 65(8): 938-945.
23. Tee, Y.B., Talib, R.A., Abdan, K., Chin, N.L., Basha, R.K., and Yunos, K.F.M. 2016. Comparative study of chemical, mechanical , thermal , and barrier properties of poly (lactic acid) plasticized with epoxidized soybean oil and epoxidized palm oil. *BioResources*, 11(1): 1518-1540.
24. Zullo, R. and Iannace, S. 2009. The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure. *Carbohydrate Polymers*, 77(2): 376-383.
25. Yuan, Y., & Lee, T. R. 2013. Contact angle and wetting properties. In *Surface science techniques*, 51: 3-34.
26. Kijchavengkul, T., Auras, R. and Rubino, M. 2008. Measuring gel content of aromatic polyesters using FTIR spectrophotometry and DSC. *Polymer Testing*, 27(1): 55-60.

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