

Thermal and Mechanical Properties of Poly(butylene succinate) Films Reinforced with Silica

Nanthaporn Sangviroon¹ and Pranut Potiyaraj^{2,a}

¹ *Interdisciplinary Program in Petrochemistry & Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*

² *Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*

Abstract. In recent year, bioplastics have become more popular resulting from the growing concerns on environmental issues and the rising fossil fuel price. However, their applications were limited by its mechanical and thermal properties. The aim of this research is thus to improve mechanical and thermal properties of PBS bioplastic films by reinforcing with silica. Due to the poor interfacial interaction between the PBS matrix and silica, glycidyl methacrylate grafted poly(butylene succinate) (PBS-g-GMA) was used as a compatibilizer in order to improve the interaction between bioplastic films and filler. PBS-g-GMA was prepared in a twin-screw extruder and analyzed by the FTIR spectrometer. PBS and silica were then mixed in a twin-screw extruder and processed into films by a chill-roll cast extruder. The effects of silica loading on thermal and mechanical properties of the prepared bioplastic films were investigated. It was found that the mechanical properties of PBS/silica composite films were improved when 1%wt of silica was added. However, the mechanical properties decreased with increasing silica loading due to the agglomeration of silica particles. The results also show that the silica/PBS films with PBS-g-GMA possessed improved mechanical properties over the films without the compatibilizer.

1 Introduction

Nowadays, biodegradable polymeric materials attract much more attention due to the fact that plastic waste has caused serious environment pollution. Poly(butylene succinate) or PBS is an aliphatic biodegradable polyester which is now commercially available. PBS is synthesized by polycondensation of succinic acid with 1,4-butanediol. It is possible that the raw materials were synthesized from renewable resources rather than petrochemical products. Despite its good processability and chemical resistance, its softness and poor barrier gas thus limit the applications of PBS [1].

Some researchers have thus attempted to improve properties of PBS by mixing with reinforcing filler i.e. carbon black, organoclay, or silica. However, it is difficult to disperse the filler particles in polymer matrix homogeneously because filler particles have strong tendency to agglomerate, which is caused by the poor interaction between filler particles and polymer matrix, resulting in reduced mechanical properties.

One way to overcome these drawbacks and to prepare materials with enhanced properties is to incorporate a compatibilizer in order to enhance the dispersibility of filler particles and improve interfacial adhesion between filler particles and polymer matrix.

Glycidyl methacrylate grafted polymers have been used as compatibilizers in some previous research because of its epoxide functional groups, which is highly electrophile and capable of reacting with a variety of functional groups such as carboxylic acids, amides, and alcohols [2].

^a pranut.p@chula.ac.th

In this study, PBS-g-GMA was prepared by the reactive melt-grafting extrusion method. Then composites were processed into films by a chill roll cast extruder. The effects of PBS-g-GMA and silica loading on thermal and mechanical properties of PBS/silica composite films were investigated.

2 Experimental

2.1 Materials

PBS granules (GS PLATM FZ91PD) were of film grade purchased from Mitsubishi Chemical. Silica (ULTRASIL[®] 9000 GR) was kindly supported by Evonik with a specific surface area of 235 m²/g and an average particle size of 13.3 μm. Dicumyl peroxide (DCP) (Sigma Aldrich) was used as an initiator and glycidyl methacrylate (GMA) (Sigma Aldrich) was used as a reagent without further purification.

2.2 Preparation of PBS-g-GMA

Firstly, PBS, GMA and DCP were physically premixed. The reactive grafting process was carried out in a twin-screw extruder (Prism TSE 16 TC, Thermo, UK) at 140°C with the screw speed of 30 rpm. The amount of GMA and DCP used were fixed at 10 and 2 phr. respectively. The degree of grafting of GMA onto PBS is 2.95 % as determined through the titration method.

2.3 Preparation of Composite Films

PBS, PBS-g-GMA pellets and silica were initially dried in the oven at 60°C for 24 h prior to further processing. Polymers were physically premixed at the ratios shown in Table 1. and melt-mixed in a twin-screw extruder at 160°C with a screw speed of 30 rpm. Then, the pelletized compounds were dried in the oven at 60°C for 24 h before casting into film by chill-roll cast extruder (LCR-300HDCO-EX, Labtech Engineering, Thailand). The PBS and its composite films were around 0.10-0.15 mm in thickness.

3 Characterization

3.1 FT-IR analysis

The Fourier transform infrared spectroscopy analysis was carried out on the PBS-g-GMA at ambient temperature by using a Perkin-Elmer One FT-IR Spectrometer (USA). It was performed through the scanning wavenumber from 4000 to 400 cm^{-1} with 64 scanning times.

3.2 Mechanical Testing

Tensile properties that are tensile strength, tensile modulus and elongation at break were measured according to ASTM D882 using a Universal Testing Machine (LLOYD LR100K, West Sussex, UK) with a gauge length of 125 mm and using the cross head speed of 12.5 mm/min and a 100 N load cell. The tear strength was measured according to ASTM D1938 using a Universal Testing Machine (LLOYD LR100K, West Sussex, UK) with the cross head speed of 250 mm/min. and a 100 N load cell.

3.3 Thermal Testing

The differential scanning calorimetry (DSC) analysis was carried out using METTLER TOLEDO DSC-1 machine (Switzerland) in a nitrogen atmosphere. Samples of 2 mg were used for every new measurement. Sample was heated from -50°C to 150°C at a heating rate of 5°C/min. The sample was then cooled from 150°C to -50°C at a same heating rate. The second heating was performed from -50°C to 150°C. Finally, it is cooled to -50°C.

Table 1. Composition of PBS composite compounds.

Sample (%wt)	PBS	PBS-g-GMA	Silica
PBS	100	-	-
PBS/G5	95	5	-
PBS/S1	99	-	1
PBS/S2	98	-	2
PBS/S3	97	-	3
PBS/G5/S1	94	5	1
PBS/G5/S2	93	5	2
PBS/G5/S3	92	5	3

4 Results and Discussion

4.1 FT-IR spectra

FTIR spectra for neat PBS and PBS-g-GMA are shown in Figure 1. Two extra shoulders characteristic of ester carboxyl groups were observed at 1,731 cm^{-1} in the modified PBS-g-GMA spectrum. The shoulders represent free acid in the modified polymer PBS-g-GMA and thus indicated the successful grafting of GMA onto PBS [3].

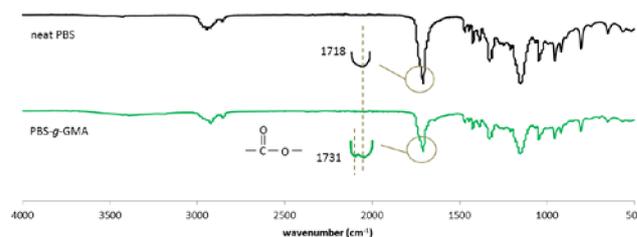


Figure 1. FT-IR spectra of neat PBS and PBS-g-GMA after purification

4.2 Mechanical Testing

The mechanical properties including tensile strength, Young's modulus, elongation at break and tear strength of PBS and its composite films were displayed in Figure 2. The PBS and its composite films were tested along in the machine direction (MD) and in the transverse direction (TD).

For the composite films without PBS-g-GMA, the tensile strength and tensile modulus increased with the addition of 1%wt of silica. However, as then amount of silica increased, tensile strength and tensile modulus were reduced. The elongation at break of composite films was lower than neat PBS at every ratio. Due to the aggregation of silica particles, interfacial adhesion between silica particles and PBS was weakened thus contribute to crack propagation and hence potential composite failure [4]. When the PBS-g-GMA was incorporated, tensile strength, tensile modulus as well as elongation at break of composite films were higher than those of neat PBS film.

The tear strength of composite films was lower than that of neat PBS film except for the films with 1%wt silica which possessed a slightly higher tear strength comparing with neat PBS. The addition of PBS-g-GMA can improve interfacial adhesion by improving interfacial interaction between silica particles and PBS matrix, hence PBS phase can be transfers stress to silica particles resulting increased mechanical properties [5].

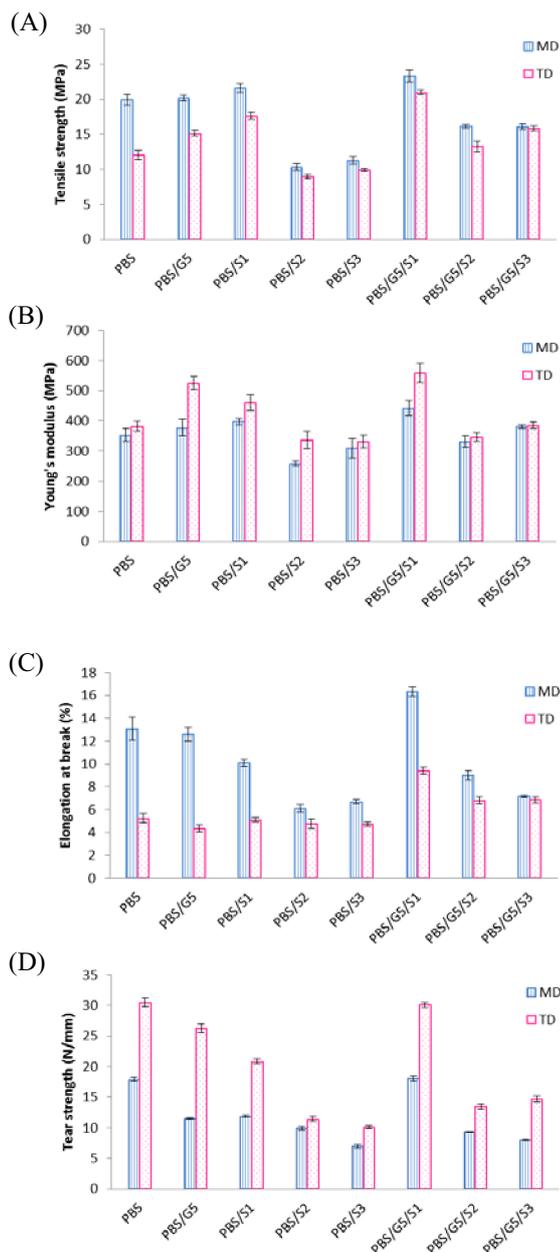


Figure 2. Mechanical properties of PBS and their composite films. (A) Tensile strength, (B) Young’s modulus, (C) Elongation at break and (D) Tear strength.

4.3 Thermal Testing

Thermal behavior of PBS and its composites are shown in Table 2. The temperature was evaluated from the second scan to ensure the results because the first heating is to eliminate the thermal history in the samples. Shinha Ray *et al.* [6] reported that two different types of crystalline lamella are presented in PBS. The lower melting temperature (T_{m1}) is related to the original crystallites melting while the higher melting temperature (T_{m2}) corresponds to the recrystallized crystals melting.

From the results, it was observed that the lower melting temperature, crystallization temperature (T_c) and degree of crystallinity (x_c) slightly increased with the presence of PBS-*g*-GMA as a compatibilizer. This may be due to the improved interaction between PBS and

silica. For the composite films without PBS-*g*-GMA, it shows that x_c increased with the addition of 1%wt of silica because silica acted as a nucleating agent, and then decreased by increasing the silica content possibly due to aggregation of silica particles, thus resulting in slowing down of the mobility of PBS chains [7].

Table 2. Melting and crystallization behavior of PBS and its composite films.

Sample	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	x_c (%)
PBS	92.6	106.2	114.3	57.4
PBS/G5	93.1	106.9	114.6	57.3
PBS/S1	88.5	103.5	114.4	58.9
PBS/S2	89.0	103.3	114.5	54.9
PBS/S3	88.9	103.5	114.7	55.8
PBS/G5/S1	94.9	107.4	114.4	69.6
PBS/G5/S2	94.7	107.5	114.8	67.4
PBS/G5/S3	94.9	106.8	114.0	66.4

5 Summary

PBS/silica composite films were prepared at various ratios of the filler and their mechanical properties were investigated. It was found that the mechanical properties of PBS/silica composite films were improved when 1%wt of silica was added. However, the mechanical properties decreased with increasing silica loading due to the agglomeration of silica particles. The results also show that improvements in the mechanical properties were obtained when PBS-*g*-GMA was used as a compatibilizer as the filler dispersion and filler-matrix interfacial interactions. DSC measurements revealed that PBS-*g*-GMA had little influence on the crystallization and melting behavior of PBS/silica composite films.

Acknowledgement

This research has been supported by the Ratchadaphiseksomphot Endowment Fund 2013 of Chulalongkorn University (CU-56-416-AM).

References

1. J. Bian, L. Han, X. Wang, X. Wen, C. Han, S. Wang, L. Dong, *J. Appl. Polym. Sci.* **116**, 902 (2010)
2. N. Papke, J. Karger-Kocsis, *J. Appl. Polym. Sci.* **74**, 2616 (1999)
3. C.S. Wu, H.T. Liao, J.J. Jhang, *Polym. Bull. Vol.* **70**, 3443 (2013)
4. S.I. Han, J.S. Lim, D.K. Kim, M.N. Kim, S.S. Im, *Polym. Degrad. Stab.* **93**, 889 (2008)
5. Z. Xiuju, S. Juncai, Y. Huajun, L. Zhidan, T. Shaozao, *J. Thermoplast. Compos. Mater.* **24**, 735 (2011)
6. S.S. Ray, M. Bousmina, K. Okamoto, *Macromol. Mater. Eng.* **290**, 759 (2005)
7. Y.J. Phua, W.S. Chow, Z.A. Mohd Ishak, *Polym. Eng. Sci.* **53**, 194 (2013)