Effects of dicumyl peroxide on cell formation of biopolymer blend-activated carbon composite foams

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Abstract. Immiscible biopolymer blends of polylactic acid (PLA) and polybutylene succinate (PBS) with a weight ratio of 80/20 were compatibilized by different concentrations (0, 0.1, 0.3 and 0.5 parts per hundred resin (phr)) of dicumyl peroxide (DCP) in the presence of 3 phr of activated carbon (AC). Influences of DCP on the melt rheology at foaming temperature, cell formation and morphology and foam properties of PLA-PBS-AC composites using 5 phr of azodicarbonamide (ADC) as a blowing agent were reported. It was found that the melt viscosity, relating to the melt flow index (MFI) of PLA-PBS-AC composite foams increased with increasing DCP loadings due to more compatibility between PLA and PBS. Closed cells with thick cell walls were obtained with the addition of DCP. Also, the cell size and cell density tended to decrease by DCP adding since lower cell expansion and coalescence occurred at higher polymer surface tension. The crystallinity ($X_c$) and thermal properties of PLA and PBS in composite foams were almost unchanged when DCP was filled in the system. The PLA-PBS-AC composite foam having 0.3 phr of DCP provided the lowest foam density ($\rho_f$) and the highest void fraction ($V_f$) of 0.5766 g cm\textsuperscript{-3} and 54\% respectively.

1. Introduction
At these days, polymer foam packaging is seriously susceptible to environmental and disposal problems since it is not feasibly available to economically recycling process owing to high cost of the waste management. Furthermore, most of based polymers are not biodegradable, resulting in a major concern in terms of sustainability, ecology and recyclability, especially for the single-use packaging. Therefore, a requirement for the utilization of bio-based and/ or biodegradable materials in foam packaging has been extensively gained attention in order to efficiently mitigate the composting issue, nevertheless maintains all existing polymer foam properties and performances as specified. PLA is classified as a bio-based and biodegradable aliphatic polyester which has great potential to be utilized as a replacement material for typical polymers, derived from petroleum-based substances. However, it is too hard and brittle for use in packaging applications. Thus, its toughness is usually developed by mixing with PBS since PBS is another biodegradable polymer, having excellent toughness and high chemical resistance [1-3]. In addition, the compatibility between PLA and another polymer is an absolutely crucial issue to obtain the required level of properties and performances from their blends. Therefore, the compatibilizer was usually consumed in the melt blending to ameliorate the properties of polymer blends such as melt rheology, morphology and physical and mechanical properties. In the previous work, triphenyl...
phosphite was utilized as a reactive compatibilizer in PLA/poly (ε-caprolactone) (PCL) blends which obviously exhibited the improvement of the elasticity of blends [4]. Moreover, the PLA/poly(butylene adipate-co-terephthalate) (PBAT) blend was prepared with the filling of glycidyl methacrylate (GMA) as a compatibilizer for the reactive blending. The obtained results revealed that the toughness of such blends increased together with the improvement of other properties such as melt rheology, topology and miscibility [5]. The reactive blends of PLA and PBS were fabricated using DCP performed as a radical initiator in the extrusion process [6]. The DCP loadings of 0.2 and 0.3 phr exhibited the appropriate beneficial on mechanical properties. Furthermore, the enhancement of PLA and poly (ethylene terephthalate glycol-modified) (PETG) compatibility was reported by employing epoxy-based compatibilizer [7]. The cell structure of PLA/PETG foams was great uniformity with small pores and large expansion ratio at a suitable compatibilizer dosage in the blends.

Hence, the objective of this study was to prepare composite foams containing PLA, PBS and AC with the addition of DPC via a reactive melt extrusion process. The effect of DCP on melt rheology through MFI measurement, relating to the bubble creation and morphology and foam properties of composite foams was investigated. The Xc as well as thermal properties of PLA and PBS in composite foams were also determined.

2. Experimental procedures

2.1. Raw materials

PLA (2003D) and PBS (FZ91PM) with the MFI of 6 and 5 g (10 min)\(^{-1}\) respectively were supplied from BC Polymer Marketing Co., Ltd., Thailand. AC (CGC-11A 200C) was purchased from Gigantic Carbon Co., Ltd., Thailand, possessing average surface area and particle size of about 1050 m\(^2\) g\(^{-1}\) and 74 µm respectively. ADC (Sunfoam SB00P) with particle size around 10 µm obtained from Lautan Luas (Thailand) Co., Ltd., Thailand was used as an exothermic blowing agent in the foaming process. An antioxidant (Annox 20) and chain extender (Joncryl ADR4370) received from Optimal Tech Co., Ltd. and Merit Solution Co., Ltd. Thailand respectively were also filled in the system. DCP received from Sigma-Aldrich was used as a compatibilizing agent.

2.2. Melt mixing and sheet extrusion processes

Polymer composites containing various DCP dosages at 0, 0.1, 0.3 and 0.5 phr were prepared at selected PLA:PBS ratio and ADC and AC concentrations of 80:20 wt%, 5 phr and 3 phr respectively, based on our previous work [8]. The amount of antioxidant and chain extender were maintained at 0.5 and 0.7 phr respectively. Aforementioned components were dry blended in a plastic bag prior to the melt mixing process using twin screw extruder (LTE20-32, Labtech Engineering Co., Ltd., Thailand). The screw diameter, screw length and screw L/D ratio were 20 mm, 64 cm and 32 respectively. The mixing screw and die temperatures were set up in the range of 130-180°C. The speeds of feeding and mixing screws were 12 and 80 rpm respectively. The prepared composite was dried at 80°C for 12 h until the moisture content was about 0.02% and then kept in an aluminum packaging. Afterward, the composite foam sheet was fabricated using a single screw extruder with L/D ratio of 25 (HAAKE Rheomex, LMS Instruments Co., Ltd., Thailand) at 220°C with a screw speed of 200 rpm. The thickness of composite foam sheet was controlled by using rollers with a rolling speed of 35 rpm at room temperature.

2.3. Characterizations

The \(\rho_f\) of 1 cm \(\times\) 1 cm foam sheets was analyzed by helium gas displacement method using an automatic gas pycnometer (Ultrapyc 1200e, Science Engineering and Service Co., Ltd., Thailand) at 17.0 psi and 30°C. The \(V_f\) was determined by using equation (1) from the average density of PLA and PBS resins (\(\rho_p\)) and the density of foam samples (\(\rho_f\)).
The cell topology was detected by using a Schottky field-emission scanning electron microscope (SEM, SU5000, Coax Group Corp. Ltd., Thailand). The specimen was immersed in liquid nitrogen for ease of fractured surface preparation. Then, the platinum was coated on the sample surface by sputtering deposition. The Image J software was utilized to determine the bubble dimension and cell density based on SEM micrographs. The cell density per unit area of composite foams was calculated by using equation (2).

\[ V_r = 100 \times \left[ 1 - \frac{\rho_f}{\rho_p} \right] \]  

where \( A \) is the area of the SEM image (cm\(^2\)), \( n \) is the quantity of cells in the SEM picture, \( \rho_p \) is the average density of PLA and PBS resins and \( \rho_f \) is the density of the composite foam. The MFI was characterized using a melt flow indexer (Davenport model 10, Lloyd Instruments, Thailand), following ASTM D1238 at 220°C with an applied load of 2.16 kgf. The \( X_c \) and thermal properties of PLA, PBS in composites were obtained from thermograms using a differential scanning calorimeter (DSC, Mettler Toledo (Thailand) Ltd.) under N\(_2\) flow. The sample was firstly heated from -60 to 200°C at a scanning rate of 10°C min\(^{-1}\) to eliminate the melt history. After that, the sample was cooled down at 10°C min\(^{-1}\) from 200 to -60°C and hold at -60°C for 5 min before the 2\(^{nd}\) scanning to 200°C at 10°C min\(^{-1}\). The \( X_c \) was derived from the melting enthalpy of PLA (\( \Delta H_m,PLA = 93.7 \text{ J g}^{-1} \)) and PBS (\( \Delta H_m,PBS = 110.3 \text{ J g}^{-1} \)) at 100% crystalline and the crystallization enthalpy from the melting peak (\( \Delta H_c \)) (see equation (3)).

\[ X_c (\%) = \frac{\Delta H_c}{\Delta H_m} \times 100 \]  

3. Results and discussion

![Figure 1](image)

Figure 1. MFIs of composite foams at a variety of DCP concentrations.

The melt rheology of composite foams was indirectly analyzed from the MFI measurement at 220°C as shown in figure 1. The MFI of composite foams tended to decrease from 34 to 26 g (10 min\(^{-1}\)) with increasing DCP contents from 0 to 0.5 phr, suggesting that the melt viscosity of polymer blends increased due to the partial enhancement of PLA and PBS compatibility. In the melt mixing process, DCP acted as a radical initiator, resulting in the formation of crosslinking and /or branching structures. Such structures performed as nucleating sites for the generation of PLA-PBS copolymers which became
a compatibilizer for the PLA and PBS fractions and, thereby, attenuated the compatibility of both polymers [6]. Moreover, the variation of MFIs had a trend to decline (see error bars) with the addition of DCP in composite foams, compared with the one having 0 phr of DCP. The gas pressure generated during the bubble creation did not greatly affect the polymer melt flow when the miscibility between PLA and PBS improved.

Figures 2-5 depict the glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting temperature ($T_m$) and $X_c$ of PLA and PBS in composites at various DCP loadings. The $T_g$ of PBS was lower than -60°C which could not be obtained because of the instrument limitation. In addition, the portion of PBS in composite foams was quite low (20 wt%), thus the effect of $T_g$ on the formation of cell foams could be negligible. The $T_g$ of PLA was around 56-58°C, almost unchanged with the DCP variation as presented in figure 2. It was expected that the $T_g$ of both polymers did not influence the bubble formation since the foaming process was performed at 220°C after polymers were melted. The $T_m$ of PLA (148-150°C) and PBS (112-113°C) also slightly varied with increasing DCP dosages, implying that the amount of DCP inconsiderably influenced the crystallization behavior of both polymers (see figure 3). The cold crystallization temperature of PLA ($T_{cc, PLA}$) and crystallization temperature of PBS ($T_{c, PBS}$) in the composite foam with no DCP were 120°C and 89°C respectively as indicated in figure 4. The $T_{cc, PLA}$ and $T_{c, PBS}$ of composite foams were somewhat constant with increasing DCP concentrations. The $T_{cc, PLA}$ was higher than $T_{c, PBS}$, thus the crystallization of PLA occurred before that of PBS, meaning that the crystallization of PLA had more effects on cell morphology than that of PBS did. However, the $X_c$ of PLA insignificantly enhanced as the DCP dosage was increased (see figure 5) since the formation of bubbles might impede the arrangement of polymer chains to be an ordered structure during polymer solidification. Hence, the $X_c$ of PLA might have lower impacts on bubble growth and coalescence than the polymer melt viscosity did. It should also be noted that the crystallization of polymers assists to stabilize the cell structure, nonetheless high crystallinity may obstruct the bubble expansion as a result of high proportion of hard segments in polymers [9-12].

Figure 2. $T_g$ in PLA-PBS-AC composites at different DCP loadings.

Figures 6(a)-6(d) show SEM micrographs and cell size distributions of PLA-PBS-AC composite foams at different DCP dosages. Closed cells with thicker cell walls were observed by DCP addition because the bubble coalescence and expansion hardly happened at high polymer surface tension [13]. The average cell size of the composite foam containing no DCP was around 120-200 µm with narrower cell size distribution than that of composite foams having 0.1, 0.3 and 0.5 phr of DCP. With the addition of DCP, the average bubble size of composite foams had a trend to decrease and exhibited a wide range of variation. The composite foam possessing 0.3 phr of DCP had the broadest cell size distribution in the range of 100-120 µm to 220-240 µm. The cell density of composite foams decreased ((1.6-0.6) x 10⁶ cells cm⁻³) with DCP filling in the system from 0 to 0.5 phr, as presented in figure 7, owing to the enhancement of cell wall thickness. However, the cell density inconsiderably varied with increasing the amount of DCP from 0.1 to 0.5 phr.
Figure 3. \(T_m^{PLA}\) (a) and \(T_m^{PBS}\) (b) in PLA-PBS-AC composites at various DCP dosages.

Figure 4. \(T_c^{PLA}\) (a) and \(T_c^{PBS}\) (b) in PLA-PBS-AC composites at different DCP contents.

Figure 5. \(X_c^{PLA}\) (a) and \(X_c^{PBS}\) (b) in PLA-PBS-AC composites at different DCP concentrations.
Figure 6. SEM images and cell size distributions of PLA-PBS-AC composite foams at different DCP loadings (phr): (a) 0, (b) 0.1, (c) 0.3 and (d) 0.5.

Figure 7. Bubble densities of PLA-PBS-AC composite foams at different amounts of DCP.
Figures 8 (a) and 8(b) present that the $\rho_f$ of composite foams tended to decrease from 0.6368 to 0.5766 g cm$^{-3}$ while the $V_f$ enhanced from 49 to 54% with the addition of DCP in the range of 0 to 0.5 phr. The composite foam containing 3.0 phr of DCP exhibited the lowest $\rho_f$ of about 0.5766 g cm$^{-3}$ and the highest $V_f$ of approximately 54% due to the balance of polymer melt viscosity and $X_c$, PLA effects on the formation of cell foams.

![Figure 8. Foam densities (a) and void fractions (b) of composite foams at different contents of DCP.](image)

4. Conclusions
The existence of DCP seemed to increase the melt viscosity of PLA-PBS-AC composite foams since more compatibility between PLA and PBS occurred via a reactive blend. DCP played a role as nucleating sites for the PLA-PBS copolymer formation, acting as a compatibilizing reagent for the PLA and PBS portions. The $X_c$ and thermal properties of PLA and PBS in composites were scarcely altered with the addition of DCP, indicating that the cell creation and morphology were mainly affected by the polymer surface tension more than the polymer crystallinity. The balance of melt viscosity and $X_c$, PLA is required to obtain optimum cell formation, cell dimension, cell density and foam properties. As a result, the composite foam containing the PLA/PBS proportion of 80/20 by weight, 5.0 phr of ADC, 3.0 phr of AC and 0.3 phr of DCP provided the lowest $\rho_f$ and the highest $V_f$, compared with other DCP loadings.

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References
[1] Bhatia A, Gupta R K, Bhattacharya S N and Choi H J 2007 Korea-Aust. Rheol. J. 19 125-31
[2] Harada M, Ohya T, Iida K, Hayashi H, Hirano K and Fukuda H 2007 J. Appl. Polym. Sci. 106 1813-20
[3] Zhou J, Yao Z, Zhou C, Wei D and Li S 2014 J. Appl. Polym. Sci. 131 40773
[4] Wang L, Ma W, Gross R A and McCarthy S P 1998 Polym. Degrad. Stab. 59 161-8
[5] Zhang N, Wang Q, Re J and Wang L 2009 J. Mater. Sci. 44 250-6
[6] Ji D, Liu Z, Lan X, Wu F, Xie B and Yang M 2014 J. Appl. Polym. Sci. doi: 10.1002/APP.39580
[7] Wang X, Liu W, Zhou H, Liu B, Li H, Du Z and Zhang C 2013 Polymer 54 5839-51
[8] Ketkul K, Threepopnatkul P, Aussawasathien D and Hrimchum K 2017 Key Eng. Mater. 751 344-49
[9] Kang J W, Kim J M, Kim M S, Kim Y H and Kim W N 2009 Macromol. Res. 17 856-62
[10] Wang X X, Kumar V and Li W 2012 Cell. Polym. 31 1-18
[11] Corre Y M, Maazouz A, Duchet J and Reignier J 2011 *J. Supercrit. Fluids.* **58** 177-88
[12] Zhai W T, Ko Y, Zhu W L, Wong A and Park C B, 2009 *Int. J. Mol. Sci.* **12** 5381-97
[13] Liao X, Nawaby A V and Whitfield P S 2010 *Polym. Int.* **59** 1709-18