Composites Science and Technology 119 (2015) 115–123

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Effect of plate-like particles on properties of poly(lactic acid)/poly(butylene adipate-co-terephthalate) blend: A comparative study between modified montmorillonite and graphene nanoplatelets

Sutinee Girdthep [a], Nopparat Komrapit [a], Robert Molloy [b], Saisamorn Lumyong [c], Winita Punyodom [a], Patnarin Worajittiphon [a], *

[a] *Polymer Research Laboratory, Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*
[b] *Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*
[c] *Department of Biology, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

ARTICLE INFO

Article history:
Received 21 June 2015
Received in revised form
29 September 2015
Accepted 6 October 2015
Available online 13 October 2015

Keywords:
Polymer-matrix composites (PMCs)
Mechanical properties
Thermal properties
Graphene nanoplatelets

ABSTRACT

Surface-modified montmorillonite (mMMT) and graphene nanoplatelets (GNPs), both possessing plate-like structure, were adopted as property enhancers for a blend based on poly(lactic acid) and poly(butylene adipate-*co*-terephthalate). Unlike mMMT, GNPs contributed to higher stretchability of the solvent-cast films compared to that of the polymer-clay composite films. Fine dispersion of GNPs throughout the polymer host promoted several improved properties of the blend. Compared to the mMMT at identical filler amount, GNPs enhanced thermal stability and water vapor barrier property while decreased light transmittance in controllable fashion by simply tuning the GNP loading content (0.1–1 phr).

In contrast, the clay did not show any obvious trend of property enhancement. Thus, GNPs functioned as promising property improver for this selected blend. Finally, the polymer-graphene composite could find further application in conductive coating of metal electrodes. This paper shows the simple preparation of polymer composite films by using fillers without any complicated functionalization. The findings will also benefit further facile processing of engineering composites.

1. Introduction

Polymer composites based on biodegradable polymers have drawn much attention over the world since increasing accumulation of plastic garbage globally and scarcity of raw material source of petroleum-based polymers have become main environmental problems. Poly(lactic acid) (PLA) is a biopolymer produced from natural resources with the ability to degrade in compost pile within a relatively short time period. PLA is used extensively for production of packaging products. Nevertheless, PLA is usually mixed with other polymers and fillers to reduce brittleness of PLA-based products. Our earlier attempt has shown that poly(butylene adipate-co-terephthalate) (PBAT) effectively increases PLA toughness in the preparation by the melting process [1]. There can be morphological differences among fillers or reinforcing phase, for example, fiber, rod, spherical particles, plates, etc. The most widely used filler for packaging services is the one whose structure is plate-like because the fine embedment of such fillers in polymer matrix can create tortuous paths for gas or water vapor molecules, and thus the relevant barrier properties are improved [2]. Although our earlier compressed polymer sheets were characterized thoroughly, the filler for the barrier property improvement was only one clay type, modified kaolinite. Apart from the clay we studied, montmorillonite (MMT), a commercially available type of clay found in nature, has been adopted as the reinforcing phase for PLA. Usually, modified MMT (mMMT) was used rather than its pristine form to facilitate exfoliation of the clay in polymers for improving composite properties [2,3].

Graphene has gained significant attention as useful filler in a wide range of applications including packaging due to its superb versatility [4]. Being also of plate-like morphology at the nanoscale and thus having high active surface area, graphene nanoplatelets (GNPs) have been incorporated into PLA for barrier enhancement purpose [4]. GNPs and graphene oxide (GO) were fillers in the

---

* Corresponding author.
E-mail address: pworajittiphon@gmail.com (P. Worajittiphon).

http://dx.doi.org/10.1016/j.compscitech.2015.10.005
0266-3538/

comparative work by Pinto et al. to investigate their influence on the properties of solvent-cast PLA films [4]. When compared to virgin PLA films, both nanocomposite films containing low loading (<1 wt%) of GNPs and GO showed higher yield strength, higher Young's modulus, and lower oxygen and nitrogen gas permeabilities as measured by time lag permeation method. However, property enhancement of PLA by GNPs and GO was not significantly different. In fact, the cost of GO as currently prevalent in the market is higher than that of GNPs [5,6], thus utilizing GO is likely not practical in larger-scale production. Therefore, GNPs have been of interest in this research.

The focus of this study is to compare the effect of mMMT and GNPs on PLA/PBAT blend properties typically required for packaging applications. An extended use of this PGC is also shown as conductive coating of metal electrodes. To our knowledge, a compatibilized blend of PLA and PBAT has not yet been used as a model polymer matrix for a comparative study of the functionality of mMMT and GNPs in improving polymer blend properties. This would, for the first time, answer the question of which plate-like material, without any complicated functionalization, is more potential for such a polymer system and possibly for the others.

2. Experimental

2.1. Materials

The PLA pellets (4043D) were a product of NatureWorks (Cargill Dow LLC, MN, USA) with the number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights of *ca.* 130,000 g mol^{-1} and 150,000 g mol^{-1}, respectively. PBAT (Ecoflex® F blend C1200) was supplied by BASF (Germany) as pellets with an $\overline{M}_n$ of 24,400 g mol^{-1}. All the polymer pellets used throughout this report were dried at 60 °C for 24 h before use. A colorless liquid of tetrabutyltitanate (TBT) supplied by Fluka, Sigma–Aldrich (St. Louis, USA) was used to improve the compatibility between PLA and PBAT via transesterification reaction [1].

GNPs from Cheap Tubes Inc. (VT, USA) with lateral dimension of 1–2 μm and average thickness of <4 nm were used as received. Commercial montmorillonite (≤20 μm) produced by Nanocor® Inc. (IL, USA) and supplied by Sigma–Aldrich (USA) was modified by 15–35 wt.% octadecylamine and 0.5–5 wt.% aminopropyltriethoxysilane. Chloroform was of analytical grade, supplied by Labscan (Thailand).

No modification was applied to the GNPs to achieve filler homogeneous dispersion. Contrarily, octadecylamine was chosen for MMT modification in this research since this functional group on MMT surface can form hydrogen bonds with PLA [7].

2.2. Preparation of neat polymer, blend, and composite films

All films were prepared by solution casting method using chloroform at 50 °C for 2 h under continuous stirring. mMMT and GNPs were separately dispersed ultrasonically using a Vibra-Cell™ VCX130 sonicator (130 W) at 35% amplitude for 30 min in the same solvent prior to mixing with the polymer solution. The mixture was then poured onto a glass petri dish before being left at an ambient condition for 48 h and subsequently moved into a vacuum dried oven for another 24 h for complete solvent removal. Based on our previous report, the weight ratio of the PLA-based blend herein was similarly selected at a PLA/PBAT weight fraction of 70/30 [1].

Here, we used the as-received fillers and controlled weight, rather than volume fraction, to demonstrate the possibility of using them for further facile processing of engineering composites. Composite composition is assigned as 70/30/5, meaning that this particular formula contains a PLA/PBAT weight ratio of 70/30 with the TBT content of 5 phr. In addition, PCCA and PGCA stand for PLA/PBAT/TBT at a 70/30/5 ratio with mMMT and GNPs of A and A phr, respectively.

2.3. Characterization

The mechanical properties of the films were measured using a universal tensile testing machine (LRX, Lloyd Instrument) based on the ASTM D882 Type V with a crosshead speed of 50 mm min^{-1} and gauge length of 50 mm. Representative stress–strain curves of the PCC and the PGC films are shown in Supporting Information. The film surface morphology was investigated using a Scanning Electron Microscope (SEM) (JSM-5910LV, JOEL, Japan) coupled with a Shimadzu EDX-700 HS energy dispersive spectrometer to verify the physical compatibility of the two polymers and the presence of the filler in the polymer matrix. The SEM specimens were coated by a thin gold layer. The dispersion states of both mMMT and GNPs in the polymer host were analyzed using a TTRAX III (Rigaku, Japan) X-ray diffractometer with a Cu–K$_\alpha$ as an X-ray source at a scanning rate of 2° min^{-1}. The light transmittance characteristic of the films of the films was measured using a UV–visible spectrometer (Lambda 25, Perkin Elmer). The morphologies of the fillers were revealed under a Transmission Electron Microscope (TEM) (H-7500, Hitachi, Japan) at an accelerating voltage of 200 kV. The thermal properties of the films were determined using a Perkin–Elmer Pyris DSC7 Differential Scanning Calorimeter, from −20 °C to 200 °C. The samples were heated at a rate of 10 °C min^{-1}, and then quickly cooled and reheated for the second heat treatment. The thermal stability of the films was studied with a Thermogravimetric Analyzer (TGA) (TGA7, Perkin Elmer, USA) by heating the sample (*ca.* 5 mg) from 50 °C to 600 °C at a 20 °C min^{-1} heating rate. The water vapor permeability (WVP) measurement of the films was applied from ASTM E96. Briefly, the top of an aluminium cell containing silica gel (0% RH) was sealed by a dried film and subsequently kept under 38.0 °C and 90% RH. The antibacterial performance of the films was determined by using a visible cell count method. *Salmonella* spp., *Candida albicans*, *Staphylococcus aureus*, *Escherichia coli*, and *Aspergillus niger* were used as model micro-organisms in this study. The bacteria and fungi were incubated in a nutrient broth agar at 37 °C and in a potato dextrose broth agar at 30 °C, respectively. The electrical conductivity was measured at an ambient temperature in terms of the electrical current flowing through a simple electrolysis cell having PGC1 (1 phr GNPs) as a dip-coating layer (*ca.* 20 μm) on the copper electrode. The reference electrode was a similar copper wire without any coating. The electrodes were submerged in a dilute acidic aqueous solution under an applied voltage of 12 V. All the standard deviation values in the quantitative results were obtained from successive measurements performed in triplicate.

3. Results and discussion

3.1. Effect of plate-like fillers on properties of partially compatibilized blend (PLA/PBAT/TBT)

3.1.1. Physical appearance and mechanical properties

The effect of mMMT and GNPs on film transparency was studied by varying the filler content in the compatibilized blend films with a selected PLA/PBAT/TBT ratio at 70/30/5. As can be observed from Fig. 1a, the PGC films appear darker with increasing GNP content, compared to the PCC films, corresponding to % transmittance result (Fig. 1b and c).

This observation suggests that the films become more impermeable to light as the GNP content increases. In contrast, the PCC films consistently show their color in pale white independently on