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Research paper

Preparation and characterization of kaolin/starch foam

Kaewta Kaewtatip *, Varaporn Tanrattanakul, Wilaiwan Phetrat

Bioplastic Research Unit, Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

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ABSTRACT

The objective of this work was to study the effect of the kaolin content on the properties of starch foams. The kaolin/starch foams were made with kaolin contents that ranged from 0 to 15 m% by baking in a hot mold. The starch and kaolin/starch foams were stored at room temperature with a relative humidity (RH) of 55% for 7 days prior to testing. An increase in the kaolin content increased the foam density. The izod impact strength increased up to 1151.37 J/m^2 at the highest kaolin content (15 m%). The improvement was about five times the izod impact strength of pure starch foam. Moreover, the presence of any kaolin reduced the water absorption ability of the starch foam. Scanning electron microscopy revealed that kaolin increased the size of the starch foam cells and was itself well dispersed. Kaolin/starch foams showed a higher thermal stability than pure starch foam.

1. Introduction

Currently, the accumulation of synthetic plastic wastes has become a worldwide environmental problem. Biodegradable polymers have created much interest because they might help to solve this problem. Starches derived from plants such as cassava, rice, potato and corn are classical renewable materials and can be processed into foam polymers through common thermoplastic processing such as extrusion (Cha et al., 2001; Xu et al., 2005) or compression molding (Glenn et al., 2001; Lawton et al., 2004). However, starch foam has a number of disadvantages such as it has poor mechanical properties, poor thermal stability and high water absorption (Cinelli et al., 2006; Lee et al., 2008).

The addition of additives can play an important role in improving the properties of starch foam. Natural rubber latex was shown to increase the flexural modulus (Tanrattanakul and Chumeka, 2010) and water resistance of starch foams (Shey et al., 2006). Many research groups have tried to improve the properties of starch foam using different types of fiber such as aspen (Lawton et al., 2004), corn (Cinelli et al., 2006), cellulose (Pablo et al., 2008), kraft (Nattapon et al., 2012), jute and flax fibers (Nattakan et al., 2004). These fibers can improve the mechanical properties and water absorption of starch foam because of their strong interaction between the fibers and the starch matrix. Starch foam mixed with poly(lactic acid) (PLA), poly(hydroxyester ether) (PHEE), or poly(hydroxybutyrate-co-valerate) (PHBV) had significantly lower densities and higher expansion than the pure starch foam (Willett and Shogren, 2002). Mixing natural (Lee and Hanna, 2008) or organically modified montmorillonite (Lee et al., 2008) produced an increase in the Young's modulus, thermal stability and water resistance of starch foam. Kaolin is a natural clay that has a huge advantage because of its abundance, low cost, is environment friendly and has suitable properties for usage. Kaolinite exhibits complex structures consisting of octahedral sheets of $AlO_2(OH)_4$ and tetrahedral sheets of SiO_4 (Atta et al., 2012; Bergaya et al., 2006; Ma and Bruckard, 2010; Songfang et al., 2011). Adding kaolin to thermoplastic starch led to an increase in the tensile strength, Young's modulus and water resistance (de Carvalho et al., 2001). The addition of kaolin was also shown to improve the thermal stability and to retard the crystallization of the thermoplastic starch (Huang et al., 2006; Kaewtatip and Tanrattanaku, 2012). However, there have been no reports on the effects of kaolin on the properties of starch foam.

The objectives of this research were to prepare kaolin/starch foams and to study their properties. The effect of the aging time on the water absorption of starch and kaolin/starch foams was also investigated.

2. Experimental

2.1. Materials

Native cassava starch (PD 10369) and kaolin (Wizkay TU-90) were kindly supplied by Siam Modified Starch Co., Ltd. and WIZARD Chemical Co., Ltd., respectively. Typical properties of Wizkay TU-90 kaolin are as follows: the particle sizes are finer than 1 μm; particles larger than 325 mesh are 0.02% maximum; the brightness 90–93%; free moisture 1% maximum; pH 6–9; bulk density 40–50 lbs/ft^3 and specific gravity 2.58. The starch was dried at 105 °C for 48 h in an oven and kept in a desiccator prior to use. The glycerol was from Ajax Finechem. Guar gum and magnesium stearate were from Sigma-Aldrich, Inc.

* Corresponding author. Tel.: +66 74288360; fax: +66 74446925.
E-mail addresses: jumpolymer@hotmail.com, kaewta.k@psu.ac.th (K. Kaewtatip).

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2.2. Foam preparation

Native cassava starch (100 g), guar gum (1 g), magnesium stearate (2 g) and kaolin (0, 3, 6, 9, 12 and 15 m%, dry starch basis) were mixed with a mixer (Kenwood, KM 262) at room temperature for 10 min. Glycerol (5 g) and distilled water (100 g) were added to the mixture. The batters were further mixed for 10 min and then were thermo-molded (15 cm × 15 cm × 4 mm) by using a compression molding machine, KT-7014 produced by Kao Tieh Ltd. (Taipei, Taiwan) at 180 °C under a pressure of 1000 psi for 5 min.

2.3. Characterization of foams

The izod impact test was performed according to ASTM D256. Dimensions of the un-notched specimens were 12.7 mm × 63.5 mm × 4 mm. The experiment was carried out by using a 2 J pendulum. Testing was performed at 25 ± 3 °C and 55 ± 2% RH after equilibrating the samples at 55 ± 2% RH and 25 ± 3 °C for 7 days. Ten specimens were tested for obtaining a mean result for each sample.

The density was calculated from the ratio between the mass and volume. Pieces of samples (dimensions 30 × 150 × 4 mm) were stored at 55% RH for 7 days before testing. Ten specimens were tested for every sample.

Morphology of the fractured surfaces of the starch and kaolin/starch foams was examined by using a scanning electron microscope (SEM) (Quanta 400, FEI). The specimen was coated with a thin layer of gold. The operating voltage used was 15 kV.

The thermal decomposition temperatures of the starch and kaolin/starch foams were obtained using a PerkinElmer® TGA 7. The thermogravimetric analyzer (TGA) was operated at a heating rate of 10 °C/min from 50 to 600 °C under a nitrogen atmosphere.

2.4. Water absorption measurement

Pieces of samples (dimensions 15 × 15 × 4 mm) were stored at 55% RH for 7 and 45 days before testing, they were weighed then dried in the oven at 105 °C for 24 h then immediately reweighed. The water absorption can be calculated using Eq. (1) (Huang et al., 2004; Ma et al., 2007):

$$\text{Water absorption}(\%) = [(w_1 - w_2)/w_2] \times 100 \quad (1)$$

where w_1 was the mass of sample before drying and w_2 was the mass of sample after drying. All measurements were performed in triplicate.

3. Results and discussions

3.1. Density

Density was one important factor that was changed in the kaolin/starch foam. The density of starch foam was 0.21 g/cm^3 and the density of the kaolin/starch foams with a kaolin content of 3, 6, 9, 12 and15 m% was 0.23, 0.24, 0.25, 0.27 and 0.29 g/cm^3, respectively. Undoubtedly, a filler like kaolin causes an increase of viscosity of the batter and this reduces its expansion (Cinelli et al., 2006; Shogren et al., 1998). Lee et al. (2008) have prepared tapioca starch, poly(lactic acid), and Cloisite NA$^+$ nanocomposite foams and also showed that the addition of filler increased the density of the foam. Laura et al. (2006), who studied the influence of fibers on the mechanical properties of cassava starch foams also showed a similar trend that the density of the starch foam increased when the fiber content was increased.

3.2. Thermal stability

The TGA curves of starch and kaolin/starch foams with different kaolin contents are shown in Fig. 1. There were two steps of mass loss in all samples. First, a mass loss from 50 °C to 110 °C, that was assigned to evaporation of water (Chivrac et al., 2010; Yin et al., 2008). The mass loss from 300 to 340 °C involved the decomposition of starch at its decomposition temperature (Kaewtatip and Tanrattanakul, 2008; Martins et al., 2009). However, the percentage mass loss in the thermograms of the different samples was different. For the starch foam itself the loss was 83.57% (Fig. 1a). When the kaolin content increased from 3 m% to 15 m%, the percentage mass loss decreased from 77.36% to 70.50% (Fig. 1b–c). This result indicated that the starch foam was degraded more rapidly than the kaolin/starch foam. That may be due to the kaolin acting as an insulator to retard the passage of volatile degradation products in the starch foam (Lee and Hanna, 2009; Wang et al., 2005). This confirmed that kaolin improved the thermal stability of the starch foam.

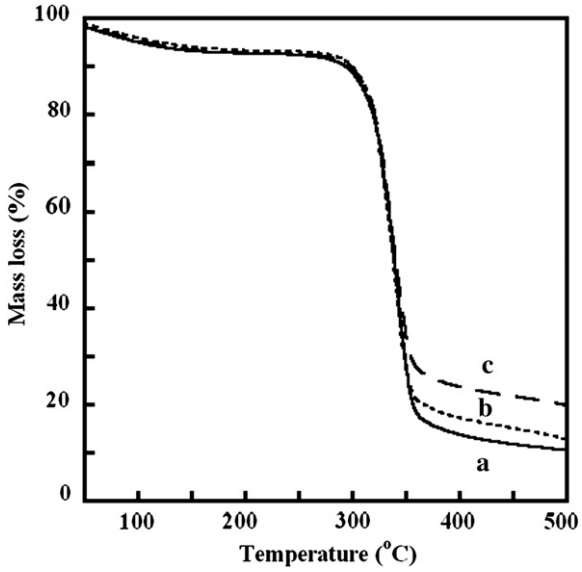

Fig. 1. Thermogravimetric curves of starch foam (a) and kaolin/starch foam with: 3 m% (b) and 15 m% (c) of kaolin content.

3.3. Morphology

SEM micrographs of cross-sections of starch and kaolin/starch foams containing different amounts of kaolin (3 and 15 m% kaolin) are presented in Fig. 2.

Starch foam has a smaller and denser cell structure (Fig. 2a). Kaolin/starch foams with 3 m% (Fig. 2b–c) and 15 m% (Fig. 2d–e) kaolin content show a different cell size and structure from the starch foam itself. The cell size of starch foam was 0.37 ± 0.23 mm, whereas the cell size of kaolin/starch foams with 3 m% and 15 m% kaolin content were 0.57 ± 0.16 mm and 0.81 ± 0.7 mm, respectively.

The cell size of the kaolin/starch foams was increased because kaolin delays the thermal collapse of the steam bubble and encourages the formation of larger foam cells. This result is in agreement with those from other authors (Benchamaporn et al., 2007; Ghazali et al., 1999).

3.4. Izod impact strength

The izod impact strength of starch and kaolin/starch foams is shown in Fig. 3. The izod impact strength of starch foam was 246.06 J/m^2 and this was considerably increased with added kaolin from 334.65 J/m^2 to 1151.60 J/m^2 when the kaolin content increased from 3 m% to 15 m%, respectively. The maximum izod impact strength of kaolin/starch foam (1151.60 J/m^2) was about 5 times higher than that for starch foam itself. The results are in agreement with the SEM observations that kaolin was well dispersed and showed good adhesion to the