A novel biodegradable nanocomposite based on poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) and silylated kaolinite/silica core–shell nanoparticles

Qian Zhang a,b,c, Qinfu Liu a,* James E. Mark c, Isao Noda d

a School of Geological Science and Survey Engineering, China University of Mining and Technology, Beijing 100083, China
b School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454009, China
c Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, USA
d The Procter & Gamble Company, 8611 Beckett Road, West Chester, OH 45069, USA

Abstract

A novel biodegradable nanocomposite was fabricated based on poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) and silane-modified kaolinite/silica core–shell nanoparticles (SMKS), via solution-casting method using chloroform as solvent. Unmodified (ORK) and glycidoxypropyltrimethoxysilane (G-silane) surface-modified kaolin (SMK) were also introduced into PHBHHx matrix for comparison. SMKS significantly improved the mechanical properties of the PHBHHx compared to that of ORK and SMK. The composite filled with a low loading of SMKS increased the tensile strength and toughness from 18.2 to 23.5 MPa and 2.6 to 4.2 MPa, respectively. Transmission electron microscopy (TEM) indicated that SMKS was finely distributed in the PHBHHx matrix compared with the other two kinds of fillers. These significant improvements in these mechanical properties were attributed to the fine dispersion of SMKS into the polymer and covalent interaction between polymer chains and the surface of SMKS.

1. Introduction

Recently, an increasing number of biodegradable polymers have been developed, with the aim to solve the environmental problem caused by the disposal of large volumes of non-biodegradable materials (Okada, 2002; Alata et al., 2007; Williams, 2007). The copolymer PHBHHx is one of the most promising biodegradable semi-crystalline aliphatic polyesters of the polyhydroxalkanoate family (Choi and Park, 2003; Cakmak et al., 2005; Noda et al., 2005; Lee et al., 2008). This is primarily due to the fact that it has a unique combination properties, including full anaerobic degradability, moisture resistance, good barrier properties, relatively high shelf stability (under distribution and home-storage conditions), processability on conventional equipment, and easy dyeability (Furukawa et al., 2007).

It has potential applications in the manufacture of storage bags, shopping bags, slip covers, coatings in automobiles and furniture (Cheng et al., 2008; Lee et al., 2008). This particular copolymer has the advantage of biodegradability, but is somewhat lacking in strength (Noda et al., 2004; Venkitachalam et al., 2005), which restricts its use in certain applications. One way to overcome this problem is to modify natural polymers by incorporation of inorganic fillers that can further extend their applications in aggressive environments. Such additions of nanoparticles to form nanocomposites has in fact been the focus of recent research to improve the performance properties of such polymers (LeBaron et al., 1999; Zhang et al., 2007; Zini et al., 2007). Examples of desired property improvements include improved thermal, mechanical, and other physical properties in comparison to the corresponding neat polymer (Ray et al., 2002; Horch et al., 2004; Matti et al., 2007; Zhang et al., 2008). In order to achieve this, surface of nanoparticles is usually modified so as to promote their uniform dispersion throughout the polymer and improve interaction with the organic matrix. Much of the work in this area, however, has focused on montmorillonite and silica (Ansarifar et al., 2005; Tiwari et al., 2008; Zulfigar et al., 2008) and there are relatively few reports on other kinds of clay minerals in this application. Of interest here is kaolin, or “China clay” found in hydrothermal, residual and sedimentary deposits around the world. Recently there has been increased research on organic modified kaolin as a filler in polymer to reinforce the mechanical properties and reduce the cost of polymer products (Ansari and Price, 2004; Buggy et al., 2005; Liu et al., 2008; Sukumar and Menon, 2008).

Recently some methods for silylation of kaolinite have been reported, in which the kaolinite particles were intercalated with small molecules such as urea, potassium acetate, dimethyl sulphoxide and so on to expand the interlayer space which make the interlayer hydroxyl groups to be accessible for the further organic molecule chemical grafting (Letaief...
et al., 2006; Janek et al., 2007; Tonle et al., 2007; Letaief and Detellier, 2008). The hydroxyl groups at the particle edges are considered to be the major reactive sites of kaolinite surface. However, these edges have been estimated to occupy approximately 10% of the whole kaolinite surface (Wierer and Dobias, 1988; Jesionowski, 2003). The surface of kaolinite, like other clay minerals, is chemically inert, making the covalent attachment of functionalized molecule difficult. The adhesion between the kaolinite particles and the modifying compound is not strong as they are not covalently bound over the whole surface but either electrostatically bound. In order to overcome this problem, methods, such as acid hydrolysis and various plasma treatments have been attempted to increase the reactivity of the kaolinite external surface by providing additional reactive hydroxyl groups (Ming and Spark, 2003; Lego et al., 2008; Liberelle et al., 2008).

In this work, a new method is reported for silylation of kaolinite. The method includes initial deposition of silica on the kaolinite surface by the sol–gel method using tetraethylorthosilane (TEOS) as the silica precursor (Stöber et al., 1968; Rouse and Ferguson, 2003; Zhu et al., 2005). This silica shell provided large amount of functional silanol groups for the further modification with silane. These nanoparticles were introduced into PHBHHx matrix to fabricate PHBHHx/SMKS nanocomposites by a solution-casting method. The present study throws light on the effect of SMKS as filler on the mechanical properties of PHBHHx composites. The properties of PHBHHx composites filled with ORK or SMK were also measured for comparison. The morphology and dispersion of these nanoparticles in PHBHHx matrix were also investigated.

2. Experimental

2.1. Materials

PHBHHx (Fig. 1) was provided by the Procter & Gamble Co., West Chester, Ohio and was used as received. It was a random copolymer consisting of 93.5 mol% 3-hydroxybutyrate, and 6.5 mol% 3-hydroxyhexanoate. Kaolinite powder with 20–50 nm average in particle thickness, 300 nm average in diameter and 32 m$^2$/g specific surface area, was obtained as an industrial product from Zaozhuang SanXing High-Tech Material Co. Ltd, China. The detailed information was described previously (Liu et al., 2008). G-silane and the TEOS were purchased from Beijing Chemical Reagents Company, China. The solvent chloroform was purchased from Aldrich.

![Fig. 1. Structure of PHBHHx.](image)

2.2. Nanoparticles preparation

Silylated kaolinite/silica core–shell nanoparticles have been prepared by the sol–gel technique using TEOS as silica precursor (Stöber et al., 1968) and G-silane as surface modifier. Typically, 5.0 g of kaolin were dispersed in 90 ml solution of ethanol, ammonia and deionized water in 250 ml three-necked round flask. The dispersion was treated ultrasonically for 45 min, and the desired amount of TEOS was added at 60 °C, followed by continuous stirring for 5 h. At the end of this process, hydrolyzed G-silane was injected into the slurry and allowed to react for 30 min. Finally, the slurry was filtered and was washed with deionized water several times, and then dried at 105 °C for further use.

2.3. Nanocomposite fabrication

The PHBHHx/SMKS nanocomposites (in 100/1, 100/3, 100/5, 100/7, 100/10) were prepared by solution-casting. First, PHBHHx was dissolved in chloroform and left overnight at room temperature to insure that all PHBHHx had been dissolved. Second, SMKS was dispersed in chloroform by ultrasonic treatment for 30 min and then this slurry was slowly added into PHBHHx solution and stirred for 12 h, followed by ultrasonication for another 1 h. Finally, the product was dried and thermal compressed for the characterizations of morphology and mechanical properties. PHBHHx/ORK (100/5) and PHBHHx/SMK (100/5) composites were also prepared similarly.

2.4. Characterization

TEM images of the SMKS, ORK and SMK nanoparticles were obtained using a Phillips CM 20 instrument operated at an acceleration voltage of 150 kV. The TEM images of the nanocomposites were taken with a JEM 1230 EX-II instrument operated at an acceleration voltage of 60 kV. These samples were ultrathin sliced up into less than
100 nm in thickness using a Super NOVA 655001 instrument (Leica, Swiss) with a diamond knife and were viewed without staining. The fracture surfaces from direct tensile testing of PHBHHx nanocomposites were observed with a FEI XL 30 scanning electron microscope (SEM) at 20 kV acceleration voltages. Specimens were coated with a thin gold film prior to SEM observations. FTIR spectra were recorded on a Perkin Elmer Spectrum using the KBr-disk technique. The values of the Young’s modulus and the tensile strength of samples having 30×5×1 mm$^3$ were measured using a fully-computerized INSTRON mechanical tester (Model 1122) with the initial gauge length 30 mm at speed rate of 10 mm/min at room temperature. The tensile properties including the Young’s modulus, toughness, elongation at break, and tensile strength (stresses at break) and values were obtained as an average of at least three measurements.

3. Results and discussion

3.1. Preparation of silylated kaolinite/silica core–shell nanoparticles

TEM images of the SMKS nanoparticles (Fig. 2) clearly show the distribution of silica on the surface of kaolinite particles. Specifically, a thin layer of silica about 10 nm (Fig. 2a) and some silica spheres 30×5×1 mm$^3$ were measured using a fully-computerized INSTRON mechanical tester (Model 1122) with the initial gauge length 30 mm at speed rate of 10 mm/min at room temperature. The tensile properties including the Young’s modulus, toughness, elongation at break, and tensile strength (stresses at break) and values were obtained as an average of at least three measurements.

3.2. Microstructures of the PHBHHx nanocomposites

TEM images of the PHBHHx nanocomposites (Fig. 5) clearly show the distribution of silica on the surface of kaolinite particles. Specifically, a thin layer of silica about 10 nm (Fig. 2a) and some silica spheres 30×5×1 mm$^3$ were measured using a fully-computerized INSTRON mechanical tester (Model 1122) with the initial gauge length 30 mm at speed rate of 10 mm/min at room temperature. The tensile properties including the Young’s modulus, toughness, elongation at break, and tensile strength (stresses at break) and values were obtained as an average of at least three measurements.

**Fig. 4.** Schematic representation of the proposed structure models for silane-modified kaolinite/silica core–shell nanoparticle procedures (a) ORK, (b) KS and (c) SMKS.

**Fig. 5.** TEM images of the PHBHHx nanocomposites (a) PHBHHx/ORK (100/5), (b) PHBHHx/SMK (100/5) and (c) PHBHHx/SMKS (100/5).
3.3. Mechanical properties

Room temperature tensile properties of the neat PHBHHx and the PHBHHx/SMKS nanocomposites in various loading concentrations are presented in Fig. 6. The properties include (i) Young’s modulus, (ii) tensile strength (defined as the stress at break), (iii) toughness and (iv) elongation at break. The Young’s modulus increased with increasing filler loading. The toughness was sharply increased with the increasing filler loading and reached a maximum value of 4.2 MPa at 3 phr filler content and then decreased with the further increasing filler loading. The tensile strength increased linearly up to 22.6 MPa at 1 phr filler content and no significant changes were observed above this filler content. The elongation at break was strongly improved at 1 phr filler content and then decreased sharply with the additional filler content.

From all the above results, particular interest is the observation that even very small amounts of the SMKS gave significant reinforcement. The increase in Young’s modulus and tensile strength was not so obvious when SMKS loading was above 5 phr and the properties of toughness and elongation at break were even reduced.

The mechanical properties of pure PHBHHx and its composites filled with ORK, SMK and SMKS, respectively with the same loading of 100/5 (PHBHHx/filler) were tested for comparison (Table 1). All composites showed significant improvement in the Young’s modulus and tensile strength compared to neat PHBHHx. SMKS endows PHBHHx the greatest Young’s modulus and tensile strength compared to ORK and SMK. Significant decreases in toughness and elongation at break compared to blank PHBHHx were observed in PHBHHx/ORK and PHBHHx/SMK. This was attributed to aggregate formation of ORK and

Fig. 6. Effect of filler concentration on (a) Young’s modulus, (b) toughness, (c) tensile strength and (d) elongation at break of PHBHHx/SMKS nanocomposites.

Fig. 7. SEM micrographs of tensile fracture surfaces, (a) neat PHBHHx, (b) PHBHHx/SMK (100/5) and PHBHHx/SMKS (100/5).
SMKs within the polymer matrix (Fig. 5a and b). These large aggregates, which are several microns in diameter, provide original sites for the crack propagation. On the other hand, the hybrid nanocomposite filled with SMKS exhibited the toughness of 3.7 MPa, which increased strongly compared to pure PHBHHx. These dramatic improvements in these properties were attributed to the fine dispersion of SMKS into the polymer matrix and covalent interaction between polymer chains and the surfaces of SMKS.

3.4. Fractographic observations (scanning electron microscopy)

The SEM observation, often called a fractograph, is useful for clarifying the fracture mechanism. The roughness of the fracture surface has generally been associated to fracture properties and critical strain energy release rates. A smooth featureless fracture surface is attributed to brittle failures, and rougher fracture surfaces are attributed to tougher composites (Wang et al., 2006). Fig. 7a, b and c show the tensile fracture surfaces of neat PHBHHx, PHBHHx/SMK (100/5) and PHBHHx/SMKS (100/5) respectively. In case of neat PHBHHx, a semi-crystalline polymer, the fracture surface was even which is consistent with no plastic deformation before rupture. For the PHBHHx, SMKs nanoparticles were well dispersed in the PHBHHx matrix and to covalent interactions between the polymer chains and the more filled surface of SMKS nanoparticles. TEM images confirmed that SMKS nanoparticles were well dispersed in the PHBHHx matrix. SEM observations of fracture surfaces indicated that samples filled with SMKs had a rough surface and became stress whitened compared to control samples.

4. Conclusions

SMKS nanoparticles were prepared by the sol–gel technique using TEOs as silica precursor and G-silane as surface modifier. This silica shell on the surface of kaolinite with many silanol groups greatly promoted silylation of kaolinite. The PHBHHx composite filled with a low loading of SMKS showed an increase in the tensile strength and toughness from 18.2 to 23.5 MPa and 2.6 to 4.2 MPa respectively. These strong improvements in mechanical properties were attributed to the more finely dispersed SMKS nanoparticles into the polymer matrix and to covalent interactions between the polymer chains and the modified surface of SMKS nanoparticles. TEM images confirmed that SMKS nanoparticles were well dispersed in the PHBHHx matrix. SEM observations of fracture surfaces indicated that samples filled with SMKs had a rough surface and became stress whitened compared to control samples.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Toughness (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHBHHx</td>
<td>261 ± 18</td>
<td>18.0 ± 0.2</td>
<td>2.6 ± 0.4</td>
<td>16.2 ± 0.1</td>
</tr>
<tr>
<td>PHBHHx/ORK (100/5)</td>
<td>402 ± 12</td>
<td>19.4 ± 0.9</td>
<td>1.4 ± 0.2</td>
<td>11.9 ± 0.3</td>
</tr>
<tr>
<td>PHBHHx/SMK (100/5)</td>
<td>400 ± 6</td>
<td>21.4 ± 0.5</td>
<td>2.1 ± 0.5</td>
<td>13.9 ± 0.2</td>
</tr>
<tr>
<td>PHBHHx/SMKS (100/5)</td>
<td>432 ± 14</td>
<td>23.2 ± 0.4</td>
<td>3.7 ± 0.4</td>
<td>15.4 ± 0.4</td>
</tr>
</tbody>
</table>

Note: ORK is unmodified kaolin, SMK is surface-modified kaolin, and SMKS is surface-modified silica-coated kaolin.

Acknowledgements

The authors grateful acknowledge the financial support provided JEM by the National Science Foundation through grants DMR 0314760 and DMR 0803454 (Polymers Program), Qian Zhang also thanks the China National 863 project of China (2008AA06Z109) for financial support.

References


Venkitachalam, R., Mark, J.E., Noda, I., 2005. Drying biodegradable poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) gels in the elongated state to improve their mechanical properties. Journal of Applied Polymer Science 95 (6), 1519–1523.


