

Green Composite of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) Reinforced with Porous Cellulose

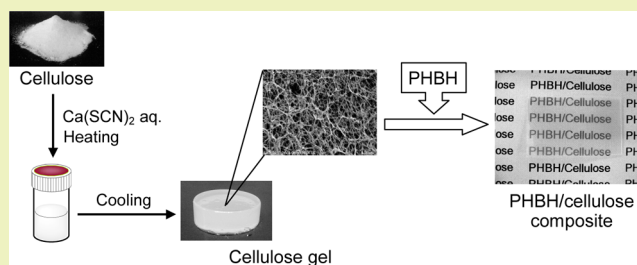
Nao Hosoda, Takashi Tsujimoto,* and Hiroshi Uyama*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

Supporting Information

ABSTRACT: In this study, a green composite from bacterial polyester, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), and cellulose was developed. Cellulose gel was prepared from a $\text{Ca}(\text{SCN})_2$ aqueous solution, and subsequent washing by ethanol gave regenerated porous cellulose without shrinkage. The PHBH/cellulose composite was fabricated by immersion of porous cellulose in a polymer solution. The cellulose content of the composite was controlled by changing the cellulose concentration of the $\text{Ca}(\text{SCN})_2$ aqueous solution. The resulting composites showed a relatively good transparency with improvements in mechanical properties such as tensile strength, toughness, and brittleness. Furthermore, the thermal stability of the composites was improved by the introduction of cellulose. These composites from renewable resources are expected to contribute to the development of biobased materials in composite science.

KEYWORDS: Renewable resources, Polyhydroxyalkanoate, Porous cellulose, Reinforced materials, Mechanical property, Green composites



INTRODUCTION

Recently, biobased plastics have received much attention as an alternative to conventional plastics derived from petroleum resources.^{1,2} The use of biobased materials is highly significant for reduction of greenhouse gas and fossil resource-savings in social viewpoints, which is one of the most promising solutions to problems concerning the global environment and energy resources.

A series of poly(3-hydroxyalkanoate)s (PHAs), including the poly(3-hydroxybutyrate) (PHB) homopolymer and related copolymers, is a naturally occurring thermoplastic that behaves as an intercellular-carbon and energy-storage compound in microorganisms such as bacteria.^{3–5} PHB is a highly crystalline and brittle polymer but possesses a melting point and mechanical properties comparable to those of petroleum-based synthetic polymers.^{6–11} PHB-related copolymers are developed to overcome the shortcomings of PHB. PHBH is a copolymer consisting of randomly arranged 3-hydroxybutyrate (3HB) and 3-hydroxyhexanoate (3HH) units. PHBH has a lower melting point and more highly ductile properties than PHB. The amount of the 3HH fraction in PHBH strongly influences the properties of this polymer such as crystallinity, melting point, strength, and crystallization rate. It was reported that the crystallinity of PHBH decreases from 60% to 18% as the 3HH fraction increases from 0% to 25%, and PHBH becomes soft and flexible with an increase in the 3HH fraction.¹² However, the low crystallinity induces a low strength modulus and thermal stability of PHBH, and the final products are tacky due to a low glass transition temperature.¹³

Composite materials are important for structural application, where the combination of high strength and stiffness are required.^{14,15} In recent years, there has been an increasing interest in the development of biobased and/or biodegradable composite materials, which are sometimes called green composites.^{16–20} One approach to making a green composite is to use cellulose fibers.

Cellulose is the most abundant material in the world, and about 1.5×10^{12} tons of cellulose grow every year.²¹ Cellulose from wood, straw, and cotton is widely used in several industries, such as the paper industry, chemical industry, textile industry, and food industry. Compared to inorganic fibers, cellulose fibers have several advantages such as their renewable nature, low density, high specific strength, etc.^{22,23} Cellulose fibers such as native fibers, their fragments, and regenerated fibers were used as reinforcement components for common polymers.^{24–35} The main drawback of cellulose fibers for reinforcement applications is incompatibility with polymer matrices due to their strong hydrophilic nature. Agglomeration is a common problem when polymers are filled with cellulose fibers because of poor adhesion between the cellulose fibers and polymer matrix. Therefore, it is a major challenge on how to obtain good dispersion of cellulose in a polymer matrix.

Cellulose cannot be manufactured by the melt processing technique and casting method in a common solvent due to the strong hydrogen bonding between intra- and inter-molecules.

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Therefore, many researchers have studied solvents for cellulose. Several solvent systems such as LiCl/*N,N*-dimethylacetamide (DMAc), Ca(SCN)₂/water, LiOH/urea/water, and ionic liquids were reported and used for the modification or the preparation of cellulose gel.^{36–39} In this study, porous cellulose prepared by using a Ca(SCN)₂ aqueous solution was used as a reinforcement material, and a novel green composite from PHBH and cellulose was developed by the immersion process. The resulting composites showed optical transparency with increases in mechanical properties and thermal stability.

EXPERIMENTAL SECTION

Materials. PHBH containing 11 mol % 3-HH ($M_w = 3.2 \times 10^5$) was a gift from Kaneka Co., and cellulose (Whatman CF-11) was purchased from Wako Pure Chemical Industries, Ltd. Other reagents and solvents were commercially available and were used as received.

Preparation of PHBH/Cellulose Composite. The following procedure was typically used in the preparation of PHBH/cellulose composites. Calcium thiocyanate (Ca(SCN)₂) was dissolved in deionized water to saturation (59 wt %) at room temperature. Cellulose was dispersed in this solution, and the mixture was heated at 120 °C for 20 min to give a transparent solution. The solution was cooled at room temperature to form cellulose gel. After 24 h, the gel was washed several times with ethanol, and cellulose was regenerated to a porous material (Figure S1, Supporting Information). For the preparation of the PHBH/cellulose composite, porous cellulose was immersed in 5 wt % of a PHBH chloroform solution, followed by drying at room temperature to remove the solvent. Then, the sample was pressed at 160 °C under a pressure of 5 MPa for 5 min. This was followed by rapid quenching at 0 °C to produce a PHBH/cellulose composite.

Measurement. Thermogravimetric (TG) analysis was performed using a SEIKO TG/DTA7200 at a heating rate of 10 °C/min under nitrogen. Scanning electron microscopic (SEM) analysis was carried out by a HITACHI SU-3500 instrument.

The thermal properties of the sample were investigated under a nitrogen atmosphere by using a SEIKO DSC6220 differential scanning calorimeter (DSC). The sample was melted at 180 °C for 2 min and then cooled to –50 °C at a cooling rate of 10 °C/min. The temperature was maintained for a duration of 2 min, and the sample reached 180 °C at a heating rate of 10 °C/min. Polarized optical microscopic analysis was carried out using an OLYMPUS BX51 microscope equipped with an IMOTO MHS-2000 heating stage. The sample was placed on a glass slide, melted at 180 °C on a heating stage, and subsequently cooled at room temperature.

Dynamic viscoelasticity analysis was carried out by using a SEIKO DMS6100 with frequency of 1 Hz at a heating rate of 3 °C/min. Tensile properties were measured by a Shimadzu EZ Graph. A cross-head speed of 10 mm/min was used. The sample was cut into a plate shape of 40 mm × 5 mm × 150 μm. Thermal expansion was measured by a SEIKO TMA/SS6100 in tensile mode under 10 mN tension with 10 mm span at a heating rate of 3 °C/min.

RESULTS AND DISCUSSION

Synthesis of PHBH/Cellulose Composite. The PHBH/cellulose composite was prepared by the immersion method. In this study, a porous material based on cellulose gel was used as the reinforcement filler for PHBH. Cellulose was dissolved in a Ca(SCN)₂ aqueous solution at 120 °C, followed by cooling at room temperature to form a white cloudy gel similar to agar gel. The salt in the cellulose gel was extracted by rinsing with ethanol, and cellulose was regenerated as a white porous material retaining its shape. The formation of the porous cellulose was dependent on the cellulose concentration in a Ca(SCN)₂ aqueous solution. The immersion method relies on penetration of dissolved PHBH into the pore of cellulose by

diffusion. The regenerated cellulose with a porous structure was immersed in a PHBH chloroform solution, followed by drying at room temperature to remove the solvent. Figure 1 shows a

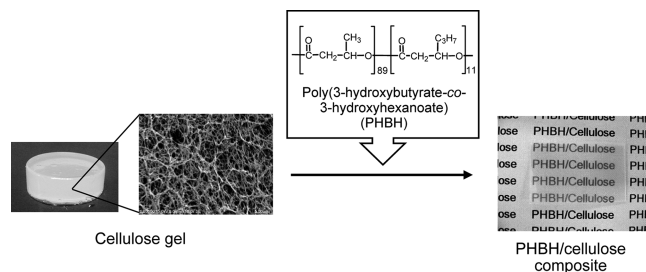


Figure 1. Preparation of PHBH/cellulose composite.

photograph of the PHBH/cellulose composite after hot pressing at 160 °C. The resulting composite was transparent, and the letters (PHBH/Cellulose) in the background could be seen through the sample. This result suggests structural homogeneity above visible wavelengths, resulting from the nanometric fibrous structure of cellulose. With a higher cellulose content, however, some turbidity was observed due to heterogeneous coagulation of cellulose (Figure S2, Supporting Information).

TG analysis was performed to evaluate the cellulose content of the composite. Figure 2 shows typical TG curves of neat

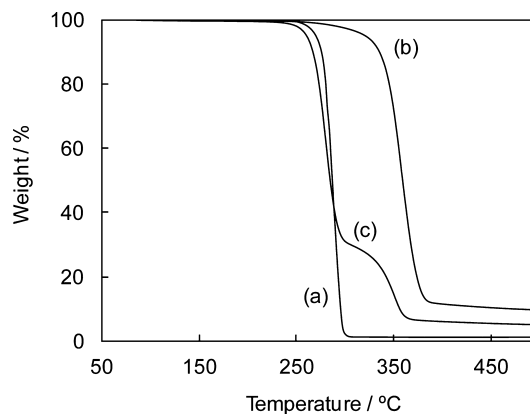


Figure 2. Typical TG curves of (a) neat PHBH, (b) cellulose, and (c) PHBH/cellulose-32.

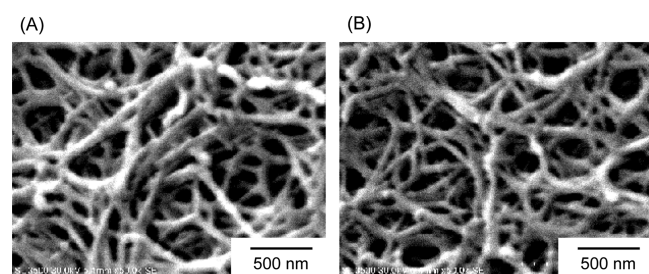
PHBH, cellulose, and PHBH/cellulose composite. The weight of neat PHBH and porous cellulose rapidly decreased at 292 and 361 °C, respectively. The TG curves of PHBH/cellulose composites showed stepwise degradation behaviors and allowed assessment of the cellulose content of the composite from a weight decrease at about 360 °C. In this study, three composites were prepared. The sample code, cellulose concentration in a Ca(SCN)₂ aqueous solution, cellulose content of the composite, and decomposition temperature are summarized in Table 1. The cellulose content depended on the cellulose concentration in a Ca(SCN)₂ aqueous solution, indicating that the cellulose content of the composites could be controlled.

Figure 3 shows SEM images of the porous cellulose and the residue after soaking of the composite in chloroform for 24 h. The cellulose gel had a highly porous structure consisting of a fibrillar network, which was ascribed to the phase separation of

Table 1. Preparation of PHBH/Cellulose Composite

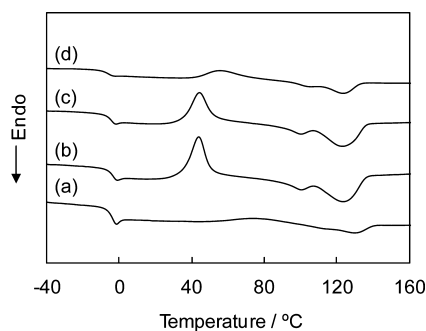
code	cellulose concentration ^a (wt %)	cellulose content ^b (wt %)	decomposition temperature (°C)	
			T_{d1}	T_{d2}
PHBH	– ^c	0	290	– ^d
PHBH/cellulose-16	1.0	16	287	344
PHBH/cellulose-32	2.5	32	283	352
PHBH/cellulose-45	4.0	45	283	350
cellulose	– ^c	100	– ^d	361

^aCellulose concentration in $\text{Ca}(\text{SCN})_2$ aqueous solution. ^bCellulose content of PHBH/cellulose composite. ^cNo data. ^dNot observed.

**Figure 3.** SEM images of (A) porous cellulose and (B) residue of PHBH/cellulose composite after soaking in chloroform.

the cellulose solution. The morphology of the residue of the composite after soaking in chloroform was similar to that of the porous cellulose, indicating that fibrillar cellulose is not aggregated during the washing by ethanol and preparation of the composite. Furthermore, the residue weight after soaking was close to TG results.

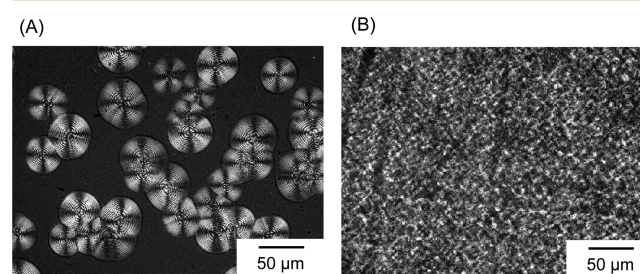
Thermal Properties of PHBH/Cellulose Composite. DSC measurements of neat PHBH and PHBH/cellulose composites were performed to evaluate the effects of the porous cellulose on thermal behaviors of PHBH (Figure 4). In

**Figure 4.** DSC curves of heating scan for (a) neat PHBH, (b) PHBH/cellulose-16, (c) PHBH/cellulose-32, and (d) PHBH/cellulose-45.

the second heating scan, glass transition, cold crystallization, and melting of PHBH were observed. The glass transition temperature (T_g) of PHBH was hardly changed by the incorporation of cellulose. Similar results were reported in several studies.^{40,41} On the other hand, the cold crystallization temperature of the PHBH/cellulose composites decreased, and the exotherm peaks at around 40 °C became sharper compared with those of neat PHBH. This behavior resulted because the cellulose component accelerated the crystallization of PHBH

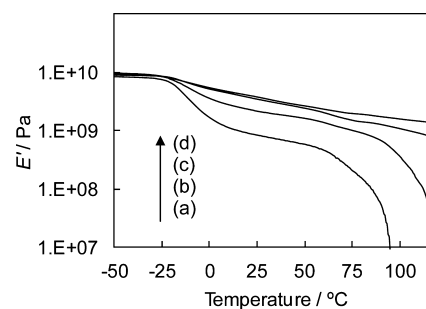
(Figure S3, Supporting Information). The three-dimensional network of cellulose reduced the energy barrier of nucleation to form a small critical nucleus of PHBH. Neat PHBH and PHBH/cellulose composites exhibited two melting peaks, demonstrating the melting–recrystallization–melting process, and the intensity of the lower melting peak of the bimodal endotherms increased due to the incorporation of cellulose. This is accounted for by the melting of the unstable crystal and thin lamella of PHBH formed by the hindrance of the cellulose network. Although the crystallization of PHBH was effectively accelerated in PHBH/cellulose-16 and PHBH/cellulose-32, the crystallization of PHBH was inhibited at higher cellulose content (PHBH/cellulose-45). This may be due to the confinement of PHBH chains caused by a large amount of cellulose.

The crystallization behaviors of PHBH were also investigated by polarized optical microscopy (Figure 5). Polarized optical

**Figure 5.** Polarized optical micrographs of (A) neat PHBH and (B) PHBH/cellulose-32.

micrographs were taken 10 min after quenching from the melt at 180 °C. In neat PHBH, the spherulite with characteristic banding and a Maltese cross was observed. The spherulite size of neat PHBH was relatively large, and the nuclear density was quite low. A polarized micrograph of the PHBH/cellulose composite at 180 °C was slightly bright due to the crystallized cellulose, although the fibrous structure was not observed (Figure S4, Supporting Information). The PHBH component crystallized during the cooling process, and the porous cellulose increased the number of PHBH crystals and dramatically reduced the crystal size. This observation agrees with DSC results.

Mechanical Properties of PHBH/Cellulose Composite. To evaluate the reinforcement effect of the porous cellulose, dynamic viscoelasticity analysis was performed. Figure 6 shows the temperature dependence of the storage modulus of neat PHBH and PHBH/cellulose composites. The storage modulus

**Figure 6.** Dynamic viscoelasticity of (a) neat PHBH, (b) PHBH/cellulose-16, (c) PHBH/cellulose-32, and (d) PHBH/cellulose-45.

of neat PHBH at lower temperature (below T_g) was almost constant at around 9.0 GPa and dropped around -20 and 60 °C, which derives from the glass transition and melting of PHBH, respectively. The incorporation of porous cellulose increased the storage modulus in the rubbery region, and the reinforcement effect depended on the cellulose content of the composite. The storage modulus of the PHBH/cellulose composite with high cellulose content was relatively higher above even the melting temperature of PHBH, suggesting the porous cellulose improved thermal stability.

The strain–stress curves of neat PHBH and PHBH/cellulose composites are shown in Figure 7, and the mechanical

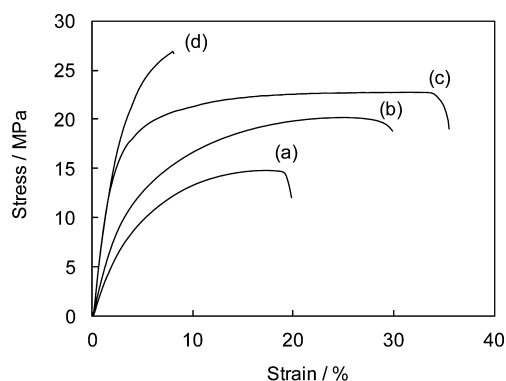


Figure 7. Strain–stress curves of (a) neat PHBH, (b) PHBH/cellulose-16, (c) PHBH/cellulose-32, and (d) PHBH/cellulose-45.

properties such as Young's modulus, maximum strength, strain at break, and toughness are summarized in Table 2. Mechanical

Table 2. Mechanical Properties of PHBH/Cellulose Composite

code	Young's modulus (MPa)	maximum strength (MPa)	strain at break (%)	toughness (MJ m^{-3})
PHBH	271	15	20	2.2
PHBH/cellulose-16	378	20	29	4.9
PHBH/cellulose-32	732	22	36	7.2
PHBH/cellulose-45	746	27	8	1.5

properties of fiber-reinforced materials are affected on some factors such as fiber volume, aspect ratio, fiber–matrix adhesion, and orientation. Tensile strength is dependent on the compatibility between the fiber and matrix, while modulus is influenced by fiber impregnation or the aspect ratio of the fiber.⁴² The Young's modulus and tensile strength of the PHBH/cellulose composites increased compared with those of neat PHBH. These behaviors are related to the three-dimensional porous structure of cellulose and the interaction between PHBH and regenerated porous cellulose owing to their relatively polar nature. These data indicate that porous cellulose acts as reinforcement material. The strain at break of the PHBH/cellulose composites was larger than that of neat PHBH. The brittleness of poly(3-hydroxyalkanoate) such as PHB and PHBH is attributed to large spherulites and secondary crystallization.^{43–45} The porous cellulose dramatically decreased the spherulite size of PHBH by the nucleating effect of cellulose. Moreover, the toughness of PHBH/cellulose-32, defined as the area of the strain–stress curve, was more than 3 times larger compared with that of neat PHBH. This data

implies that the resulting composites possess a great ability to absorb energy before breaking.

The coefficient of thermal expansion (CTE) is reduced by the transfer of thermal stress from the polymer matrix to the high aspect ratio fibrous material such as glass fiber or cellulose fiber.^{46,47} Figure 8 shows the thermomechanical analysis results

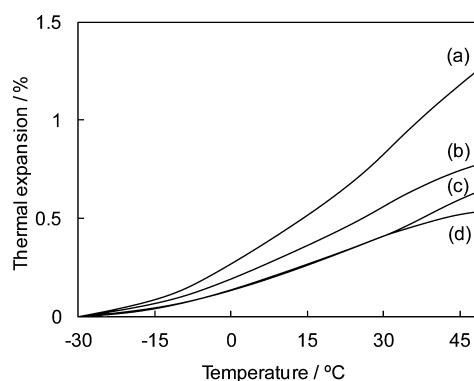


Figure 8. Thermal expansion of (a) neat PHBH, (b) PHBH/cellulose-16, (c) PHBH/cellulose-32, and (d) PHBH/cellulose-45.

of neat PHBH and PHBH/cellulose composites. The CTEs of PHBH/cellulose composites in glassy state (below T_g) were 22–42 ppm/K, where the values were smaller than those of neat PHBH. Above T_g , the CTE of neat PHBH remarkably increased. On the other hand, the incorporation of porous cellulose suppressed the thermal expansion of the PHBH/cellulose composites as the cellulose content increased. These results indicate that the three-dimensional network structure of cellulose is effective in restricting thermal expansion of PHBH matrix.

CONCLUSIONS

In this study, a green composite from bacterial polyester and cellulose was developed, and the thermal and mechanical properties of the composite were evaluated. Regenerated porous cellulose prepared from a $\text{Ca}(\text{SCN})_2$ aqueous solution was impregnated with PHBH by immersion of the porous cellulose in a polymer solution, and subsequent drying gave a full biobased composite. The resulting composites showed relatively good transparency due to the nanoscale network structure of cellulose. The porous cellulose accelerated the crystallization of PHBH, and the spherulite size of PHBH decreased. The Young's modulus and tensile strength of PHBH/cellulose composites were larger than those of neat PHBH. The incorporation of porous cellulose also increased the strain at break, indicating that the resulting composites are effectively reinforced without sacrificing toughness. Furthermore, the porous cellulose resulted in low thermal expansion of the composites.

Given that the present composite is derived from renewable resources, the biomass content of the PHBH/cellulose composite was 100%. Therefore, the resulting composite should contribute greatly to the reduction of greenhouse gas emissions. This study provides a new methodology for the preparation of high-performance biobased polymeric composites. Further investigations on biobased composites are under way in our laboratory.

■ ASSOCIATED CONTENT

■ Supporting Information

Typical nitrogen adsorption/desorption isotherm of porous cellulose (Figure S1). Photographs of PHBH/cellulose composites (Figure S2). DSC curves of cooling scan for neat PHBH and PHBH/cellulose composites (Figure S3). Polarized optical micrographs of neat PHBH and PHBH/cellulose composite at 180 °C (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*Tel: +81-6-6879-7365. Fax: +81-6-6879-7367. E-mail: tsujimoto@chem.eng.osaka-u.ac.jp (T.T.).

*Tel: +81-6-6879-7364. Fax: +81-6-6879-7367. E-mail: uyama@chem.eng.osaka-u.ac.jp (H.U.).

Notes

The authors declare no competing financial interest.

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