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Effects of TS-1 zeolite structures on physical properties and enzymatic degradation of Poly (butylene succinate) (PBS)/TS-1 zeolite hybrid composites

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ABSTRACT

The objective of this study was to investigate how the water uptake features and carrier characteristics of the TS-1 zeolite affected the physical and rheological properties, morphological parameters, and enzymatic hydrolysis of Poly (butylene succinate) (PBS). The introduction of TS-1 zeolite as catalyst was developed for the preparation of PBS/TS-1 zeolite hybrid composites (PTHC) without heavy metal toxic substance in the context on clean technology. The TS-1 zeolite can act as a catalyst as well as a reinforcement filler with the result that PTHC can show marked increases in tensile properties and elongation at breakage in the solid state. The rheological properties of PTHC with high zeolite contents showed low values of complex viscosity, as compared with PTHC with low TS-1 zeolite contents, due to the volatilization of water released from the zeolite pores during esterification. The introduction of the TS-1 zeolite in the PBS matrix was not significantly affected by changes in the size of the long period, lamella thickness, or the amorphous region, indicating that PBS chains do not penetrate into zeolite pores, as confirmed by SAXS profiles. In enzymatic hydrolysis over 90 days, the enzymatic hydrolysis rates of PTHC significantly accelerated with increasing TS-1 zeolite contents, compared with Homo PBS. This result indicated that TS-1 zeolite can act as a carrier for enzyme activation, resulting in enzymatic hydrolysis, occurring from the amorphous area on the surface into the inside of the film.

1. Introduction

Zeolites, generally defined as high-ordered microporous materials, have been used as heterogeneous catalysts in many reactions, such as aromatization, cracking, esterification, alkylation, and methanol conversions. They have also been used in petroleum refining as drying agents, ion exchangers, animal food additives, nuclear effluent treatment, and membranes in numerous industrial fields [1–7]. Zeolite activity in these applications depends on the active sites, high surface area, and pore volumes. Thus, many researchers have studied the synthesis of new ordered microporous materials for various applications [8–16].

Among the many zeolite types, titanium silicate-1 (TS-1) zeolite has been found to have strong catalytic activity [17–23]. The titanium in TS-1 replaces silicon in a tetrahedral site of the MFI silicate lattice. TS-1 combines the advantages of having the high coordination ability of Ti^{4+} ions with the hydrophobicity of the silicate framework. In particular, the adsorption of water molecules in the pores is closely associated with the surface structure, stability, and activity of Ti sites in TS-1[18–21].

The pores in zeolite have cationic ions for charge balance, and some pores are filled with zeolitic water, resulting in cationic ions that can readily be transported in pores. Thus, TS-1 zeolite is an inorganic ion exchanger with high ion exchange capabilities. High thermal energy readily allows zeolitic water to be desorbed from the zeolite pore. The desorbed zeolite has a strong inclination to quickly fill up pores with water molecules and small polar molecules because this is a natural phenomenon to decrease lattice energy.

Considering the unique characteristics of TS-1 zeolite, it is likely that TS-1 zeolite would have a great effect on biodegradable polymer products with superior properties on the following basis. Firstly, the use of TS-1 zeolite as a catalyst in the synthesis of biodegradable polymer is important in terms of clean technology. The catalytic activity of TS-1 zeolite is closely related to the presence of isolated framework titanium species, strong acid sites on the well-defined microporous structures that are responsible for the shape selectivity, microporous size, the distribution of Ti, and the stability of structures. Despite the limited premises of TS-1 zeolite as efficient heterogeneous catalysts, it is widely recognized that TS-1 zeolite is a highly efficiently heterogeneous catalyst as well as being appropriate for heavy metal-free catalysts. Secondly,

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it should not rule out the possibility that TS-1 zeolite can act as a reinforcement filler. TS-1 zeolite consists of a silicate framework with a bulk particle size (100 nm ~ 1*u*m). Thus, the introduction of TS-1 zeolite should facilitate the preparation of hybrid materials as alternatives to enhance the physical properties of biodegradable polymers by the introduction of organic/inorganic particles, such as clay [24,25], silica [26], polyhedral oligosilsesquioxane (POSS) [27], and chitosan [28]. Thirdly, the selective adsorption features of TS-1 zeolite by high ion exchange capabilities would be expected to utilize TS-1 zeolite as trap functional carrier. Using these unique characteristics, a study on zeolites is being carried out for application to the immobilization of enzymes for biosencing as a carrier [29,30].

This makes possible the synthesis of multifunctional biodegradable hybrid materials by considering the unique feature of TS-1 zeolite such as shape selective catalyst, silicate framework and molecular adsorption.

Studies on polymer–zeolite hybrid materials have been reported over recent decades [31–36]. Graeser and Spange [31] investigated the cationic polymerization of various substituted vinyl ethers with HY zeolite and the combined properties of novel hybrid materials. Several papers [35–37] have shown that zeolite can act as reinforcement filler and nucleation agent in polymer matrices to increase thermal and mechanical properties. However, to date no study has been reported regarding biodegradable polymer hybrid materials using zeolite.

We expected that the unique characteristics of TS-1 zeolite would lead to enhanced physical properties and biodegradability of biodegradable polymers. In this study, TS-1 zeolite can act as catalyst, a reinforcement filler and affect the biodegradation rate at the same time. We prepared composite materials composed of Poly (butylene succinate) (PBS) and TS-1 zeolite by *in situ* polymerization with no conventional catalyst. This study described the consequences of the water uptake features and carrier characteristic of TS-1 zeolite on physical properties during melt processing and biodegradability.

We anticipate that PBS/TS-1 zeolite hybrid materials may have advantages in applications in the agriculture sector, packaging technologies, coatings, and drug delivery vesicles because of the unique characteristic of TS-1 zeolite.

2. Experimental

2.1. Materials

The TS-1 zeolite was kindly provided by the Korea Institute of Ceramic Eng. & Tech (KICET). The amount of Ti(IV) incorporated in the used TS-1 zeolite framework is consistent with a Si:Ti ratio of 62 based on X-ray fluorescence spectrometry. We also purchased 1,4 butanediol (99%) and succinic acid (99%) from Sigma–Aldrich (St. Louis, MO, USA). Reagents were used without further purification.

2.2. Preparation of the PBS/TS-1 zeolite hybrid composite

The PBS/TS-1 zeolite hybrid composite (PTHC) was prepared with TS-1 zeolite (~ 2.0 wt% of succinic acid weight) by a two-step *in situ* polymerization processing. First, TS-1 zeolite (0.5–2 wt%) was dispersed in 1,4 butanediol (0.6 mol) using an ultrasonic processor (VCX500, 500 W, 20 kHz; Sonic, Danbury, CT, USA) for 30 min before the ester interchange reaction. While the slurry was stirred vigorously, succinic acid (0.5 mol) was added without a heterogeneous catalyst. The mixture was then heated to 190 °C in an oil bath and subjected to mechanical stirring at 250 rpm under a nitrogen atmosphere. The temperature was increased to 240 °C at 10 °C/min with gradually reduced pressure to ensure that water and low-molecular-weight condensates were removed continuously, and the mixture was maintained at 240 °C for 3 h. The resulting samples were repeatedly washed with water and dried in a vacuum for 24 h at 50 °C. Sample codes were denoted by zeolite name and content. For example, “TS20” represents a PTHC with 2.0 wt% zeolite content.

2.3. Characterizations

The N_2 adsorption–desorption isotherm of TS-1 zeolite were performed using a Quantachrom Autosorb-1 after the sample had been degassed at 200 °C. Thermogravimetric analysis coupled with infrared spectroscopy [TG-IR, TG 209 °C Iris® (Netzsch, Exton, PA, USA) coupled with a Tensor 27 FTIR (Bruker Optics, Billerica, MA, USA)] was used to determine the qualitative and quantitative identification of the adsorbed water gases released directly from the sample during the thermal melting behavior as a function of temperature and time. The TGA was performed at a heating rate of 10 °C/min from 20 °C to 150 °C under a nitrogen atmosphere at a flow rate of 20 mL/min. IR spectra were collected at a 4 cm^{-1} resolution over the range of 600–4000 cm^{-1} on a continuous basis.

Mechanical tests were conducted using a tensile strength evaluator (Instron 4465; Instron Corp., Norwood, MA, USA) with a crosshead speed of 10 mm/min at room temperature. The rheological behaviors of all samples were measured using a dynamic oscillatory viscometer (ARES; Rheometric Scientific Inc., Piscataway, NJ, USA) with parallel plate geometry, 120 mm diameter, and a 1.0-mm gap distance between the parallel plates.

The experiment was performed with a frequency sweep ranging from 0.5 to 500 rad/s at a 10% strain level at 150 °C. SAXS experiments were conducted at the 4C1 SAXS Beamline of the Pohang Accelerator Laboratory (Korea). The storage ring was operated at 2.5 GeV and a ring current of 150–200 mA. The X-ray wavelength was 0.1608 nm and the beam size at the focal point was less than 1 mm^2, focused by a platinum-coated silicon premirror through a double-crystal monochromator. The scattering intensity was detected with a two-dimensional CCD camera. The scattering angle was calculated with a Bragg spacing of 32.78 nm for a SEBS crystal at $q = 0.19165\ \text{nm}^{-1}$ as a reference peak for SAXS. The samples were melted at 150 °C in the melting chamber to eliminate their thermal histories, quickly heated to the designated isothermal crystallization temperature (80 °C and 92 °C), and maintained for 30 min to allow for complete crystallization. The scattering profiles were monitored with exposure times of 27.7 s.

The static contact angles of the PTHC were measured using the sessile drop method with a contact shape analyzer (DSA 100; Krüss, Hamburg, Germany) to study the effect of the zeolite on hydrophilicity. Distilled water was used to measure the evolution of the contact angle with time. Water droplets (2 μL) were dropped onto the surface of the 0.3-mm-thick amorphous film. Before testing, the film samples were dried in desiccators at a normal state (20 °C) for 48 h to achieve conditioning. Each reported value is the average of at least five time replicates.

The enzymatic hydrolysis test of samples was carried out at 37 ± 0.5 °C in reciprocating shaking water bath for 90 days. Each of the films (20 mm × 30 mm, 0.3 ± 0.02 mm) was placed in a glass bottle with 30 mL of 0.2 M phosphate-buffered saline solution with 1.7 mg of lipase (Sigma–Aldrich; *Pseudomonas* sp.). Samples were removed from the solution every week, washed with distilled water several times, dried for 24 h under reduced pressure, and weighed for 90 days.

Wide-angle XRD (WAXD) experiments were conducted with Cu K_α radiation ($\lambda = 1.54$ Å) on an X-ray generator (Rigaku Corp., Tokyo, Japan) operating at 40 kV and 100 mA to investigate structural changes in the PTHC after enzymatic hydrolysis. Samples were scanned at a rate of 5°/min from 3° to 50° in 2θ.