

Research Article

Mechanical and Thermal Characteristics of Bio-Nanocomposites Consisting of Poly-L-lactic Acid and Self-Assembling Siloxane Nanoparticles with Three Phases

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Biopolymer nanocomposites (bio-nanocomposite) consisting of poly-L-lactic acid (PLLA) and siloxane nanoparticles with three phases, a high-density siloxane phase (plural cores), an elastomeric silicone phase, and a caprolactone oligomer phase, were developed to increase the mechanical properties of PLLA. The nanoparticles, average size of 13 nm, were self-assembled by aggregation and condensation of an organosiloxane with three units: isocyanatepropyltrimethoxysilane (IPTS), polymethylpropylloxysiloxane (PMPS), and a caprolactone oligomer (CLO), which form each phase. The bio-nanocomposite was produced using PLLA and the nanoparticles. Bending and tensile testing showed that the use of these nanoparticles (5 wt% in PLLA) greatly increases the tenacity (breaking strain) of PLLA while maintaining its relatively high breaking (maximum) strength. The elongation of the nanocomposite was more than twice that of PLLA while the elasticity modulus and breaking (maximum) strength were comparable to those of PLLA. The nanoparticles also increased the impact strength of PLLA. The use of the nanoparticles almost did not show adverse affect on the thermal resistance of PLLA. The nanocomposite's heat resistance indicated by the glass transition temperature and heat distortion temperature was fairly kept. The decomposition temperature of the nanocomposite somewhat increased.

1. Introduction

Polymer nanocomposites, usually consisting of polymers and nanometer-sized particles, have gathered high attentions because of their attracting characteristics [1]. In particular, inorganic nanometer-sized particles (nanoparticles) are mainly used as reinforcing fillers because they improve key characteristics of these composites at a relatively low content [2, 3]. For example, clay nanoparticles [4], metal oxide nanoparticles such as silica [5] and titania nanoparticles [6], and carbon nanotubes [7] increase the mechanical properties, especially the elasticity modulus, of many kinds of polymer composites. However, currently available nanoparticles insufficiently improve the tenacity (elongation at breaking point) of nanocomposites, which is necessary if nanocomposites are used in durable products such as electronic

equipments and automobiles. This is mainly because these nanoparticles lack rubber-like elasticity although they have an affinity for a polymer matrix. Adding a typical elastomer such as rubber or plasticizer (e.g., a long chain alkyl ester) with a high affinity for a polymer matrix, however, reduces the breaking strength and elasticity modulus of the composite due to their lack of rigidity [8, 9].

Nanoparticles with multiplephases, a high-density phase (core) with rigidity and outside phases with rubber-like elasticity and affinity for matrix polymers, should improve the tenacity of nanocomposites without degrading their breaking strength. Metal oxide nanoparticles are typically formed by hydrolysis and condensation reactions of organic metal compounds, mainly silicon alkoxides [10–14] and perhydropolysilazane [15], in solvents or polymers, that is,

a sol-gel method. However, the formation of multiple-phased nanoparticles using these organic metal compounds is difficult due to their limited chemical structures. Moreover, the use of conventional surface treatment agents such as organic metal alkoxides to uniformly form multiple phases on nanoparticles while preventing their coagulation is practically difficult because such treatment is an extremely complex process.

Poly-L-lactic acid (PLLA), a representative mass-produced biopolymer made of biomass (starch), is attractive for use in environmentally sensitive applications because its use prevents petroleum exhaust and reduces plastic waste due to its biodegradability after disposal. Although it has a relatively high breaking strength, its tenacity is extremely inadequate for it to be used in a variety of applications including durable products like those mentioned previously because of its stiff structure, which is due to the hard crystalline region. Studies on PLLA nanocomposites have focused on the usual nanoparticles such as clay and calcium carbonate ones [8, 16, 17]. However, to the best of the authors' knowledge, the use of multiphased nanoparticles to increase the tenacity of PLLA has not been reported.

We briefly reported self-assembling siloxane nanoparticles with three phases and a biopolymer nanocomposite (bio-nanocomposite) consisting of PLLA as a biopolymer and the nanoparticles that improve the tenacity of PLLA [18]. The nanoparticles consist of a high-density siloxane phase (plural cores), an elastomeric silicone phase, and a caprolactone oligomer phase. Self-assembly by aggregation and condensation of an organosiloxane with three units forms each phase. Testing showed that the use of the nanoparticles greatly increases the tenacity (breaking strain) of PLLA while maintaining its relatively high breaking strength.

In this paper, we report the detailed characterization of the nanoparticles with three phases and the mechanical and thermal characteristics of the bio-nanocomposite consisting of PLLA and the nanoparticles. The nanoparticles' outside and inside structures and size distribution were investigated. The influence of using the nanoparticles on PLLA's bending, tensile and impact strengths, heat resistance, and thermal decomposition resistance was revealed.

2. Experiment

2.1. Materials. Polymethylmethoxysiloxane (PMMS) (methoxy/methyl molecular ratio: 1/1, siloxane number: 8.0; Shin-etsu Kagaku Co., Japan; KC-89S), isocyanatepropyltrimethoxysilane (IPTS) (Azumax Co, Japan; SII645), and ϵ -caprolactone (Daicel Co., Japan; PLCCE) were used to produce the tested organosiloxanes. The analytical reagents, acetone, n-propanol, butanol, hexane, pyridine, tetrahydrofuran, dimethylsulfoxide (DMS) hydrogen chloride, methane sulfonic acid, thin octylate, and ammonium solution (28%), were obtained commercially and used as received. The poly-L-lactic acid (PLLA) (Mn: 900,000; TE-4000) was provided by Unitika Co. (Japan). The silica nanoparticles (average diameter: 12 nm; AEROJIL 200) were provided by Nippon Aerojil Co. (Japan).

2.2. Synthesis of Organosiloxanes. Organosiloxane with three units, isocyanatepropyltrimethoxysilane (IPTS), polymethylpropyloxysiloxane (PMPS), and a caprolactone oligomer (CLO), was prepared as follows.

PMPS was prepared by replacing the methoxy groups of polymethylmethoxysiloxane (PMMS) with propyloxy groups. PMMS (14.7 g, 25 mmol), n-propanol (45.0 g, 750 mmol), methane sulfonic acid (0.096 g, 10 mmol), and hexane (100 mL) were mixed and heated at 80°C for 5 hours in a nitrogen atmosphere while removing the formed methanol. After the reaction, the methane sulfonic acid was neutralized by adding pyridine (0.079, 10 mmol), and the resulting salt was removed using a paper filter. The remaining propanol was removed by evaporation. Almost all (more than 90%) methoxy was replaced by propyloxy, as determined by hydrogen-nuclear magnetic resonance (H-NMR) (Bruker Co., USA; BRUKER AVANCE 400; 400-MHz operation). (¹H-NMR [CDCl₃ (ppm)]: 0.14–0.27 (m, 24 H, Si-CH₃), 0.87–0.93 (m, 30 H, Si-OCH₂CH₂CH₃), 1.37–1.47 (m, 20 H, Si-OCH₂CH₂CH₃), 3.67–3.78 (m, 20 H, Si-OCH₂CH₂CH₃)).

The CLO was prepared by polymerizing ϵ -caprolactone by using butanol as an initiator; ϵ -caprolactam (22.8 g, 200 mmol), butanol (5.0 g, 67 mmol), and thin octylate (0.081 g, 0.020 mmol) were mixed for 10 hours at a room temperature. The unreacted materials were removed by evaporation. The resulting CLO had a molecular weight (Mn) of 550 as measured using a gel permeation chromatography (GPC) analyzer (Shimadzu Co., Japan; 10A-VP, standard material: Polystyrene, solvent: THF). The CLO was confirmed to be soluble in melted PLLA at 180°C.

The PMPS and CLO were then combined. PMPS (5.4 g, 6.0 mmol), CLO (3.3 g, 6.0 mmol), methanesulfonic acid (0.0058 g, 0.60 mmol), and toluene (20 mL) were mixed, and the resulting propanol was removed by evaporation. The methane sulfonic acid in the solution was neutralized by adding pyridine (0.047 g, 0.60 mmol), and the resulting salt was removed using a paper filter. The unreacted PMPS and CLO in the resulting compound were removed with a column with polystyrene particles. The reaction of the hydroxyl in the CLO with the propyloxy in PMPS was mostly completed (more than 90%), as determined by H-NMR. (¹H NMR [CDCl₃ (ppm)]: 0.14–0.27 (m, 24 H, Si-CH₃), 0.87–0.98 (m, 27 H, Si-OCH₂CH₂CH₃), 0.96 (t, 3 H, CH₃CH₂CH₂CH₂OCO-), 1.37–1.47 (m, 18 H, Si-OCH₂CH₂CH₃), 1.41 (m, 9 H, - (OCH₂CH₂CH₂CH₂CH₂CO)_n-OCH₂CH₂CH₂CH₃), 1.52–1.68 (m, 16 H, - (OCH₂CH₂CH₂CH₂CH₂CO)_n-OCH₂CH₂CH₂CH₃), 2.32 (m, 7 H, - (OCH₂CH₂CH₂CH₂CH₂CO)_n-), 3.67–3.78 (m, 18 H, Si-OCH₂CH₂CH₃), 3.85 (t, 2 H, Si-OCH₂CH₂CH₂CH₂CH₂CH₂OCO-), 4.09 (m, 7 H, - (OCH₂CH₂CH₂-CH₂CH₂CO)_{n-1}-OCH₂CH₂CH₂CH₃)).

The resulting compound consisting of PMPS and CLO was connected with IPTS, to produce the organosiloxane with IPTS, PMPS, and CLO. To promote reaction with the isocyanate in the IPTS, an adequate amount of the propyloxy group in the PMPS-CLO compound was changed to silanol by mixing the compound (3.8 g, 2.0 mmol),

diluted hydrogen chloride (pH 2.5, 1.5 g), and acetone (30 mL) for one hour. The hydrogen chloride in the solution was neutralized by adding sodium hydroxide (0.42 g, 10 mM), and then the water was removed by adding magnesium sulfate (50 g), which was recovered using a paper filter. The acetone was removed by evaporation. Approximately 13% of the propyloxy was changed to silanol, as determined by H-NMR. (^1H NMR [CDCl_3 (ppm)]: 0.14–0.27 (m, 24 H, Si– CH_3), 0.87–0.98 (m, 24 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.96 (t, 3 H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCO}$ –), 1.37–1.47 (m, 15 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.41 (m, 9 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ – $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.52–1.68 (m, 16 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ – $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.32 (m, 7 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ –), 3.67–3.78 (m, 15 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.85 (t, 2 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCO}$ –), 4.09 (m, 7 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ – $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.05–5.78 (br, 1 H, Si–OH)). The amount of silanol was almost the same as that of the isocyanate in the IPTS. The resulting PMPS-CLO compound containing the silanol (3.4 g, 2.0 mmol), ITMS (0.51 g, 2.5 mmol), and thin octylate (0.0081 g, 0.0020 mmol) was mixed in a nitrogen atmosphere at room temperature for 24 hours. The unreacted IPTS and PMPS-CLO compound in the final compound was removed using the same column. The reaction ratio of IPTS with the PMPS-CLO compound was 90%, as determined by H-NMR. (^1H NMR [CDCl_3 (ppm)]: 0.14–0.27 (m, 24 H, Si– CH_3), 0.62 (m, 2 H, Si– $\text{CH}_2\text{CH}_2\text{CH}_2$ –), 0.87–0.98 (m, 24 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.96 (t, 3 H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCO}$ –), 1.37–1.47 (m, 15 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.41 (m, 9 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ – $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.52–1.68 (m, 16 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ – $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.60 (m, 2 H, Si– $\text{CH}_2\text{CH}_2\text{CH}_2$ –), 2.32 (m, 7 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ –), 3.08 (m, 2 H, Si– $\text{CH}_2\text{CH}_2\text{CH}_2$ –), 3.55 (m, 9 H, Si– OCH_3), 3.67–3.78 (m, 15 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.85 (t, 2 H, Si– $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCO}$ –), 4.09 (m, 7 H, –($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$) $_n$ – $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.45 (s, 1 H, NH)).

As references, an organosiloxane with IPTS and PMPS units and an organosiloxane with PMPS and CLO units were prepared using each unit and the methods described previously.

Moreover, the structures of these resulting organosiloxanes: the organosiloxane with IPTS, PMPS, and CLO units, the organosiloxane with IPTS and PMPS units, the organosiloxane with PMPS and CLO units, and the PMPS alone were measured by GPC as previously described to determine molecular weights and element analysis to determine the contents of carbon, hydrogen, and nitrogen (Elementar Co., Germany; vario MICRO cube, Burning furnace: 950°C, Reducing furnace: 550°C, Helium: 200 mL/min, Oxygen: 25–30 mL/min). The molecular weights and element contents are listed in Table 1, indicating that they mostly agreed with the calculated values.

2.3. Formation of Nanoparticles. Three-phased nanoparticles were formed by aggregation and condensation of the

organosiloxane with three units (IPTS, PMPS, and CLO) in two steps. The stepwise reactions were ascertained by H-NMR analysis for methoxy, propyloxy, and silanol.

The first step was core formation through hydrolysis and condensation of the methoxy in the IPTS unit. The organosiloxane with three units (1.9 g, 1.0 mmol), water (1.8 g, 100 mmol), ammonium solution (28%, 1.6 g), and tetrahydrofuran (THF, 10 mL) were mixed for 24 hours at room temperature. About 90% of the methoxy was consumed by hydrolysis, but the increase in silanol resulting from the methoxy was barely detected, demonstrating that most of the silanol formed siloxane bonds. Reaction of the propyloxy in the PMPS unit did not occur. The THF, water, and ammonia were removed by evaporation.

The second step was elastomeric silicone phase formation in the nanoparticles through hydrolysis and condensation of the propyloxy in the PMPS unit by heating at a high temperature in DMS, which has a higher boiling point (189°C). DMS (200 mL) was added to the resulting nanoparticles after the first step, followed by heating at 180°C for 20 minutes. After this step, there was almost complete (more than 90%) hydrolysis and condensation of the propyloxy in the nanoparticles.

The reference particle consisting of cores and elastic silicone phase (average diameter: 10 nm) was formed using the organosiloxane with IPTS and PMPS through the first step as aforementioned. The reference particle consisting of elastic silicone and CLO phases (average diameter: about 100 nm) was formed using the organosiloxane with PMPS and CLO through the second step as previously mentioned.

2.4. Production of Bio-Nanocomposites. A bio-nanocomposite consisting of PLLA and the three-phased nanoparticles was prepared as follows. After the first step (core formation), the THF, water, and ammonia were removed by evaporation. The resulting nanoparticles (5.0 g) were mixed with PLLA (95.0 g) in chloroform (500 mL), followed by removal of the solvent by evaporation. The resulting composite was extruded at 180°C for 10 minutes using a screw-type mixer (Thermo Electron Co., Germany; Mini Lab Haake Rheomex CTW5) and molded by pressing while heating at 180°C for 10 minutes at 100 kg/cm², followed by crystallization of the PLLA in the composite by heating at 100°C for 4 hours.

As references, PLLA composites containing the commercial silica nanoparticles, the two-phased nanoparticles, or the organosiloxane with PMPS and CLO were prepared using the method described previously. The two-phased nanoparticles (average diameter: 10 nm) were formed using the organosiloxane with IPTS and PMPS units through the core formation step as previously mentioned (the first step).

2.5. Measurements of Nanoparticles and Bio-Nanocomposites. The three-phased nanoparticles were observed with a scanning electron microscope (SEM) (Hitachi High-Technologies Co., Japan; HD-2300). Their size distribution and average diameter were measured with a light scattering analyzer (Microtrac Co., Japan; Nanotracer UPA-UT151).

To investigate the inside structure of the nanoparticles, the amounts of silicon and carbon in the nanoparticles were

TABLE 1: Molecular weights and element content of organosiloxanes.

Organosiloxane	Molecular weight (Mn)	Element content ratio (wt%)
	Measured/calculated	Measured/calculated
PMPS ⁽¹⁾	904/1062	C: 42.5/42.9 H: 8.8/8.9 N: <0.3/0
IPTS ⁽²⁾ + PMPS + CLO ⁽³⁾	1449/1695	C: 47.2/47.4 H: 8.6/8.6 N: 0.5/0.8
IPTS + PMPS	1083/1225	C: 41.5/41.1 H: 8.6/8.4 N: 0.6/1.1
PMPS + CLO	1433/1532	C: 48.9/49.9 H: 8.8/9.5 N: <0.3/0

⁽¹⁾ Polymethylpropyloxysiloxane.

⁽²⁾ Isocyanatepropyltrimethoxysilane.

⁽³⁾ Caprolactone oligomer.

determined using an SEM energy dispersive X-ray analyzer (SEM-EDX) (Hitachi High-Technologies Co., Japan; HD-2300).

The mechanical characteristics of the bio-nanocomposite, reference composites, and PLLA were measured by bending and tensile testing in accordance with JIS K 7171 using a bending and tensile testing instrument (Instron Co., USA; INSTRON 5567). The test pieces of the molded resin samples in the bending test were 2 mm thick, 40 mm long, and 25 mm wide. The test pieces in tensile testing were 1.2 mm thick, 70 mm long, and 4 mm wide. Furthermore, Izod-impact testing was conducted in accordance to JISK7110 using an impact testing instrument (Toyo Seiki CO., Japan; Universal Impact Tester C1). The test pieces with notch were 3.0 mm thick, 40 mm long, and 25 mm wide.

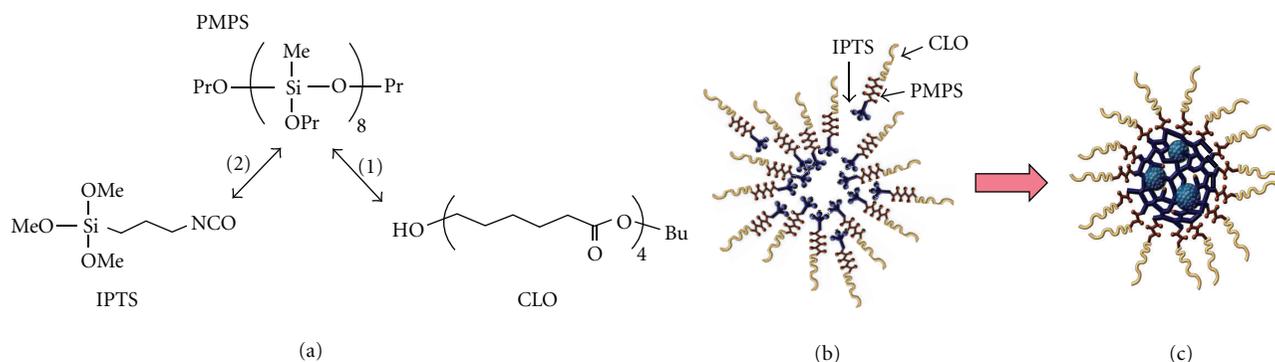
To evaluate thermal properties of the bio-nanocomposites and PLLA, their glass transition temperature (T_g) and melting temperature were measured by using differential scanning calorimetry (DSC) analysis of the samples (Perkin Elmer Co, USA; Perkin Elmer DSC-7 differential scanning calorimeter). The same thermal history as before the measurement was created by heating each sample from -20 to 220°C at a scanning rate of 20°C per minute, then keeping it at 220°C for 5 minutes, and finally quenching it to room temperature. Furthermore, heat distortion temperature of the molded resin samples was measured in accordance with JIS K 7191-2 using a heat distortion temperature measurement (Ueshima Seisakusho CO., Japan, TM-4126). The test pieces were 3.2 mm thick, 40 mm long, and 25 mm wide. The measurement was conducted by heating at a scanning rate of 2 centigrade per minute and loading at 1.8 MPa and 0.45 MPa. Thermal gravimetric analysis (TGA: Seiko Instruments Inc., Japan, EXSTAR 6000) of the resin samples was conducted in nitrogen by heating at 10 centigrade per minute.

3. Results and Discussions

3.1. Self-Assembly of Three-Phased Nanoparticles and Their Characterization. Scheme 1 illustrates the process used to prepare the organosiloxane with three units and the assumed self-assembly of the nanoparticles with three phases through aggregation and condensation of the organosiloxane, which consists of three units: isocyanatepropyltrimethoxysilane (IPTS), polymethylpropyloxysiloxane (PMPS), and a caprolactone oligomer (CLO).

IPTS was selected to form the high-density siloxane phase (plural cores) because it contains methoxy groups, which are highly polar and reactive, at a high molecular ratio, and thus preferentially aggregates and condensates, producing a rigidly cross-linked (high-density) siloxane network that forms more than one core in the particle. PMPS was selected to form the elastomeric silicone phase with an appropriate (nanometer) size around the cores because it contains propyloxy groups, which have moderate polarity and reactivity, at a low molecular ratio in an adequate-length siloxane chain (siloxane number: 8.0). Its use produces a loosely cross-linked (relatively low-density) siloxane network after the core formation. The CLO was selected to form the outside phase due to its low polarity compared with those of IPTS and PMPS and its high affinity for the PLLA matrix (it is highly soluble in melted PLLA). The organosiloxane was synthesized by mixing PMPS with CLO at a molecular ratio of 1 : 1 and then mixing the resulting compound with IPTS at a molecular ratio of 1 : 1.

The organosiloxane with three units dissolved in a solvent aggregated and formed the nanoparticles with three phases due to condensation by using water and a base catalyst (Schemes 1(b) and 1(c)). To avoid confusing the formation of the high-density siloxane cores with the formation of the elastomeric silicone phase around them, we initiated



SCHEME 1: Preparation of organosiloxane with three units (a) and self-assembly of three-phased nanoparticles through aggregation (b) and condensation (c) of organosiloxane.

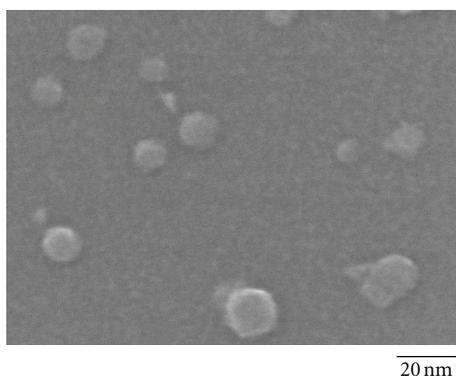


FIGURE 1: Observation of three-phased nanoparticles using scanning electron microscope.

two-step condensation of the organosiloxane by taking advantage of the higher reactivity of the methoxy groups in the IPTS unit than that of the propoxy groups in the PMPS unit. The first step was core formation through hydrolysis and condensation of the methoxy groups in the IPTS unit. The second step was elastomeric silicone phase formation through hydrolysis and condensation of the propoxy groups in the PMPS unit by heating.

As shown in Figure 1, the formed nanoparticles were observed with a scanning electron microscope (SEM). The size distribution, measured by light scattering analysis, indicated a relatively narrow size range, with an average diameter of 13 nm (Figure 2).

The inside structures of the nanoparticles were investigated by scanning electron microscopy and energy dispersive X-ray (SEM-EDX) analysis. Figure 3 shows the result for the amounts (intensities) of silicon and carbon that were detected along the cross section of a representative single nanoparticle in the nanoparticles shown in Figure 1. The amount of silicon originating from the IPTS and PMPS units was remarkably higher at several points around the center. This indicates that the nanoparticle had plural high-density siloxane cores formed mainly from the IPTS unit and that, around the cores, there was a relatively low-density siloxane

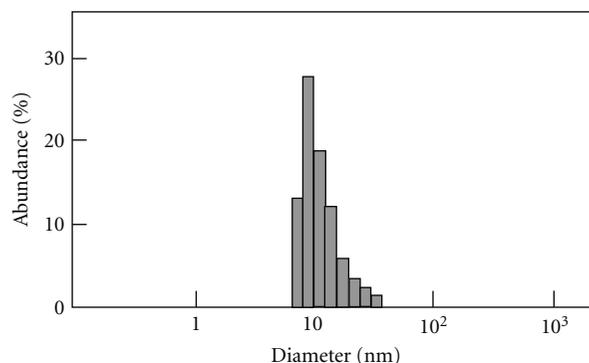


FIGURE 2: Size distribution of three-phased nanoparticles.

phase formed mainly from the PMPS unit. The amount of carbon, which originated from all the units, especially the CLO unit, did not significantly vary throughout the particle. This indicates that there was a relatively high concentration of carbon in the outer layer of the particle, meaning that the CLO unit formed the outside phase fairly well.

From these results, it seems reasonable that three-phased nanoparticles can be formed by self-assembly of the organosiloxane with three units, as shown in Schemes 1(b) and 1(c). The IPTS unit mainly performs the aggregation of the organosiloxane. The aggregated IPTS unit mainly forms the high-density cross-linked siloxane phase (plural cores) through preferential hydrolysis and condensation reactions of its methoxy groups. After the core formation, the PMPS unit mainly forms the middle phase, the relatively low-density cross-linked siloxane network (elastomeric silicone) around the cores through hydrolysis and condensation reactions of its propoxy groups. The CLO unit mainly forms the outside phase of the nanoparticles after the organosiloxane has aggregated because of its position and relatively low polarity.

3.2. Mechanical and Thermal Properties of Bio-Nanocomposite with Three-Phased Nanoparticles. Using PLLA and the three-phased nanoparticles at 5 wt%, we prepared a bio-nanocomposite to measure its mechanical and thermal properties.

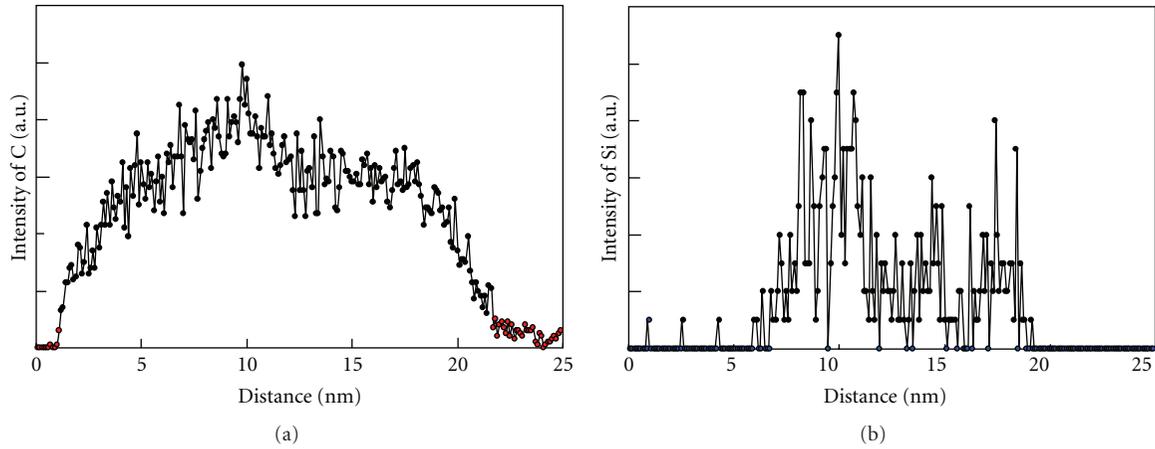


FIGURE 3: Analysis of silicon and carbon in three-phased nanoparticle by SEM-EDX: intensities of silicon (a) and carbon (b) detected along cross section of nanoparticle (The particle diameter: 23 nm).

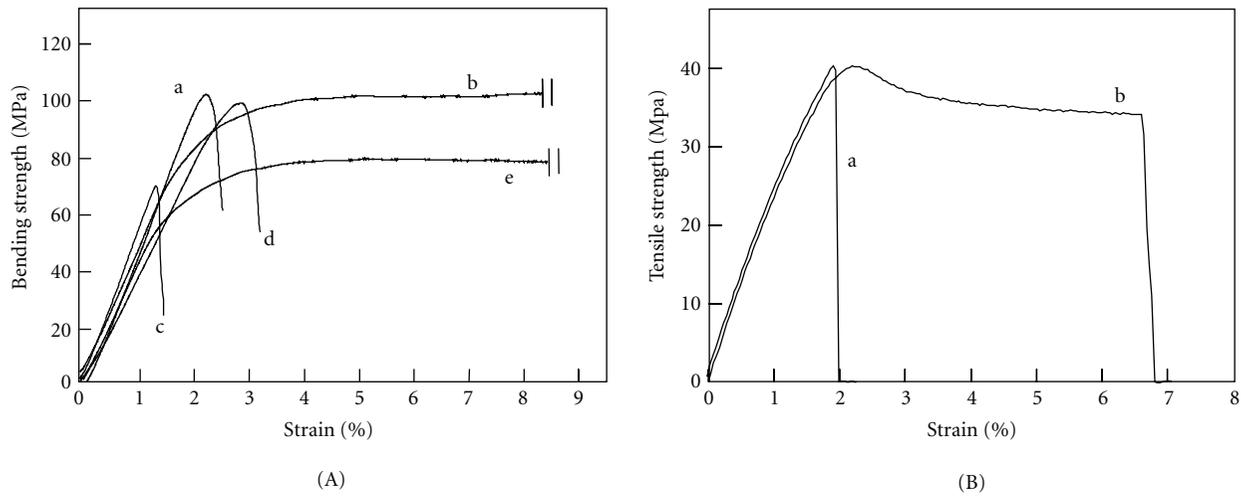


FIGURE 4: Flexural (A) and tensile (B) testing of bio-nanocomposite: (a) PLLA, (b) bio-nanocomposite consisting of PLLA and three-phased nanoparticles (5 wt%), (c) nanocomposite consisting of PLLA and silica nanoparticles (5 wt%), (d) nanocomposite consisting of PLLA and two-phased nanoparticles with cores and elastomeric silicone phase (5 wt%), and (e) composite consisting of PLLA and organosiloxane with PMPS and CLO (5 wt%).

As shown in bending and tensile tests of Table 2 and Figures 4(A) and 4(B), the three-phased nanoparticles greatly increased the PLLA's tenacity without degrading its high breaking strength. The elongation of the nanocomposite was more than twice that of PLLA while the elasticity modulus and breaking (maximum) strength were comparable to those of PLLA.

As references, PLLA composites containing commercial silica nanoparticles, two-phased nanoparticles (cores and elastomeric silicone phase), or the organosiloxane consisting of PMPS and CLO units were prepared using the method described previously. The composite containing the commercial silica nanoparticles, average diameter 12 nm, showed a slight increase in the modulus, but its strength and elongation were less than those of PLLA (Figure 4(A) (c)). The two-phased nanoparticles, average diameter of 10 nm, were formed using the organosiloxane with IPTS and PMPS

TABLE 2: Strength properties of bio-nanocomposite consisting of PLLA and three-phased nanoparticles (5 wt%).

	PLLA	Bio-nanocomposite with nanoparticles
Bending		
Strength (MPa)	100	99
Elastic modulus (GPa)	4.6	4.2
Strain (%)	2.2	9.7
Tensile		
Strength (MPa)	40	40
Elastic modulus (GPa)	2.1	1.8
Strain (%)	1.9	5.0
Izod impact strength (KJ/m ²)	4.3	5.1

TABLE 3: Thermal properties of bio-nanocomposite consisting of PLLA and three-phased nanoparticles (5 wt%).

	Glass transition temperature (°C)	Heat distortion temperature (°C) load: 0.45 MPa/1.80 MPa	Decomposition temperature (°C) /10% weight loss
PLLA	63	124/66	337
Bio-nanocomposite with nanoparticles	59	119/64	344

units through the same core formation step described previously. The composite containing the nanoparticles showed only a slight increase in elongation compared with that of PLLA (Figure 4(A) (d)). The composite containing the organosiloxane with PMPS and CLO (PMPS might be cross-linked when mixing with PLLA during heating) showed substantial increase in elongation compared with that of PLLA, but its strength and modulus were less (Figure 4(A) (e)). These mean that each phase in the three-phased nanoparticles is necessary to increase the PLLA's tenacity while maintaining its breaking strength and modulus.

These results suggest that the mechanism of the improved tenacity due to the use of the three-phased nanoparticles is as follows. During the initial period of the bio-nanocomposite deformation, the nanoparticles create a high elasticity modulus and maximize the strength because of their core rigidity and the high affinity of the outside CLO phase for the PLLA matrix. This idea is supported by the results that the reference organosiloxane with PMPS and CLO, not forming cores and also, the nanosilica, which aggregated in the PLLA composites due to its low affinity with PLLA, did not maintain such a high modulus and strength, simultaneously. In the middle and final periods of the deformation, the three-phased nanoparticles elongated the composite due to the rubber-like elasticity of the elastomeric silicone phase derived from PMPS and the plasticity of the outside CLO phase. While the nanosilica and the reference two-phased particles without the CLO phase did not perform such elongation of the PLLA composites, the organosiloxane with PMPS and CLO elongated the composite, which can support the proposed mechanism.

As listed in Table 2, Izod impact strength of the bio-nanocomposite consisting of PLLA and the three-phased nanoparticle was higher than that of PLLA (20%), indicating that the nanoparticles has a function to increase the strength. However, the effect was limited comparing with usual typical elastomers such as rubber or plasticizer [8]. It is mainly due to the nanoparticles' rigid cores, which can retard the role of the elastomeric phase in the nanoparticles as an impact absorber.

Furthermore, we have cleared the influence of adding the three-phased nanoparticles on the heat resistance of PLLA as listed in Table 3. The glass transition temperature and heat distortion temperature of the bio-nanocomposite consisting of PLLA and the nanoparticles slightly decreased comparing with PLLA, but these levels were fairly kept. Adding typical elastomers such as rubber or plasticizer reduces heat resistance of the composites [8]. However, the nanoparticles maintained the heat resistance of PLLA because of their

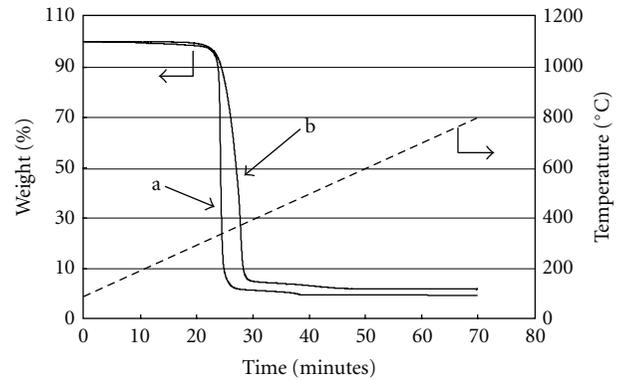


FIGURE 5: Thermal gravimetric analysis of bio-nanocomposite: (a) PLLA and (b) bio-nanocomposite consisting of PLLA and three-phased nanoparticles: 5 wt% (in N₂, 10°C/min).

cores' rigidity to retard the resin's deformation during heating as aforementioned.

The decomposition temperature of the bio-nanocomposite with PLLA and the nanoparticles somewhat increased comparing with PLLA (Table 3, Figure 5). The result was mainly caused by the formation of the cores with high-density cross-linking structures in the nanoparticles, which are resistant to the thermodegradation of the nanocomposites.

4. Conclusion

We reported on a bio-nanocomposite consisting of PLLA and self-assembling siloxane nanoparticles with three phases: a high-density cross-linked siloxane phase (plural cores), an elastomeric silicone phase around the cores, and an outside CLO phase with a high affinity for the PLLA matrix. These nanoparticles were self-assembled by aggregation and condensation of the organosiloxane with three units that, respectively, form each phase. The bio-nanocomposite was produced by mixing PLLA and the nanoparticles in a solvent and removing it. These nanoparticles increased the tenacity of the PLLA and its impacting strength. Bending and tensile test indicated that the elongation of the bio-nanocomposite consisting of PLLA and the nanoparticles was more than twice that of PLLA while the elasticity modulus and breaking (maximum) strength were comparable to those of PLLA. The izod impact strength of the bio-nanocomposite increased by 20 percent comparing with PLLA. The use of the nanoparticles almost did not show adverse affect on the thermal

resistance of PLLA. The heat resistance indicated by the glass transition temperature and heat distortion temperature of the bio-nanocomposite slightly decreased comparing with PLLA, but these levels were fairly kept. The decomposition temperature of the bio-nanocomposite somewhat increased. From these results, the bio-nanocomposite using the three-phased nanoparticles will be used in durable product applications and other new applications. These nanoparticles can also be applied to various other brittle polymers by modifying the structure of the outside phase to achieve a high affinity with these polymers.

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References

- [1] E. Manias, "Nanocomposites: stiffer by design," *Nature Materials*, vol. 6, no. 1, pp. 9–11, 2007.
- [2] F. Hussain, M. Hojjati, M. Okamoto, and R. E. Gorga, "Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview," *Journal of Composite Materials*, vol. 40, no. 17, pp. 1511–1575, 2006.
- [3] J. Jordan, K. I. Jacob, R. Tannenbaum, M. A. Sharaf, and I. Jasiuk, "Experimental trends in polymer nanocomposites—a review," *Materials Science and Engineering A*, vol. 393, no. 1–2, pp. 1–11, 2005.
- [4] A. Usuki, N. Hasegawa, and M. Kato, "Polymer-clay nanocomposites," *Advances in Polymer Science*, vol. 179, pp. 135–195, 2005.
- [5] P. Rosso, L. Ye, K. Friedrich, and S. Sprenger, "A toughened epoxy resin by silica nanoparticle reinforcement," *Journal of Applied Polymer Science*, vol. 100, no. 3, pp. 1849–1855, 2006.
- [6] Z. Evgeni, T. Roza, M. Narkis, and S. Arnon, "Particulate multi-phase polymeric nanocomposites," *Polymer Composites*, vol. 27, no. 4, pp. 425–430, 2006.
- [7] M. Moniruzzaman and K. I. Winey, "Polymer nanocomposites containing carbon nanotubes," *Macromolecules*, vol. 39, no. 16, pp. 5194–5205, 2006.
- [8] T. Li, L. S. Turng, S. Gong, and K. Erlacher, "Polylactide, nanoclay, and core-shell rubber composites," *Polymer Engineering and Science*, vol. 46, no. 10, pp. 1419–1427, 2006.
- [9] M. Shibata, Y. Someya, M. Orihara, and M. Miyoshi, "Thermal and mechanical properties of plasticized poly(L-lactide) nanocomposites with organo-modified montmorillonites," *Journal of Applied Polymer Science*, vol. 99, no. 5, pp. 2594–2602, 2006.
- [10] C. S. Ha and W. Cho, "Microstructure and interface in organic/inorganic hybrid composites," *Journal of Polymer Advanced Technologies*, vol. 11, pp. 145–150, 2000.
- [11] Y. Chujo and T. Saegusa, "Organic polymer hybrids with silica gel formed by means of the sol-gel method," *Advances in Polymer Science*, vol. 100, pp. 10–29, 1991.
- [12] R. Tamaki and Y. Chujo, "Synthesis of polystyrene and silica gel polymer hybrids utilizing ionic interactions," *Chemistry of Materials*, vol. 11, no. 7, pp. 1719–1726, 1999.
- [13] G. Z. Li, L. Wang, H. Toghiani, T. L. Daulton, K. Koyama, and C. U. Pittman, "Viscoelastic and mechanical properties of epoxy/multifunctional polyhedral oligomeric silsesquioxane nanocomposites and epoxy/ladderlike polyphenylsilsesquioxane blends," *Macromolecules*, vol. 34, no. 25, pp. 8686–8693, 2001.
- [14] G. M. Kim, H. Qin, X. Fang, F. C. Sun, and P. T. Mather, "Hybrid epoxy-based thermosets based on polyhedral oligosilsesquioxane: cure behavior and toughening mechanisms," *Journal of Polymer Science B*, vol. 41, no. 24, pp. 3299–3313, 2003.
- [15] A. Yamano and H. Kozuka, "Preparation of silica coatings heavily doped with spiropyran using perhydropolysilazane as the silica source and their photochromic properties," *Journal of Physical Chemistry B*, vol. 113, no. 17, pp. 5769–5776, 2009.
- [16] L. Petersson and K. Oksman, "Biopolymer based nanocomposites: comparing layered silicates and microcrystalline cellulose as nanoreinforcement," *Composites Science and Technology*, vol. 66, no. 13, pp. 2187–2196, 2006.
- [17] L. Jiang, J. Zhang, and M. P. Wolcott, "Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: reinforcing effects and toughening mechanisms," *Polymer*, vol. 48, no. 26, pp. 7632–7644, 2007.
- [18] M. Iji, N. Morishita, and H. Kai, "Self-assembling siloxane nanoparticles with three phases that increase tenacity of poly L-lactic acid," *Polymer Journal*, vol. 43, no. 1, pp. 101–104, 2011.



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