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Self-assembling siloxane nanoparticles with three phases that increase tenacity of poly L-lactic acid

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Polymer Journal (2011) 43, 101–104; doi:10.1038/pj.2010.107; published online 24 November 2010**Keywords:** nanoparticles; poly L-lactic acid; self-assembly; tenacity

Inorganic nanometer-sized particles (nanoparticles) are attracting attention as reinforcing fillers for use in polymer-nanoparticle composites (nanocomposites) because they improve key characteristics of these composites at a relatively low content.^{1,2} For example, clay nanoparticles,³ metal oxide nanoparticles, such as silica⁴ and titania nanoparticles,⁵ and carbon nanotubes⁶ 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 to be used in durable products such as electronic equipments and automobiles. This is mainly because these nanoparticles lack rubber-like elasticity although they do have an affinity for a polymer matrix. Adding a typical elastomer such as rubber or plasticizer (for example, a long chain alkyl ester) with a high affinity for a polymer matrix, however, reduces the breaking strength and elasticity modulus of the composite because of their lack of rigidity.^{7,8}

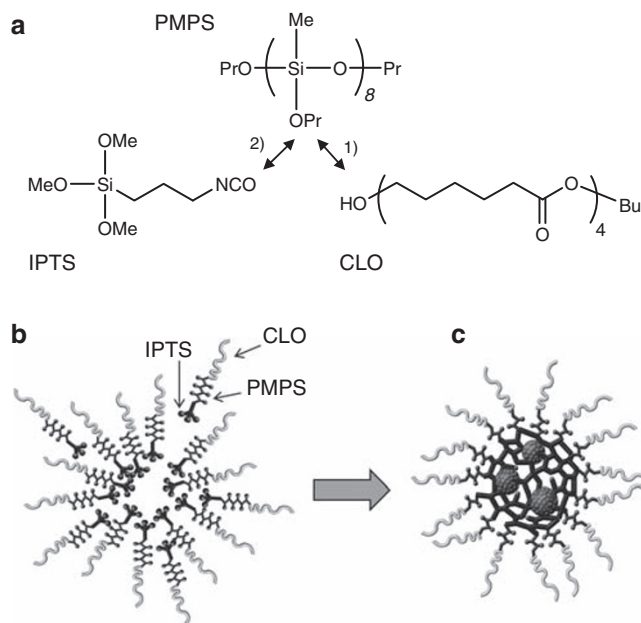
Nanoparticles with multiple-phases, a high-density phase (core) with rigidity and outside phases with rubber-like elasticity and affinity for matrix polymers, should improve the tenacity of nanocomposites without degrading their breaking strength. Metal oxide nanoparticles are typically formed by hydrolysis and condensation reactions of organic metal compounds, mainly silicon alkoxides^{9–13} and perhydropolysilazane,¹⁴ in solvents or polymers, that is, a sol-gel method. However, the formation of multiple-phased nanoparticles using these organic metal compounds is difficult because of 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 because of 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 above 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.^{7,15,16} However, to the best of the authors' knowledge, the use of multi-phased nanoparticles to increase the tenacity of PLLA has not been reported.

In this paper, we report self-assembling siloxane nanoparticles with three phases that improve the tenacity of PLLA. The particles consist of a high-density siloxane phase (plural cores), an elastomeric silicone phase and a caprolactone oligomer (CLO) phase. Self-assembly by aggregation and condensation of an organosiloxane with three units forms each phase. Testing showed that the use of these nanoparticles increases the tenacity (breaking strain) of PLLA while maintaining its relatively high-breaking strength.

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 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 crosslinked (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 crosslinked (relatively low-density) siloxane network after the core formation. The CLO was selected to form the outside phase because of 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).



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

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 (Scheme 1a). After the binding reactions had ceased, the unreacted IPTS, PMPS and CLO were removed using a column packed with polystyrene particles. The reactions were confirmed by hydrogen-nuclear magnetic resonance analysis of the functional groups in the resulting compounds. Moreover, we performed gel permeation chromatography analysis to determine the molecular weight, element analysis of carbon, hydrogen and nitrogen, and Fourier transform infrared spectroscopy to determine major bonds. These results showed that the IPTS, PMPS and CLO were combined in almost equal molecular proportions as we intend. The CLO and IPTS were probably randomly located on the PMPS in the final compound, but apart to some extent because of the difference in their polarities. The reference organosiloxanes with two units (IPTS+PMPS or PMPS+CLO) were prepared and determined based on these methods. These details of the preparation are described in the Supplementary Information.

We confirmed that the organosiloxane with three units dissolved in tetrahydrofuran aggregates and forms nanoparticles due to condensation by using water and ammonia as a base catalyst. To avoid confusion, the formation of the high-density siloxane cores with the formation of the elastomeric silicone phase around them, we initiated 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 propyloxy groups in the PMPS unit. The first step was core formation through hydrolysis and condensation of the methoxy groups in the IPTS unit at room temperature for 24 h in tetrahydrofuran. The second step was elastomeric silicone phase formation through hydrolysis and condensation of the propyloxy groups in the PMPS unit by heating at a high temperature (180 °C) for 20 min after replacing the tetrahydrofuran with dimethyl sulfoxide, which has a higher boiling point (189 °C). These stepwise reactions were ascertained by hydrogen-nuclear magnetic resonance analysis for the

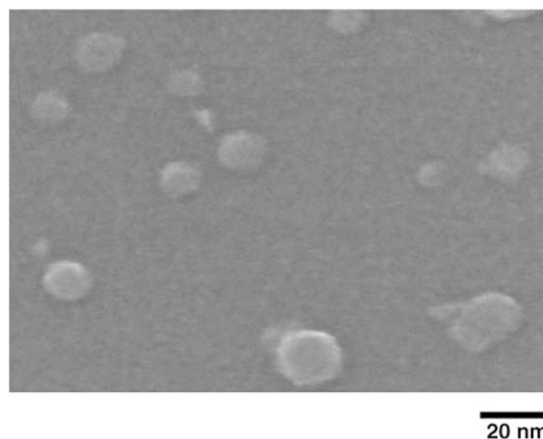


Figure 1 Observation of three-phased nanoparticles using scanning electron microscope.

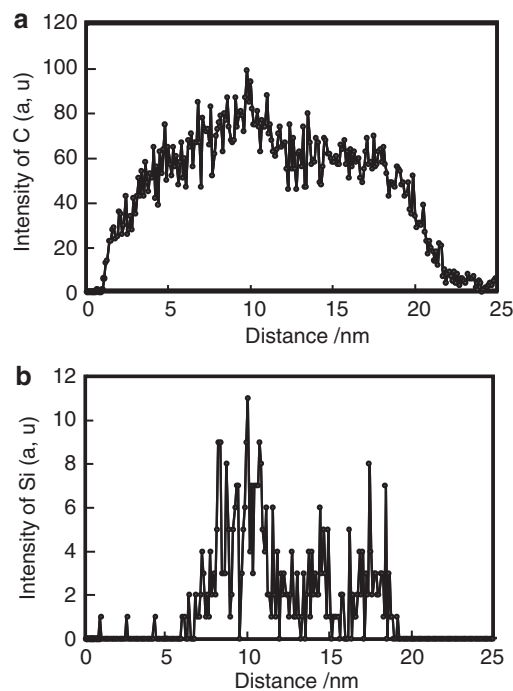


Figure 2 Analysis of silicon and carbon in three-phased nanoparticle by scanning electron microscopy and energy dispersive X-ray: intensities of silicon (a) and carbon (b) detected along cross-section of nanoparticle. The particle diameter is 23 nm.

methoxy, propyloxy and silanol. After the first step, the methoxy groups in the IPTS were almost completely hydrolyzed and condensed forming siloxane, whereas the propyloxy groups in the PMPS unit did not hydrolyze. After the second step, the propyloxy groups were almost completely hydrolyzed and condensed.

As shown in Figure 1, the formed nanoparticles were observed with a scanning electron microscope. The size distribution, measured by light scattering analysis, indicated a relatively narrow size range, with an average diameter of 13 nm. The inside structures of the nanoparticles were investigated by scanning electron microscopy and energy dispersive X-ray analysis. Figure 2 shows representative results for the amounts (intensities) of silicon and carbon that were detected along

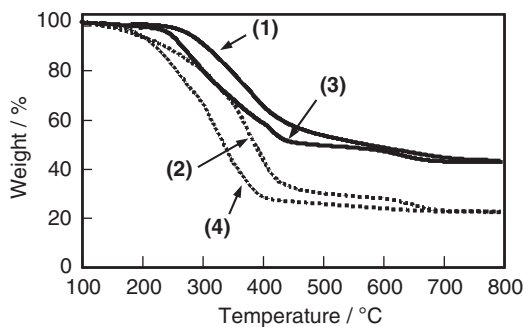


Figure 3 Thermo-gravimetric analysis of nanoparticles and organosiloxanes: (1) three-phased nanoparticle, (2) organosiloxane consisting of isocyanate-propyltrimethoxysilane, polymethylpropyloxysiloxane (PMPS) and caprolactone oligomer (CLO) to form (1), (3) two-phased particle consisting of elastomeric silicone and CLO phases, (4) organosiloxane consisting of PMPS and CLO to form (3).

cross-sections of the nanoparticles. 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 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.

Figure 3 shows the thermo-gravity analysis of the nanoparticle formed by the organosiloxane with IPTS, PMPS and CLO, the reference particle formed by the organosiloxane with PMPS and CLO (through the second step described above), and these organosiloxanes. The results indicated that the nanoparticle showed higher thermo-degradation resistance than the reference particle, which suggests the formation of the high-density crosslinking phase to retard the thermo-degradation; we considered the phase to be the cores in the nanoparticle. Furthermore, these particles showed considerably higher thermo-degradation resistances than those of the organosiloxanes. These suggest that not only the high-density cores derived from IPTS, but also the relatively low-density crosslinking silicone phase derived from PMPS were formed.

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 1b and c. The IPTS unit mainly performs the aggregation of the organosiloxane. The aggregated IPTS unit mainly forms the high-density crosslinked 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 crosslinked siloxane network (elastomeric silicone) around the cores through hydrolysis and condensation reactions of its propyloxy 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.

Using these three-phased nanoparticles at 5wt%, we prepared a molded PLLA nanocomposite to measure its tenacity by flexural and tensile testing. After the first step (core formation), the tetrahydrofuran, water and ammonia were removed by evaporation. The nanoparticles were mixed with PLLA in chloroform, followed by

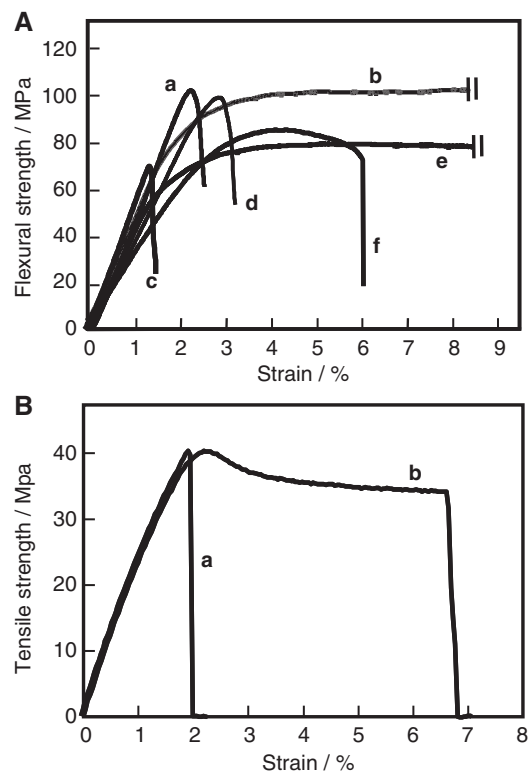


Figure 4 Flexural (A) and tensile (B) testing of poly L-lactic acid (PLLA) composites: (a) PLLA, (b) PLLA nanocomposite with three-phased nanoparticles (5wt%), (c) PLLA nanocomposite with silica nanoparticles (5wt%), (d) PLLA nanocomposite with two-phased nanoparticles consisting of cores and elastomeric silicone phase (5wt%), (e) PLLA composite with organosiloxane consisting of polymethylpropyloxysiloxane and caprolactone oligomer (CLO) (5wt%) and (f) PLLA composite with CLO (2wt%).

removing the solvent by evaporation. The resulting composite was extruded at 180 °C for 10 min using a screw-type mixer and then molded by pressing while heating at 180 °C for 10 min, followed by crystallization of the PLLA in the composite by heating at 100 °C for 4 h. It is likely that the condensation reaction to form the elastomeric silicone phase in the particle was mostly finished during the extruding and molding of the PLLA composite, because the same heating condition as that for the solvent in the second step above resulted in the same condensation reaction.

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

As references, PLLA composites containing the commercial silica nanoparticles, the two-phased nanoparticles (cores and elastomeric silicone phase), the organosiloxane consisting of PMPS and CLO units, or the CLO alone were prepared using the method described above. These details of the preparation are described in the Supplementary Information.

The composite containing the commercial silica nanoparticles, average diameter of 12 nm, showed a slight increase in the modulus, but its strength and elongation were less than those of PLLA (Figure 4A (c)). The two-phased nanoparticles, average diameter of 10 nm, were formed using the organosiloxane with IPTS and PMPS

units through the same core formation step described above. The composite containing the nanoparticles showed only a slight increase in elongation compared with that of PLLA (Figure 4A d). The composite containing the organosiloxane with PMPS and CLO (PMPS might be crosslinked when mixing with PLLA during heating) showed substantial increase in elongation compared with that of PLLA, but its strength and modulus were less (Figure 4A e). The composite containing the CLO alone decreased the elasticity modulus of the PLLA composite and insufficiently increased its elongation (Figure 4A f). The amount of CLO alone in the composite was 2 wt%, which is near to the amounts of the CLO parts of the three-phased nanoparticles and the organosiloxane with PMPS and CLO. Increasing the amount of CLO further decreased both the modulus and also the strength while it increased the elongation. 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 PLLA 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 nano-silica, which aggregated in the PLLA composites because of 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 because of the rubber-like elasticity of the elastomeric silicone phase derived from PMPS and the plasticity of the outside CLO phase. Although the nano-silica, the reference two-phased particles without the CLO phase, and CLO alone did not perform to cause such elongation of the PLLA composites, the organosiloxane with PMPS and CLO elongated the composite, which can support the proposed mechanism.

In summary, we reported on self-assembling siloxane nanoparticles with three phases: a high-density crosslinked 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 self-assemble by aggregation and condensation of the organosiloxane with three units, IPTS, PMPS and CLO that respectively form each phase. Adding these nanoparticles to PLLA increases the

tenacity of the PLLA while maintaining its high breaking strength. Their use will expand the use of PLLA 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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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)