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Highly Loaded Silicone Nanocomposite Exhibiting Quick Thermoresponsive Optical Behavior

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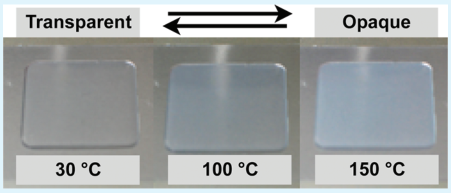
Supporting Information

ABSTRACT: Bulk silicone nanocomposites with thermoresponsive optical behavior were fabricated using silica nanoparticle fillers within a cross-linked silicone matrix. Silica nanoparticles (25 nm diameter) were surface-modified, allowing for even distribution at 6−24 wt % within and covalent bonding to the silicone matrix. Utilizing the temperature-dependent match/mismatching of the refractive indices of the silica nanoparticle filler and the silicone matrix, bulk nanocomposites are highly transparent at room temperature and demonstrate significant increases in opacity with increasing temperature up to 100−150 °C. Such a response could be cycled quickly and repeatedly with no detrimental effect on the material.



KEYWORDS: transparent nanocomposite, thermoresponsive optical property, silicone, SiO_2 nanoparticle, refractive index, thermal stability

INTRODUCTION

Polymer nanocomposites, which consist of a polymer matrix filled with inorganic fillers, typically nanoparticles (NPs), have been widely applied in a variety of engineering fields as functional materials that exhibit unique optical, electrical, thermal and mechanical properties.[1−3] In spite of polymer nanocomposites offering such attractive advantages, there have been a limited number of papers describing preparation techniques or properties of transparent nanocomposites.[3−10] Appropriate incorporation of NPs into various kinds of transparent polymeric materials is the key to improving their mechanical and physical properties while preserving their optical properties.[1,4−10] Among the various functionalities found to be effective, reversible thermoresponsive optical properties have attracted considerable attention lately and are becoming increasingly important in practical applications including optical switches and lenses for sensor and eye protection.[11−13] Most studies related to this field mainly focus on the fabrication and characterization of NPs made from poly(*N*-isopropylacrylamide) (PNIPAM)-based hydrogels[14] or PNIPAM-covered Au, Ag or Fe_3O_4 NPs,[15−17] and PNIPAM nanocomposite thin films embedded with Au NPs.[18] However, the optical transitions of these materials generally occur under 50 °C within a very narrow temperature range (1−2 °C), which causes difficulties for higher-temperature applications. In addition, their optical behavior as a function of temperature has been mainly characterized through submersion of the materials in water.[11−16,18] Research on transparent bulk nanocomposites showing thermoresponsive optical behavior within a large temperature range in air is lacking.

We first report here the preparation of a novel transparent silicone-based nanocomposite, highly loaded with silica (SiO_2) NPs (maximum 24 wt %) which were distributed evenly throughout the silicone matrix, possessing quick, reversible and durable thermoresponsive optical properties based on matching/mismatching refractive indices (RIs, n) of the NPs and matrix. Among the various polymers, we employed a silicone as the matrix material, since it is a typical transparent polymer with excellent thermal and oxidative stability, high flexibility, low toxicity, antifouling nature[19] and decent mechanical properties.[20] It is well-known that the optical properties of polymer nanocomposites are governed primarily by the RIs of the matrix and filler, and dispersion of the filler material within the matrix.[1,4−10] To achieve highly transparent nanocomposites, it is important to properly select the two different materials in order to minimize the differences in their RIs.[4,22] For example, Gilmer et al. successfully prepared transparent poly (methyl methacrylate) (PMMA)-based nanocomposites containing aromatic siloxanes by taking advantage of the matching of their RIs.[22] Unfortunately, there are only a limited number of combinations of fillers and polymers with RIs nearly equivalent to each other. In addition, to reduce light scattering and turbidity, NP diameters should be strictly regulated to less than 50 nm.[8] However, with decreasing particle size, particle agglomeration generally becomes severe and causes significant decreases in transparency even with dispersion of NPs within the polymer matrices at very low concentration (less than 0.5 wt %).[7] To avoid such unfavorable agglomeration, Palkovits et al. successfully demonstrated in situ formation of NPs 26 nm in diameter through a hydrolysis reaction of tetraethoxysilane within the PMMA matrix (5 mm thick).[8] In spite of the successful in situ formation of SiO_2 NPs in

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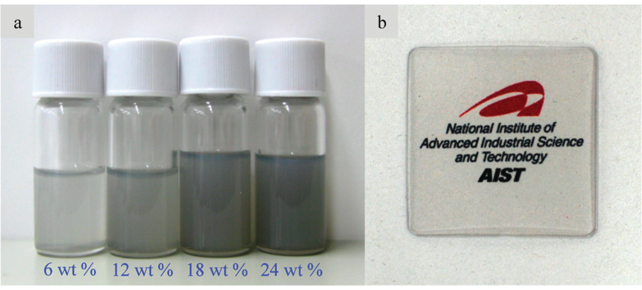

Figure 1. (a) Pictures of precursor solutions containing 6, 12, 18, and 24 wt % SiO_2 NPs (from left to right). The opacity and darkening of the solution increases with increasing NP concentration. (b) Typical picture of a ~700 μm thick nanocomposite plate containing 24 wt % SiO_2 NPs (2.7×2.7 cm^2). In contrast with the opacity of the solutions in (a), the cured sample appears nearly visually transparent.

the polymer matrix, poor transmittance of light within optical wavelengths was observed for NP concentration of only 6.67 wt %. Chang et al. employed a similar method to fabricate transparent polyimide-SiO_2 hybrid thin films, in which SiO_2 content (domain size was smaller than 20 nm) was as high as 54.9 wt %. In this case however, film thickness was regulated to ~3 μm to maintain transparency due to the extremely high SiO_2 NP loading.[10] To circumvent such difficulties in the fabrication of transparent bulk nanocomposites seen with these previous methods, an alternative method allowing homogeneous distribution of inorganic NPs in the polymer matrices, particularly at higher concentrations, is greatly required.

RESULTS AND DISCUSSION

Our process demonstrated here begins with the surface modification of SiO_2 NPs (25 nm in diameter) within a monomer liquid of the cyclic siloxane, 1,3,5,7-tetramethylcycloctetrasiloxane (D_4^H), followed by their dispersion within a mixture of D_4^H and another monomer liquid, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4^V), then cross-linking the NP-containing monomer solution using Karstedt's catalyst through a hydrosilylation reaction between the Si−H and Si-vinyl moieties from D_4^H and D_4^H-modified NPs, and D_4^V, respectively.[20,21] The cross-linking between D_4^H and D_4^V forms the silicone matrix. Due to the expected formation of the D_4^H-derived monomeric layer on the nanoparticle surfaces in the first step,[23] the affinity between the SiO_2 NPs and the monomer (D_4^H/D_4^V) solutions is dramatically increased. It improved the dispersion of the NP and reduced their aggregation within the monomer solution, leading to an increase in the transparency of the final silicone-based nanocomposites. We also studied how the composition and the atmospheric environment affected the optical properties of our nanocomposites. A sharp drop in optical transmittance through the bulk nanocomposite substrates, which undoubtedly originated from mismatching RIs of the SiO_2 NPs and silicone matrix, was observed when the temperature increased from room temperature to more than 80 °C, especially for nanocomposites with higher NP concentrations.

The original monomer solution consisting of Karstedt's catalyst and a 2:1 molar mixture of D_4^H and D_4^V was clear and transparent, and its transparency remained unchanged even after curing. However, as demonstrated in Figure 1a, the precursor solutions containing SiO_2 NPs were opaque and grayish, in particular, at higher NP concentrations. However, in spite of the lack of transparency of the precursor solutions, the resulting silicone-based nanocomposite plates (2.7×2.7 cm^2 and ~700 μm thick) were highly transparent even at the high NP concentration of 24 wt.%. In fact, as shown in Figure 1b, the AIST logo is clearly visible through that sample.

In our present case, surface modification and dispersion of the SiO_2 NPs were first performed in the D_4^H monomer liquid at 80 °C for 72 h, then D_4^V and Karstedt's catalyst (and D_4^H if needed) were added to this solution to prepare the final precursor solutions. This stepwise process effectively facilitated the dispersion of the SiO_2 NPs within the monomer (D_4^H/D_4^V) solution. The authors have previously reported that chemisorbed D_4^H molecules on an oxidized Si (Si^{SiO2}) surface formed a D_4^H-derived monomeric layer with a thickness of less than 0.5 nm.[23] We thus expect that each SiO_2 NP surface was covered with a D_4^H monolayer in a manner similar to that on the Si^{SiO2} surface. Such D_4^H-covered SiO_2 NPs have an improved affinity for the monomer solutions. In fact, unmodified SiO_2 NPs exhibit poor dispersion in the monomer solutions even at lower NP concentration of 6 wt %, showing significant phase separation. This is a clear advantage offered by our stepwise surface modification technique for SiO_2 NPs.

During the curing process, hydrosilylation reactions between the Si−H and Si-vinyl moieties on D_4^H and D_4^H-modified NPs, and D_4^V molecules, respectively, are expected to occur simultaneously.[20,21] In addition, due to the excess Si−H groups in the NP/D_4^H/D_4^V solution, it is likely that Si−O−Si linkages are also formed from the condensation reaction between the Si−H and Si−OH (derived from the hydrolysis of the Si−H groups) groups in the presence of Karstedt's catalyst.[24] Heating at 150 °C for 24 h is considered to ensure completion of all possible cross-linking by both reactions. As the cross-linking of the matrix proceeds, the D_4^H/D_4^V cross-linked silicone shell surrounding the NPs also increases in diameter. This may help decrease aggregation and promote the transparency of the resulting nanocomposites. By cross-linking the pure cyclic monomer solution through the formation of ethylene linkages by hydrosilylation and Si−O−Si linkages by silanol condensation, the density (d) increased from 0.99 (uncured liquid) to 1.06 g/cm^3 (cured solid). This difference in chemical and physical properties between the liquid siloxane monomer solution and the cured silicone matrix likely also altered the RI of the material in which the SiO_2 NPs were dispersed, to be closer to the RI of the inorganic filler. Indeed, an uncured 2:1 molar mixture of D_4^H and D_4^V, with RIs of 1.3870 and 1.4342, respectively (as reported by the manufacturer), can be expected to show an RI significantly different from that of SiO_2 ($n = 1.46$). However, the actual RI of the unfilled pure silicone matrix (cured D_4^H/D_4^V) at room temperature was measured to be 1.45 at 468 nm, and 1.44 at 589 and 656 nm, which are very close to that of SiO_2. This explains why the opaque precursor solution became a transparent solid upon curing.

Our transparent silicone-based nanocomposites exhibit a unique thermo-responsive optical property, evident by the straightforward heating test on the hot plate shown in Figure 2 (in this case, 24 wt %). Increasing the temperature to 100 °C induced a significant transition to translucency, whereas a further increase to 150 °C rendered the nanocomposites even more opaque. This is also supported by our UV−vis spectra acquired at different temperatures, as shown in Figure 3. Regardless of NP concentrations, all nanocomposite plates are highly transparent

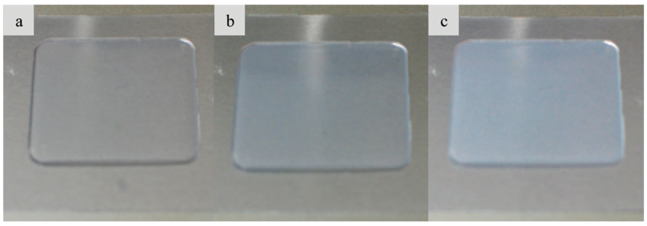

Figure 2. Pictures of the nanocomposite plate shown in Figure 1b, heated on an aluminum sheet at (a) 30, (b) 100, and (c) 150 °C. The material is highly transparent at 30 °C. Increasing the temperature of the nanocomposite produces significant increases in opacity such that the aluminum sheet cannot be observed through the material.

at room temperature. For example, even at 24 wt %, transparency of the sample remained over 75% in the visible light wavelength range (400−550 nm). By heating the samples to more than 80 °C (limitation of our instrument is 100 °C), marked decreases (5−15%) in transparency were observed, particularly at higher NP concentration (Figure 3b).

This thermoresponsive optical property appeared only when the SiO_2 NPs were added to the silicone matrix and the samples were heated, as shown in Figures 2 and 3. The unfilled pure silicone material (cured D_4^H/D_4^V) itself showed no change in transparency even at 150 °C. RIs of the SiO_2 NPs and the silicone matrix are nearly identical at ambient conditions (matching of RIs), producing highly transparent nanocomposites at room temperature. However, SiO_2 has a positive thermo-optic coefficient on the order of 1×10^{-5}/°C, whereas polymers such as our matrix exhibit negative thermo-optic coefficients on the order of 10^{-4}/°C.[26] Therefore, by increasing the temperature, the refractive index of the silicone matrix experiences a large negative change compared to the smaller positive change in that of the inorganic SiO_2 NPs, as measured by their thermo-optical coefficients.[25,26] This increase in the mismatch of RIs at higher temperatures is believed to be responsible for the unique thermoresponsive optical property. In our case, the transition of the material from transparency to opacity or the reverse is very sensitive and quickly accomplished, normally within a few seconds. Our nanocomposites also maintained their excellent thermoresponsive property even after several tens of times of thermal stress tests between room temperature and 200 °C (see the Supporting Information, Figure S-1). No cracks were visible on these surfaces. This was undoubtedly due to their excellent thermal stability. TGA analysis demonstrated that thermal decomposition of our samples hardly occurred even at 500 °C (Supporting Information, Table S-1). For example, in the case of the nanocomposite loaded with 6 wt.% SiO_2 NPs, the mass loss was about 2.3%, while those of other highly loaded samples were found to be less than 2%. In addition, our free-standing nanocomposite plates demonstrated increased density and improved mechanical properties over those of the unfilled silicone matrix. Adding 6 and 24 wt % SiO_2 NPs (d = 2.2 g/cm^3 as reported by the manufacturer) increased the density of the nanocomposite from 1.06 (cured D_4^H/D_4^V) to 1.08 and 1.14 g/cm^3, respectively. Young's modulus of the samples was measured to be 2.45 and 3.37 GPa for 6 and 24 wt % SiO_2 NPs, respectively, which are considerably higher than that of the unfilled transparent cross-linked silicone matrix material (1.46 ± 0.08 GPa) as recently reported by Zheng et al.[20]

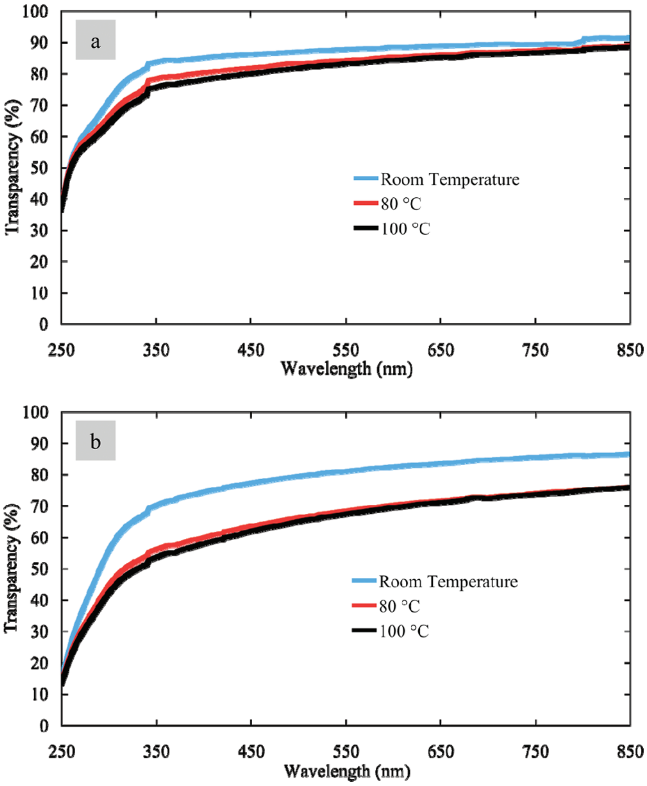

Figure 3. UV−vis spectra of nanocomposite plates containing (a) 6 and (b) 24 wt % SiO_2 NPs taken at room temperature, 80 and 100 °C. Increasing the concentration of SiO_2 NPs leads to a slight decrease in transparency in the visible range at room temperature, whereas heating the samples results in larger decreases in light transmittance with increasing loading of NPs.

CONCLUSION

Our experimental results presented here offer clear proof that our transparent silicone-based nanocomposites loaded with SiO_2 NPs show quick, reversible and durable thermo-responsive optical properties. The critical temperature for such specific behavior is considered to be more than 80 °C. Reduction in the transition temperature can be achieved by using matrix materials which exhibit larger thermo-optic coefficients. Our robust nanocomposites might be applicable to a wide variety of advanced applications including high-temperature optoelectronic devices, optical components with tunable translucency, and simple heat detectors. Optimization of the compositions and better understanding on the thermoresponsive optical behavior of our nanocomposites will also be needed in order to achieve a more tunable transparency-to-opacity transition.

EXPERIMENTAL SECTION

Materials. Silica (SiO_2) nanoparticles (NPs) 25 nm in diameter were purchased from Nanotek Inc. (Tokyo, Japan). 1,3,5,7-tetramethylcycloctetrasiloxane (D_4^H), 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4^V) and Karstedt's catalyst (2.1−2.4% Pt in xylene) were obtained from Gilest Inc. (Morrisville, PA, USA) and used as monomers and catalyst without additional purification to form silicone-based materials.

Modification of Nanoparticles. 3.0 g of SiO_2 NPs were first baked at 100 °C for 24 h, then dispersed into neat D_4^H monomer

Table 1. Formulation of the SiO_2 NP-Loaded Silicone Nanocomposites

desired wt % SiO_2 NP in final nanocomposite	initial wt % SiO_2 NP in D_4^H solution	initial mass of SiO_2 NP in D_4^H solution (g)	mass D_4^H added (g)	mass D_4^V added (g)	final ratio of D_4^H:D_4^V	final mass of solution (g)
6	20	0.3	0.308	0.392	2:1	1
12	20	0.6	0.033	0.367	2:1	1
18	40	0.45	0.208	0.342	2:1	1
24	40	0.6	0.083	0.315	2:1	1

liquid (12.0 g) in a glovebox filled with N_2 gas. This NP solution (20 wt %) was then heated in an 80 °C oil bath while stirring for 72 h. Due to this treatment, D_4^H-derived monomeric layers (0.5 nm thick) were expected to form on the SiO_2 NP surfaces.[23]

Nanocomposite Formation. Next, this original NP solution was diluted from 20 to 6 or 12 wt % D_4^H-modified NPs, by adding D_4^H/D_4^V [0.308/0.392 g (6 wt %) or 0.033/0.367 g (12 wt %)] to the solution [0.3 g (6 wt %) or 0.6 g (12 wt %)]. In our present case, the molar ratio of Si−H and Si-vinyl moieties from D_4^H and D_4^V molecules was fixed at 2:1.[20] In the case of 18 and 24 wt %, the D_4^H component was first partially evaporated slowly from the original 20 wt % NP solution under a stream of N_2 gas to increase the NP concentration to 40 wt %. Then D_4^H/D_4^V monomer liquids [0.208/0.342 g (18 wt %) or 0.083/0.317 g (24 wt %)] were added to this concentrated solution [0.45 g (18 wt %) or 0.60 g (24 wt %)] to dilute the NP concentration to 18 and 24 wt %. The components needed to prepare 1 g of the NP solution to make silicone nanocomposites with 6, 12, 18, and 24 wt % SiO_2 NPs are summarized in Table 1. Each NP solution was then sonicated for 1 h to ensure proper dispersion of the NPs, and Karstedt's catalyst was finally added such that the final precursor solution contained 10 ppm of Pt. About 0.5 mL of this final solution was gently poured into polyethylene terephthalate trays (2.7×2.7 cm^2), cured at room temperature for 24 h, and then heated at 80 °C for 24 h. The free-standing plate ~700 μm thick was then popped out of the trays and further heated at 150 °C for another 24 h.

Characterization. UV−vis spectra at different temperatures in the visible range were recorded with a V750 Spectrophotometer (JASCO Inc.) equipped with a homemade sample holder connected to a programmable temperature controller (maximum temperature of 100 °C). The thermal stability of the nanocomposites was determined through thermogravimetric analysis under nitrogen using a SDT Q600 (TA Instruments), with the temperature increasing at 10 °C/min. Nanoindentation experiments were performed using a Nano Indenter G200 (Agilent Technologies, Inc.) with a Berkovitch-type diamond tip (radius of curvature of 20 nm). From the loading and unloading curves, Young's modulus was obtained. All data acquired at indentation/displacement of 600−650 nm were determined by averaging values measured at ten different points on each sample surface. Changes in density before (fluid state) and after curing (highly viscous state) of 0.5 mL of precursor solution were characterized by measuring the weight difference. RI of the unfilled pure silicone matrix (cured D_4^H/D_4^V, ~700 μm thick) at room temperature was measured by a spectroscopic ellipsometer (M-2000, J. A. Woollam Co.).

ASSOCIATED CONTENT

Supporting Information. Durability of thermoresponsive optical property following multiple temperature cycles and TGA data are shown. This material is available free of charge via the Internet at http://pubs.acs.org/.

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