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RESEARCH PAPER

Nano-fillers to tune Young's modulus of silicone matrix

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Abstract In this study, we investigated nanoparticles, nanofibers, and nanoclays for their filler effects on tuning the Young's modulus of silicone matrix, a material with broad in vivo applications. Nano-fillers with different shapes, sizes, and surface properties were added into silicone matrix, and then their filler effects were evaluated through experimental studies. It was found that spherical nanoparticles could clearly improve Young's modulus of the silicone matrix, while nanoclays and carbon nanofibers had limited effects. Smaller spherical nanoparticles were better in performance compared to larger nanoparticles. In addition, enhanced distribution of the nanoparticles in the matrix has been observed to improve the filler effect. In order to minimize toxicity of the nanoparticles for in vivo applications, spherical nanoparticles coated with amine, acid, or hydroxide groups were also investigated, but they were found only to diminish the filler effect of nanoparticles. This study demonstrated that spherical nanoparticles could serve as fillers to tune Young's modulus of silicone matrix for potential applications in medicine.

Keywords Silicone matrix · Nanoparticles · Nanoclay · Nanofibers · Nano-fillers · Young's modulus

Introduction

Silicone is a type of silicon–carbon-based polymer, in which a single unit is composed of the element silicon bonded with oxygen, forming a siloxane molecule (Berman et al. 2007). Depending on the length or complexity of the molecule chains, silicone may exist in the forms of liquid, gel, foam, hard resin, or rubbers. These materials exhibit physical differences, but share other similar characteristics, such as transparency, softness, water-resistance, non-toxicity, biocompatibility, and resistance to interactions with other chemicals, ultraviolet rays, ozone or oxygen. These properties have contributed to broad applications of silicone in different fields, including medical applications. A well-known application of silicone in medicine is for breast or facial implants in which silicone gel works as filling materials. In less occasions, silicone is utilized to construct prostheses in the cardio-vascular system (Dodge-Khatami et al. 2003), the urogenital tract including penile prostheses (Mouracade et al. 2008), and the skeletal system (Koyama et al. 2011). Except in implants and prostheses, recent developments have extended the applications

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of silicone in other medical fields, such as in drug delivery or nerve regeneration (Lavie et al. 1987; Patra et al. 1986; Schreider and Raabe 1981; Wong 2008; Yoda 1998). In dermatology, silicone is being used to make sensitive skin care gel adhesive (Jones 1999). The pressure sensitive gel adhesive is soft, water-resistant, non-irritating, and comfortable for skin applications, which make it suitable for applications in neonatal care, medical device attachment, wound care, skin therapy, and hypertrophic scar management.

Many applications of silicone rely on its mechanical properties, especially stiffness, such as in prostheses and breast implants. However, it should be noted that mechanical properties of different tissues show great variety, as can be seen between eyes and bones (Guo et al. 2006). To make adaptive use of silicone or related products in different human tissues, it is desirable that their Young's modulus can be tuned to meet requirements in different tissue structures. In addition, due to the age or other concerns, individuals may have different preferences for stiffness of the implants, such as in breast implants. Thus, silicone with tunable Young's modulus would be desirable to optimize its performance in applications. With increasing applications in recent years, the long-term reliability of silicone prostheses, such as breast implants, is still in doubt due to the possible mechanical weakness in the silicone gel in the silicone rubber shell (Necchi et al. 2011). Based on 42 studies for a total of 9774 breast implants, a wide range of rupture percentages from 26 to 69 % have been reported after an implantation time varying from 3.9 to 17.8 years (Marotta et al. 2002). Implant rupture releases silicone into other normal tissues or organs and causes health concerns. It is thus essential to tune Young's modulus of silicone matrix for in vivo applications.

To tune or reinforce Young's modulus of polymeric matrix, traditional methods rely on varying the ratio and concentration of the contents, degree and type of side chains, or crosslinking and interactions among its components. Different ratios of poly-L-lactic acid (PLLA) and poly-DL-lactic acid (PDLLA) have been explored to tune the mechanical properties of biodegradable poly-lactic acid (PLA) polymeric blends for medical applications (Chen et al. 2003). Through adjusting pH values, the mechanical properties of polypeptide multilayer films can be adjusted by changing the distribution of charge and Coulombic interactions (Zhong et al. 2006). The incorporation of photolabile moieties in a linker of the polymer in poly(ethylene glycol) hydrogel allows the dynamic tuning of physical and mechanical properties of photodegradable hydrogel through the irradiation in the post-gelation control (Kloxin et al. 2009). These approaches have amplified the mechanical properties of materials and expanded their applications. However, it should be recognized that these methods normally require good understanding of chemical and physical properties of all the components in materials. The treatments in these methods sometimes are harsh, intricate, or require extra energy input (Kloxin et al. 2009; Zhong et al. 2006). Furthermore, the enhancement of mechanical properties in one aspect may cause the loss in some other aspects (Williams 1996). For instance, the increase in crosslinking of silicone improves durability at the loss of its adhesiveness (Williams 1996).

To explore alternative approaches that can be used to tune or reinforce the mechanical properties of polymeric matrix, recent efforts have kept pace with the development of nanotechnology. Using nanomaterials as fillers has been proposed for tuning or reinforcing mechanical properties in various polymeric matrices (Johnsen et al. 2007; Khan et al. 2011; Kinloch et al. 2005). Due to their high surface area to volume ratio, nano-fillers have higher reinforcing efficiency compared to micro-sized particulates even at very low concentrations. The addition of a relatively small fraction of nanoparticles could significantly improve the mechanical properties of the polymer. The addition of nanophase structures of silica has increased toughness as well as the viscosity of the epoxy (Kinloch et al. 2005; Kontou and Niaounakis 2006; Ragosta et al. 2005; Zhang et al. 2006). Ceramic nanoparticles, nanoclays, graphite and carbon nanotubes have also been confirmed to reinforce mechanical properties of the polymer matrix (Cannillo et al. 2006; Cho et al. 2007; Song and Youn 2006; Zaïri et al. 2011).

The aim of this study is to investigate potential nanomaterials that may work as fillers to tune and reinforce Young's modulus of the silicone. Nanofillers with different shapes, sizes, and surface properties have been evaluated for their effects as fillers on changing the Young's modulus of the silicone matrix. Through the investigation, it was expected that the nano-fillers could be used as fillers to tune mechanical properties of silicone products. Considering large amounts of silicone products consumed annually and their broad in vivo applications, this study thus serves to incorporate recent progress in nanotechnology to improve and extend the performance of silicone-related products.

Materials and methods

Materials

Polystyrene nanospheres with diameters of 46.3 nm (NP-P46) and 103 nm (NP-P103), and silicon dioxide nanospheres of around 95 nm without NH_2 modification (SiO_2–) and with NH_2 modification (SiO_2–NH_2) were purchased from Microspheres–Nanospheres (Cold Spring, NY). Zinc oxide of 90–200 nm size (ZnO–NP) and titanium dioxide (TiO_2) nanoparticles of 50 nm were purchased from Nanostructured & Amorphous Materials Inc (Houston, TX). Nanoclay and carbon nano fibers were purchased from Sigma Aldrich (St Louis, MO). Silicone matrix was formed using Sylgard® 184 Silicone Elastomer Base and Sylgard® 184 Silicone Elastomer Curing Agent from Dow Corning (Midland, MI). Polystyrene and SiO_2 nanoparticles were supplied as suspension solution and used as received. TiO_2 and ZnO nanoparticles were prepared in solution using deionized water.

Formation of silicone nanocomposites

Unmodified silicone and nano-fillers added silicone polymeric matrices were prepared to compare their Young's moduli. First, different nano-fillers were prepared under appropriate concentrations with or without surfactant. The solutions were then ultrasonicated in an Aquasonic Sonicator Waterbath (VWR Scientific, Radnor, PA) for 30 min. Following sonication, 400 µl of Sylgard® 184 Silicone Elastomer Base, 100 µl nanoparticle solution, and 200 µl Sylgard® 184 Silicone Elastomer Curing Agent were added to individual wells of 24-well plates (Becton–Dickinson Labware, Franklin, NJ). The solutions were quickly mixed first by agitation using 20 G needles (Becton–Dickinson Labware) until no obvious solution blocks were visible in the mixtures. The mixtures were then ultrasonicated for 60 min in the same sonicator waterbath. After sonication, the plates were placed at the room temperature for 48 h, allowing complete curing of polymer before mechanical testing.

Mechanical testing

The tensile strength and fracture testing of the specimens were performed under an Instron mechanical testing machine with dynamic capacity of ±1000 N. Specimens were first removed from the wells using a dig-and-cut tool to obtain a round shape composite with a height of around 6 mm and diameter of 1 cm. The specimens were tested at a displacement rate of 1 mm/min and a test temperature of 21 °C, according to the ISO standard test method. Three replicate specimens were tested for each nanocomposite or pure silicone matrix without nano-fillers. The testing was stopped when the load force reached 500 N or in some cases, 900 N. The Young's modulus was automatically generated by the software accompanied with the testing machine in each test. Some specimens failed by unstable crack growth, while others could be processed without a crack and the original shape could be recovered following the retrieval from the testing machine.

Scanning electron microscopy

The internal or fracture surfaces of the samples were investigated using scanning electron microscopy (SEM). A high resolution LEO 1525 scanning microscope from Carl Zeiss equipped with 'Gemini' column was used for the imaging analysis. All samples were not coated during the investigation. To prepare samples without crack for SEM analysis, a small piece of 2–3 mm thin layer of specimen was cut from inside of the polymeric matrix using a clean razor. For the samples with crack, a small piece of specimen was peeled off from inside using a pair of clean tweezers.

Results and discussion

Spherical nanoparticles to enhance Young's modulus

Nanoparticles as fillers have been investigated in the mechanical studies of epoxy polymer with nanosilica, nanoclay, or other materials (Anoukou et al. 2011; Brune and Bicerano 2002; Luo and Daniel

2003). As the nanoparticles are size-defined, it is thus no surprise that the size can play an important role in the mechanical properties when exploring their effect as fillers. Theoretical understanding and mathematical modeling of size effects have been studied in starch-based nanocomposites (Chivrac et al. 2008; Sheng et al. 2004), which agreed well with experimental measurements (Zaïri et al. 2011). Thus, a parametric study was first carried out to address the influence of particle size on the overall mechanical response of nanocomposites. Two different sizes of spherical polystyrene nanoparticles, 46.3 nm (NP-P46) and 103 nm (NP-P103), were investigated for their effect as fillers in the silicone matrix. The results of mechanical property testing indicated that both nanocomposites with nanoparticle fillers had higher Young's moduli than the matrix without nanoparticles (Fig. 1). This observation confirmed that spherical nanoparticles had a filler effect in reinforcing the mechanical properties of silicone matrix. In determining the size effect of the nano-fillers, we compared the Young's moduli for these two nanocomposites. The results indicated that the silicone nanocomposite with smaller size of polystyrene nanoparticles as fillers has an average value of 432.75 MPa, 38.4 % higher than the silicone with the larger size nanoparticles as fillers.

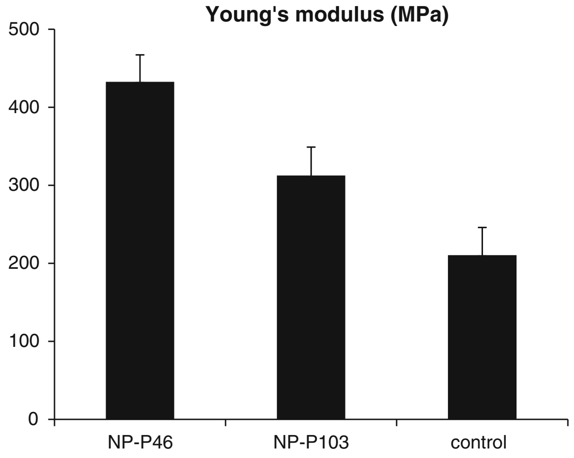

Fig. 1 Moduli of silicone matrix with two different sizes of polystyrene nanoparticles as fillers. Smaller polystyrene nanoparticles had a better performance in enhancing the Young's moduli of the composites

Surfactant enhanced nanoparticle distribution

Recent study by Uddin et al., however, suggested that nanoparticle distribution is another important factor that affects the nano-filler response (Uddin and Sun 2010). The study claimed that a high concentration of nanoparticles as fillers might actually downgrade their performance as enhancer. The main reason is the non-uniform distribution of the nano-fillers when their concentration becomes 15 % or higher. To investigate the agglomeration effect of nanoparticles in the silicone matrix, we have incorporated surfactant to improve nanoparticle distribution in the matrix. Silwet L-77 has shown to enhance transportation of nanoparticles into plant roots due to the super-spreading driven by Marangoni flow, and thus has been used in this study (Hu et al. 2010). As shown in Fig. 2, the effect of surfactant on the mechanical performance was obvious in both TiO_2 and ZnO nanoparticles as fillers. With the addition of Silwet L-77, fractures were developed in a much later stage for ZnO nanoparticles as fillers than the composite without Silwet L-77. Even no fracture was observed for TiO_2 nanoparticle fillers with the addition of Silwet L-77. The moduli of these specimens were also calculated. With Silwet L-77, higher moduli were obtained for both types of nanoparticle fillers compared to the composites without surfactant (Fig. 2a, b). Without Silwet L-77, no obvious increase in Young's modulus was observed, when ZnO nanoparticles were added to the silicone matrix. It should be mentioned that both the TiO_2 and ZnO are metal oxides and their sizes vary between 90–200 nm for ZnO nanoparticles, and 50 nm for TiO_2 nanoparticles. The moduli measured for these two nano-fillers without surfactant indicated that silicone matrix with TiO_2 fillers had a higher modulus than that with ZnO fillers. Similar observations were held in the specimens with surfactant. Since both the ZnO and TiO_2 nanoparticles have much higher Young's moduli than the silicone matrix, the difference in Young's modulus of the nanoparticle fillers would not cause the observed difference in the nanocomposites, as discussed in later theoretical analysis. Therefore, the observed higher Young's modulus from the composite with TiO_2 nano-fillers is likely attributed to the smaller size of the TiO_2 nanoparticles. This observation agrees well with the study of size effect of the polystyrene nano-fillers displayed in Fig. 1. It should be noted that the observed difference in Young's modulus between the samples without nano-fillers or surfactant in Figs. 1 and 2 is attributed to the different ratio of Elastomer Base and Elastomer Curing Agent tested in the experiments.

Toughening mechanism and plastic void growth

The above experiments indicated that organic polystyrene nanoparticles, inorganic TiO_2, and ZnO nanoparticles could improve elasticity of nanoparticle filled polymeric matrix. In addition, the enhanced distribution of nanoparticles increased the roughness of the silicone matrix. The toughening mechanisms associated with particles have been shown in previous studies to be attributed to the de-bonding of particles followed by the plastic void growth in the micro-sized particles (Kawaguchi and Pearson 2003; Lee and Yee 2000), which were also demonstrated recently in the nanoparticles (Johnsen et al. 2007). To examine whether plastic void growth contributes to the enhanced toughness of the matrix, we investigated the internal or fracture structures of the composite using SEM. We checked the internal structure of nano-fillers with or without surfactant and compared their plastic void growth. The polymer matrices undergoing investigation were not coated with gold. Thus, passive charge during the SEM scanning prevented us from looking into the structure at the nanoscale. We could still obtain microscale images of the matrix fractions, as shown in Fig. 3. The images indicated that void structures could be easily observed in the matrix with surfactant (Fig. 3a), but few could be observed in the matrix without surfactant (Fig. 3b). It should be mentioned that these void structures were likely in the microscale, and the existence of nanoscale void structures could not be confirmed. However, the existence of large amount of void structures in the matrix with surfactant implied that the void growth might be another mechanism for the surfactant-enhanced modification in addition to assisting in the dispersion of nanoparticles.

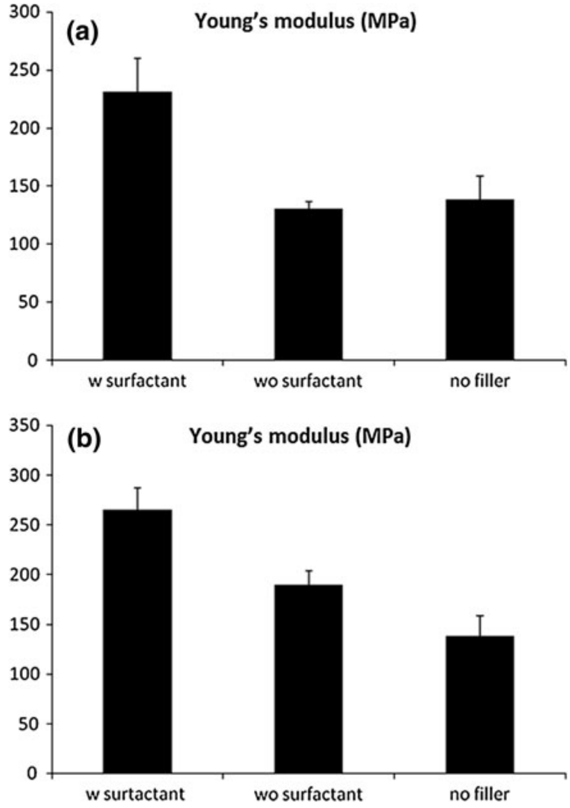

Fig. 2 Surfactant enhanced nanoparticle distribution and the mechanical performance of nanoparticles as filler for TiO_2 (**a**) and ZnO (**b**) nanoparticles

Carbon nanofibers to enhance Young's modulus

For the purpose of comparison, we also investigated other nanomaterials with probable interest based on recent studies (Anoukou et al. 2011). Nanoclay and carbon nanofibers composites have been considered among the best nano-fillers for the composites to fulfill the enhanced mechanical properties (Anoukou et al. 2011; Khan et al. 2011; Sheng et al. 2004; Shi et al. 2007; Song and Youn 2006; Zaïri et al. 2011). Chemically modified organo-nanoclay has been used to make aerospace epoxy nanocomposites which possess excellent mechanical and thermal properties with relatively low cost and ease of fabrication (Alexandre and Dubois 2000; LeBaron et al. 1999). In this study, we have added montmorillonite clay in the silicone matrix and evaluated its filler effect. The results indicated no significant difference with the addition of nanoclay (Fig. 4). Possible explanation of the phenomenon is that the montmorillonite clay is hydrophilic, while the silicone matrix is strong hydrophobic material (Efimenko et al. 2002), which makes it hard to distribute the hydrophilic nanoclay uniformly into the matrix. This has likely forced the formation of clusters in the matrix, which thus decreased or voided the filler effect.

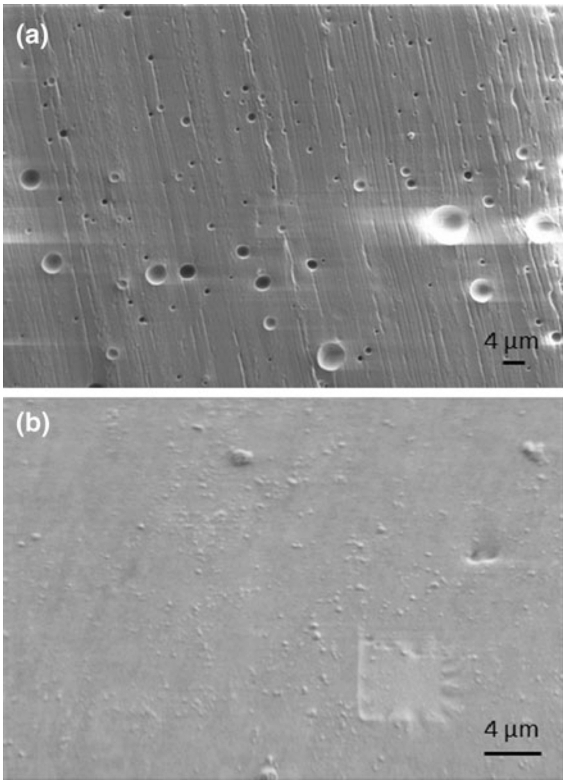

Fig. 3 SEM images of the internal or fracture structures of the TiO_2 nanoparticle-filled silicone matrix with (**a**) or without surfactant (**b**). Void growth could be obviously seen from the composites with the addition of surfactant

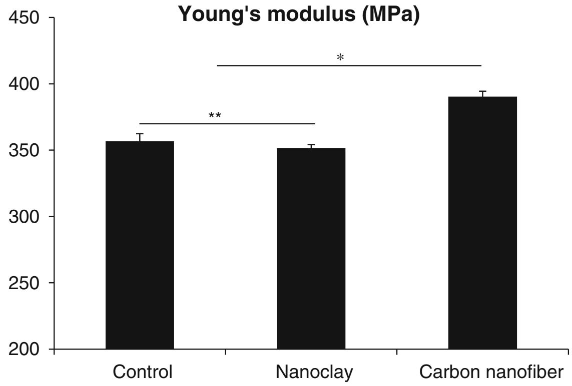

Fig. 4 Moduli of the composites with nanoclay and carbon nanofibers as fillers in the silicone matrix. Nanoclay showed no effect while carbon nanofibers increased 10 % of the Young's modulus of the composite. *Double asterisk* indicates no significant difference, and *Single asterisk* indicates a significant difference based on Student's *t* test

Carbon nanofibers were also investigated here to evaluate their potential to enhance mechanical performance of the silicone matrix as fillers. As shown in Fig. 4, enhanced mechanical performance could be obtained after the addition of carbon nanofibers. However, compared to the nanoparticles described above, the efficiency is less impressive. Only 9.4 % increase in Young's modulus was achieved. The limited increase in Young's modulus could be attributed to the limited distribution of carbon nanofibers. Carbon nanofibers were difficult to dissolve in deionized water, even with the assistance of Silwet L-77 surfactant. The pre-existed clusters thus prevented the distribution of carbon nanofibers in the Silicone Elastomer Base prior to curing. During the mixing process with the base, a small portion of carbon nanofibers could diffuse in the matrix due to their similar hydrophobicity with the silicone matrix, which then caused the filler effect.

Effects of surface chemistry of nanoparticles on Young's modulus

Surface properties are not only related to the electrostatic crosslinking by polymers, but are also important for the toxicity for in vivo applications. Recent study on mice has reported that silica nanoparticles induce fetal resorption and the restricted growth of fetuses in pregnant mice, which can be abolished by the modification of nanoparticle surface with carboxyl or amine groups (Yamashita et al. 2011). This result drew attention to investigate nanoparticles coated with proper surface properties while evaluating their filler effects. We thus examined the SiO_2 nanoparticles whose surface was coated with amine groups–NH_2. After curing, the NH_2-modified SiO_2 nanoparticles were compared to the nanoparticles without modification. As shown in Fig. 5, it was shown that after NH_2 modification, the Young's modulus of silicone matrix dropped from 160.6 to 113.2 MPa, a 29.3 % decrease; also the matrix broke at an earlier stage. Through extended research with other biocompatible chemical groups, such as –OH and –COOH, we found that these groups also downgraded the mechanical performance of the nanoparticles as fillers. It is obvious that these coated groups are hydrophilic polar groups. These coated hydrophilic groups, however, might repel with

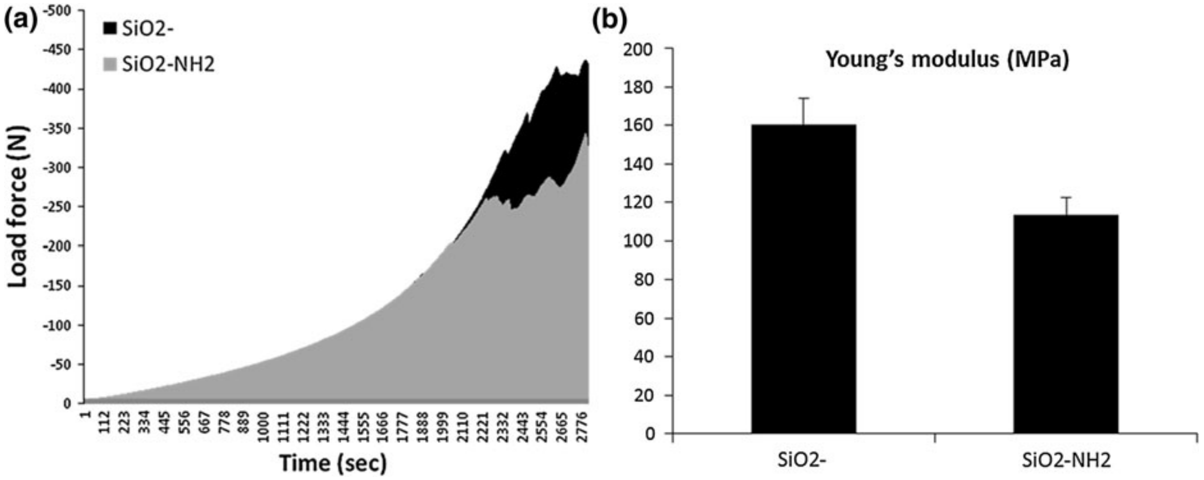

Fig. 5 Effects of surface chemistry on the mechanical effect of nanoparticles as fillers. **a** Mechanical approaching curves for silicone matrix with SiO_2 nanoparticles with or without NH_2 modification. The gray line showed the process with NH_2 modification and the black line without modification. **b** The moduli of silicone matrix filled with SiO_2 nanoparticles with or without NH_2 modification. The observations from **a** and **b** suggested that NH_2-modification diminished the filler effect of SiO_2 nanoparticles

hydrophobic silicone matrix in the interfaces, which thus diminished the filler effect of nanoparticles.

Theoretical understanding of nanoparticles as fillers in the matrix

Effect of nanoparticle fillers on the Young's modulus has been studied, and some theoretical models have been proposed to predict the moduli of particle-modified polymers (Kerner 1956; Nielsen 1966). Among these models, the rule of mixtures, the Halpin–Tsai and the Mori–Tanaka relationships, were commonly exploited. In mixtures, the Young's moduli of the composites depend on the Young's moduli of the fillers (Fig. 6a), based on the finite element modeling from Abaqus. When the Young's moduli of the fillers are 10 times higher or lower than that of the matrix, further change in Young's modulus of the fillers does not cause additional change of the Young's modulus in the composites. As in this case, the Young's modulus of the silicone matrix is much smaller than those of the fillers used in the current study. This means that the different nanoparticles used, either TiO_2 or ZnO, do not affect their filler effect in the silicone matrix, if we are only concerned about the rule of mixtures. In the rule of mixtures, a higher portion of fillers is also expected to enhance the Young's moduli of the composites, as shown in Fig. 6b, c. However, it should be noted that the rule of simple mixtures predicts that the properties of composite materials are independent of the size of inclusions, but are functions of properties of constituents, volume fraction of components, shape and arrangement of inclusions, and matrix–inclusion interfaces. This is true for systems with micron size reinforcement, but may not be right for nanocomposite systems (Gacitua et al. 2005). The effect of nanoparticle fillers depends on many variables, but especially on the relative crystalline or amorphous nature of the polymer matrix and the interactions between fillers and matrix (Jordan et al. 2005). These experimental results also suggested that the compatibility between the fillers and matrix greatly affected the mechanical properties of nanocomposites.

Although no universal patterns for the behavior of polymer nanocomposites can be concluded, still some models have been developed to explain the trends of observations (Jordan et al. 2005). The Mori–Tanaka model is used to predict the modulus of particle-modified polymer in some studies (Fornes and Paul 2003), and the model works the best for relatively high aspect ratios and thus is not proper for use in this case of spherical nanoparticles. The Halpsin–Tsai model predicts the modulus of the composite material as a function of the modulus of the matrix polymer, E_m, and that of the filler particles, E_f, as well as a function of the aspect ratio by the inclusion of a shape factor. The Young's modulus E_c of the composite can be modeled as follows:

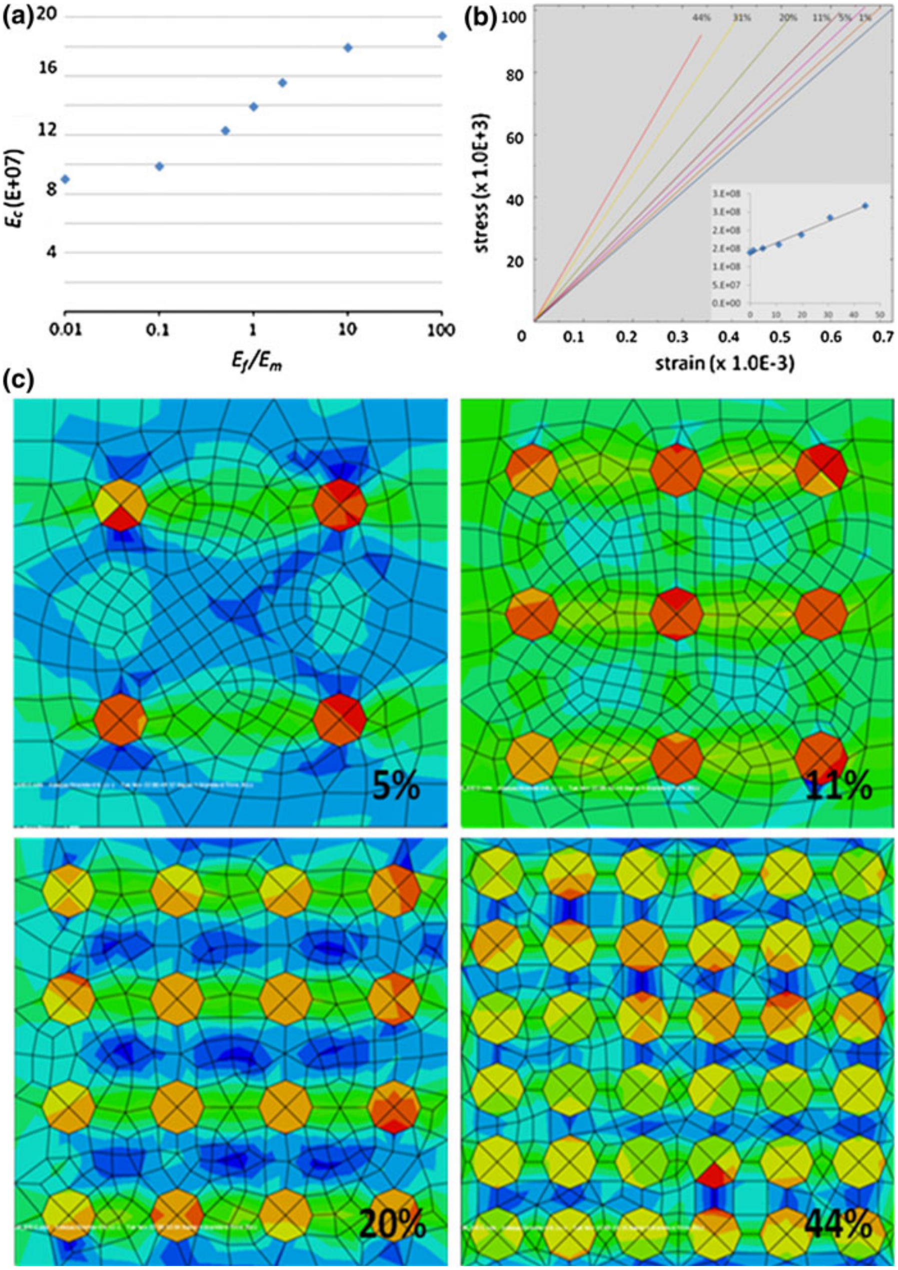

Fig. 6 Predicted moduli of nanocomposites from the finite element modeling. **a** The change of the Young's moduli of the composites (E_c) with the ratio of the Young's moduli between filler (E_f/E_m). When the E_f is too high or too low, further change in E_f doesn't cause additional change of E_c. **b** The change of Young's moduli of the composites with the increased concentration of filler particles. A higher concentration of nano-fillers will contribute to a large E_c. **c** Filler effect of four different concentrations of nanoparticles from the finite element modeling analysis. An increased concentration of nano-fillers enhanced the Young's moduli of the composites, which were reflected by the color in the four images. Color with higher wavelength means a larger Young's modulus

$$E_c = \frac{1 + \zeta \eta V_f}{1 - \eta V_f} E_m \tag{1}$$

where ζ is the shape factor, V_f is the volume fraction of particles relative to the matrix, and

$$h = \left(\frac{E_f}{E_m} - 1\right) \Big/ \left(\frac{E_f}{E_m} + \zeta\right) \tag{1.1}$$

The shape factor of ζ is related to the aspect ratio (l/t) as $\zeta = 2l/t$, where l is the length of the particle and t is its thickness. For the nanospheres used in this study, the aspect ratio is unity, and hence $\zeta = 2$ will be used. Simulation results of the Young's moduli of the composites are shown in Fig. 7 with different volume fraction V_f (0.4, 2, 5, 10, 15 %). The Young's modulus E_f of the polystyrene is approximately 3–3.5 GPa, thus 3.25 GPa is used in the simulation.

Based on the Halpin–Tsai model, it can be easily seen that with the increase of V_f, the modulus of the composites will increase correspondingly. However,

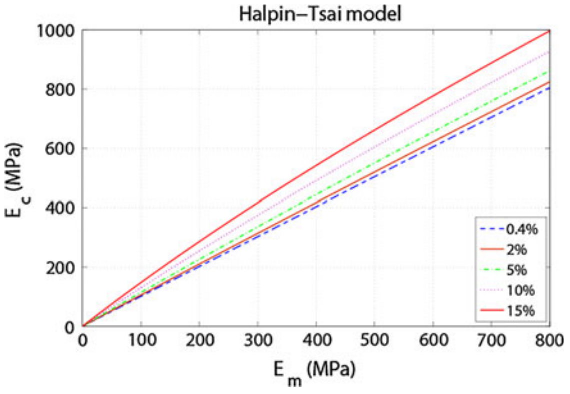

Fig. 7 Predicted moduli of nanocomposites with different concentrations of fillers from Halpin–Tsai model. Higher concentration of nano-fillers will contribute to a higher Young's modulus of the composite

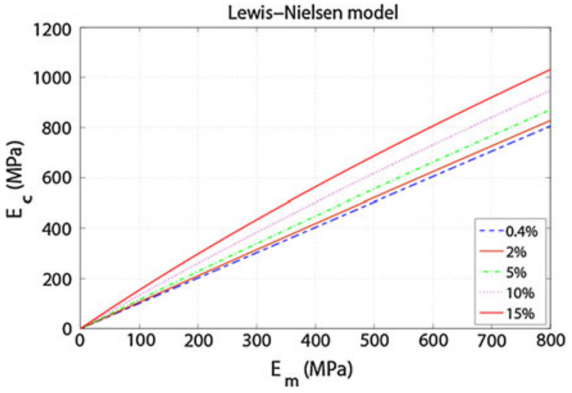

Fig. 8 Predicted moduli of nanocomposites with different concentrations of fillers from Lewise–Nielsen model. Higher concentration of nano-fillers will contribute to a higher Young's modulus of the composite

the measured moduli generally lie slightly below the estimated values, which have been proposed due to the imperfect bonding between the nanoparticles and the matrix (Johnsen et al. 2007). The filler effect can be considered further using the Lewise–Nielsen model (Nielsen 1966) and the study of McGee and McCullough (1981). The authors showed that the composite modulus can be predicted using:

$$E_c = \frac{1 + (k_E - 1)\beta V_f}{1 - \beta\mu V_f} E_m \tag{2}$$

where k_E is the generalized Einstein coefficient, and β and μ are constants. The relative modulus of the particles and the polymer matrix is considered in calculating the constant β, which is given by

$$\beta = \left(\frac{E_f}{E_m} - 1\right) \Big/ \left(\frac{E_f}{E_m} + k_E - 1\right) \tag{2.1}$$

The value of μ depends on the maximum volume fraction of particles, $V_{\max}$, and can be calculated from

$$\mu = 1 + \frac{1 - V_f}{V_{\max}}\left[V_{\max} V_f + (1 - V_{\max})(1 - V_f)\right] \tag{2.2}$$

For random close packing, non-agglomerated spheres, Nielsen and Landel quoted a value of $V_{\max} = 0.632$. This value will be used in the simulations. The value of k_E varies with the degree of matrix to particle adhesion. For a matrix with a Poisson's ratio of 0.5 containing dispersed spheres, k_E equals to 2.5 if there is no slippage at the interface, and k_E equals to 1.0 if there is slippage (Hsieh et al. 2010). The no slippage condition is assumed in this study. The simulation result of the Young's moduli of the composites is shown in Fig. 8 with different volume fraction V_f (0.4, 2, 5, 10, 15 %).

The results from model estimation showed a maximum 30 % increase in Young's moduli depending on the concentration of the nano-fillers. Compared to the measured data from Figs. 1 and 2, we could see that both models underestimated the moduli of the polystyrene nanocomposites, while they provided proximate prediction when ZnO or TiO_2 nanoparticles worked as fillers. One possible reason for the difference observed from polystyrene nanocomposites is that at a relatively low volume ratio, the interface might dominate in determining the filler effect in the nanocomposites, as suggested from other studies (Sajjad et al. 2012). Polystyrene has many phenyl groups which make them extremely hydrophobic, which might draw its strong interaction with the hydrophobic silicon matrix in the interface. These interactions will likely dominate the interface which makes the filler effect more significant than expected.

Conclusion

In this study, we have investigated the effects of different nano-fillers to tune the mechanical properties, Young's modulus, in particular, of the silicone matrix. It was concluded that smaller spherical nanoparticles, in general, provided better filler effect than the larger ones. Surfactants added to the polymer matrix could enhance the reinforcement effect of the nano-fillers, which could be attributed to the assistance with the nanoparticle dispersion, and also possibly plastic void growth in the polymeric matrix. Although surface chemistry modification with different biocompatible chemical groups might decrease the in vivo toxicity of the nanoparticles, the modification with hydrophilic groups also decreased the performance of nanoparticles as fillers in the silicone matrix. Nanoclay and carbon nanofibers proved to be less promising as fillers compared to spherical nanoparticles, due to potential limited distribution among the hydrophobic silicone matrix. The observations from this study supported the hypothesis that the hydrophobic small nanospheres could serve as promising fillers in tuning or reinforcing the mechanical properties of silicone matrix.

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