

NANO- AND MICRO-SILICA LOADED SILICONE RUBBERS' LINEAR ELASTIC CHARACTERISTICS

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Abstract

Theory and experimental data on silica-filled silicone rubbers provide the foundation for a discussion of the linear elastic characteristics of rubber composites filled with nano- and micro-particles. Lewis and Nielsen's mixture law with the apparent volume fraction could evaluate the Young's modulus of the rubber composite in the linear elastic region of the measured tensile stress-strain relations. This was confirmed because the nano-particles in the composite acted as apparent particles composed of the nano-particles and interphase layers formed on the particles. Using a model with randomly dispersed particles in three dimensions, the proportional limit strain of the composite was theoretically derived. By contrasting the evaluated limit strain with the observed outcomes of composites including nano- and micro-particles at (apparent) volume fractions below the particle percolation threshold of 0.3, we were able to establish the validity of the strain analysis. Analysis of the composites' Young's moduli and proportional limit strains revealed, in the linear elastic area, stress-strain relations.

Keywords: Nano-composite, Rubber composite, Silica particle, Silicone rubber, Interphase layer, Nano-particle, Young's modulus, Proportional limit strain

1. Introduction

Rubbers are widely used for numerous industrial applications, such as cushioning, gas storage, and sealing. In particular, flexibility or softness is one of the most important properties of rubbers and their composites because of the need of low elasticity. Generally, the elastic modulus and strength are improved by filling particles into neat rubbers (Nielsen and Landel, 1994; 2. Bergström and Boyce, 1999). The elastic moduli of the composites can be evaluated using mixture laws with the mechanical properties of the component materials. Such laws have been suggested by several researchers including Kerner (1956), Hashin and Shtrikman (1963), Lewis and Nielsen (1970), Mori and Tanaka (1973), and Guth and Gold (1945), with the law validities based on the experimental results. Because the stress-strain relations of rubber composites are usually strongly nonlinear, it is important to specify the linear elastic regions in these relations to design flexible materials. Such regions in stress-strain relations including the proportional limits have not been discussed before.

The particle size is currently reduced below the order of micro-meters to improve the mechanical properties of these composites. Generally, the effect of filled nano-particles on the mechanical behavior is not included in most mixture laws. Some researchers (Vollenberg and Heikens, 1989; Jordan et al., 2005; Fu et al., 2008) have reported that the elastic or viscoelastic moduli of composites in a rubbery state are higher than those calculated by mixture laws. The particle size effect has been recognized from several viewpoints, including the larger specific surface area of smaller particles (Camenzind et al., 2010; Edwards, 1990), the mobility (Kwon et al., 2006) and the stiffness (Sternstein et al., 2010; Wu et al., 2005) of the matrix between small particles, and special bonding between the particles and matrix (Aranguren et al., 1994).

Interphase layers around nano-particles have been shown to cause the particle size effect on the mechanical properties of nano-composites. Generally, an interphase layer can be formed by applying a coupling-agent coating on the surfaces

of the particles to bond them and the matrix polymer (Brinke et al., 2003; Li and Cho, 2013; Ge et al., 2015; Mei et al., 2016). Even when nano-particles are not coated chemically with a coupling agent, however, an interphase layer forms around the particles because of entanglement with the matrix molecules. The presence of interphase layers around nano-particles has been validated through experimental results from micro-thermal analysis (Van Assche and Van Mele, 2002), scanning electron microscopy (Zhang et al., 2006; Adachi et al., 2011), and Raman spectroscopy (Adachi et al., 2008). Therefore, such interphase layers affect the mechanical properties of nano-composites. Adachi, et al. (2018) demonstrated the nano-particle size effect on tensile deformation by examining silicone rubber composites filled with silica particles. Specially, they reported that the interphase layer around the nano-particles was made of matrix rubber in a glassy state, whereas the composite was in a rubbery state, and that the deformation properties depended on the volume fraction of apparent particles composed of the nanoparticles and interphase layer.

Silicone rubber has been widely applied in many industrial products because of its excellent properties, such as high flexibility, heat resistance, electrical insulation, water resistance, and weather resistance. Silica particles are filled into silicone rubber to improve its mechanical properties, especially the strength and elastic modulus (Yatsuyanagi et al., 2001; Salvi et al., 2002; Gauthier et al., 2004; Patwardhan et al., 2006; Galanti and Sperling, 1970; Vondráček and Schätz, 1979; Zhang et al., 2011; Yan et al., 2015). In this study, we examined the linear elastic behavior of silicone rubbers filled with micro- and nano-silica particles on the basis of experimental results and theoretical analysis. The purpose was to evaluate Young's modulus and the proportional limit in the stress-strain relations of composites having interphase layers around the nano-particles. The nano- or micro-silica particles in the specimens were not subjected to a chemical surface treatment. The Young's moduli determined from the tensile stress-strain relations validated a mixture law. A mixture law for the proportional limit proposed theoretically was clarified to be valid by comparison with the experimental results using the volume fraction of micro-particles and the apparent volume fraction of nano-particles.

2. Specimen materials

The specimens were silicone rubber composites filled with spherical nano- or micro-silica particles. The silicone rubber was made of a mixture of a base compound (KE-106, Shin-etsu Silicone) and a curing agent (CAT-RG, Shin-etsu Silicone). The weight ratio of the main compound to the curing agent was 10:1 according to the supplier recipe.

Spherical silica particles with a median diameter of 300 nm, i.e., nano-particles (SO-C1, Admatechs), or 1.5 μm , i.e., micro-particles (SO-C5, Admatechs) were filled into the silicone rubber. The Young's modulus of the particles was 72.1 GPa (Kwon et al., 2006; Adachi et al., 2008). For both sizes, the particles' surfaces were not chemically coated, so that they could disperse in the rubber without agglomerating. The volume fraction of particles in the composites ranged from 0 to 0.3.

To manufacture the rubber composites by hand, the silica particles were blended with the silicone rubber until they had all dispersed. The complete mixture was degassed in a vacuum vessel and then poured into a Teflon mold of the specimen dimensions described in the next section. The mixture in the mold was cured by heating in an oven. The curing procedure had three steps of 323 K for 0.5 h, 373 K for 0.5 h, and 423 K for 0.5 h. The heating rate between steps was 72 K/h. Cured rubber without silica particles, referred to as neat rubber, was also prepared by the same process as that for the composites. The density of the silicone rubber after curing was $1.02 \times 10^3 \text{ kg m}^{-3}$. This paper refers to the composites filled with nano- and micro-silica particles as nano- and micro-composites, respectively.

3. Experimental procedure

3.1 Viscoelastic testing

The viscoelastic properties of the neat rubber and composites were measured with a dynamic viscoelastometer (Rheogel-E-4000, UBM) by using a non-resonance tensile method. The specimens were 5 mm wide, 3 mm thick, and 35 mm long, and the distance between gripping devices was 25 mm. For tensile oscillations with frequencies from 3 to 100 Hz and an amplitude of 2 μm , the dynamic complex moduli of the specimens were measured at intervals of 1 K from 200 to 350 K. The heating rate was 1 K min^{-1} .

3.2 Tensile testing

The stress-strain relations of the rubber and composites were measured with tensile tests at room temperature. The

specimens were dumbbell-shaped: Type 3, JIS K6251 (Type 1A, ISO 37). A constant displacement rate of 10 mm/min was applied, and the tensile load was recorded using a universal material-testing machine (4444, Instron). The true stresses and logarithmic strains of the specimens were evaluated from the longitudinal and transverse strains with a gage length of 5 mm, which were measured by processing motion pictures of the specimen deformations with digital image processing software (PFV and PFA, Photron). After the tensile tests, the fracture surfaces of the specimens were observed using a low-vacuum scanning electron microscope (SU3500, Hitachi) without coating the electrically conducting material.

4. Experimental results

4.1 Viscoelastic properties

We reported the temperature dependence of the dynamic moduli of the neat rubber and composites in our previous paper (Adachi et al., 2018). Figure 1 shows the measured dynamic storage moduli of the composites at 298 and 348 K as some typical properties. In addition, the moduli were evaluated using Lewis and Nielsen's mixture law (Lewis and Nielsen, 1970), which gives highly accurate predictions, as follows:

$$E'_C = \frac{1+AB\phi}{1-B\phi} E'_M \quad (1)$$

where

$$A = \frac{1-5\nu_M}{8-10\nu_M}, \quad B = \frac{(E_P/E'_M)-1}{(E_P/E'_M)+A}, \quad \phi = \left(\frac{1-\phi_{MAX}}{\phi_{MAX}^2} \right) \phi + 1.$$

Here, E'_M and ν_M are the dynamic storage modulus and Poisson's ratio, respectively, of the silicone-rubber matrix, and E_P and ϕ are the Young's modulus and volume fraction of the silica particles. The maximum packing fraction ϕ_{MAX} is 0.637 for close-packed spheres (Kerner, 1956; Kwon et al., 2006; Adachi et al., 2008). Note that no size effect of the filled particles on the composite's E'_C value appears in Eq. (1). The results of Eq. (1) are shown as solid lines in Fig. 1.

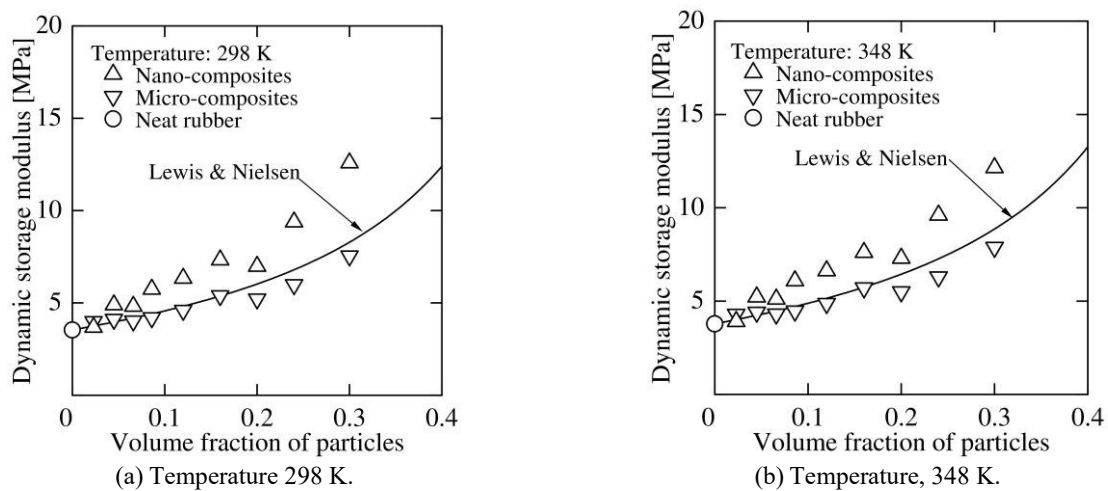


Fig. 1 Dynamic storage moduli at a frequency of 10 Hz.

The measured moduli of the nano-composites were higher than the analytical results from the mixture law, while the measured results for the micro-composites approximately agreed with the analytical results. Thus, the moduli were obtained to depend on the particle size in the composites.

4.2 Tensile deformation

Figure 2 shows the true stress-logarithmic strain curves until fracture for the neat rubber, and the nano- and micro-composites. Except for the specimens with a particle volume fraction of 0.3, the curves were J-shaped: slope increased with increasing strain, regardless of the presence or size of particles. Within the low-stress region, the curves were approximately proportional to the strain. After that, the curves increased exponentially until fractures. The slope within

the low-stress region of a stress-strain curve expresses the rubber's flexibility. The curves with a particle volume fraction of 0.3, however, differed from the others and had higher slopes. This volume fraction of 0.3 is close to the threshold of particle-percolation, 0.29 at which the particles are distributed three-dimensionally and randomly (Christian and Robert, 2001). The percolation effect causes a rubber composite to lose its low-elastic modulus region, meaning its flexibility, which is an important property of rubber. Hence, the rest of this paper focuses on the linear elastic properties of the composites and neat rubber within the low-stress region.

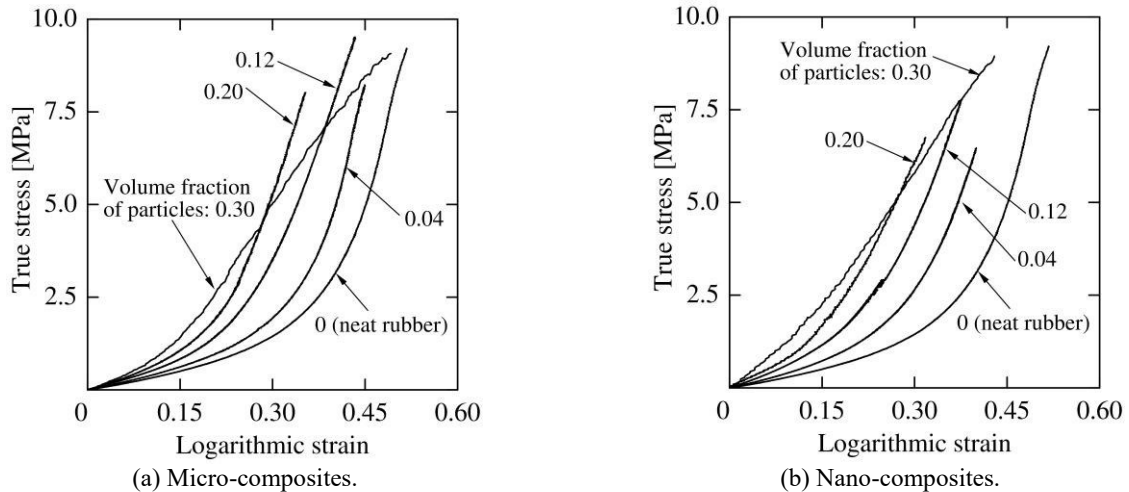


Fig. 2 True stress-logarithmic strain curves at room temperature (293 K).

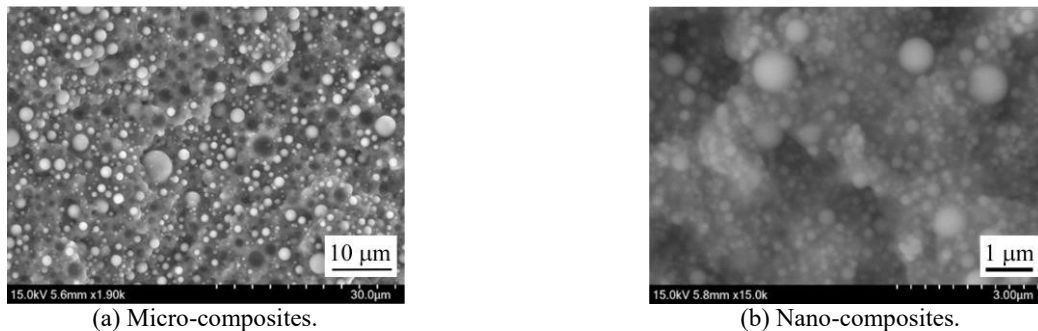


Fig. 3 Fracture surfaces. Volume fraction of particles: 0.24.

Figure 3 shows fracture surfaces of specimens after the tensile tests. The particles on the surface of the nano-composite were covered by the matrix rubber whereas the particles in the micro-composite were exposed on the surfaces. The covering matrix is called an interphase layer (Van Assche and Van Mele, 2002; Zhang et al., 2006; Adachi et al., 2011, 2008, 2018). It has been clarified to be made of the matrix rubber in a glassy state even when the composite is in a rubbery state (Adachi et al., 2018). Such interphase layers are formed by entanglement of the rubber molecules and the particles, even though a chemical coating was not applied on the particle surfaces here, according to previous studies (Adachi et al., 2018; Umboh et al., 2013, 2014). The interphase layers in some polymer composites have been reported to perform an important role in the fracture toughness of nano-composites in the glassy state (Adachi et al., 2008). Therefore, the size effect of the particles on the mechanical properties of nano-composites can be explained in terms of the interphase layers around the nano-particles. The interphase layer thus causes the higher dynamic storage moduli of the nano-composites as compared to the results of the mixture law.

5. Discussion

5.1 Interphase layer

The difference between the measured dynamic storage moduli for the nano-composites in the rubbery state and the results calculated by the mixture law, Eq. (1), which normally gives highly accurate predictions, resulted from the existence of the interphase layer around the nano-particles. The average thickness of the interphase layer was determined

by the following procedure, assuming that the particle diameters and thicknesses of the layer were uniform in the nano-composite. Hereafter, we call a particle with a surrounding interphase layer an “apparent particle”. The volume fraction of apparent particles (i.e., the apparent volume fraction), ϕ' , was calculated inversely by substituting the measured E_C' of the nano-composite and E_M' into Eq. (1). From the results of the apparent volume fraction, the thickness of the interphase layer h can be determined as

$$h = \frac{d}{2} \left\{ \left(\frac{\phi'}{\phi} \right)^{1/3} - 1 \right\}, \quad (2)$$

where d is the diameter of the nano-silica particles.

Hence, Fig. 4 shows the dependencies of the determined thickness of the interphase layer on the temperature and the actual volume fraction. In Fig. 4(a), the thickness decreased slightly with higher temperature. This variation implies that the thickness is affected by relaxation of the rubber molecules due to thermal activation. Because the dependence of the interphase layer thickness on the volume fraction of the particles is clear, however, Fig. 4(b) shows the relation between the thickness and the volume fraction at room temperature (293 K). The thickness decreased as the volume fraction increased. It is reasonable that the interphase layer formed around the nano-particles is related to the mobility of rubber molecules between the particles. The interphase layer thickness was thus approximated by the following equation, because it varied considerably with the volume fraction, but the temperature dependence was small:

$$h = 5.54 \cdot \phi^{-0.76} \text{ [nm]}, \quad (3)$$

In the rest of this paper, the apparent volume fraction of particles in the nano-composite is derived from the interphase layer thickness calculated by Eq. (3).

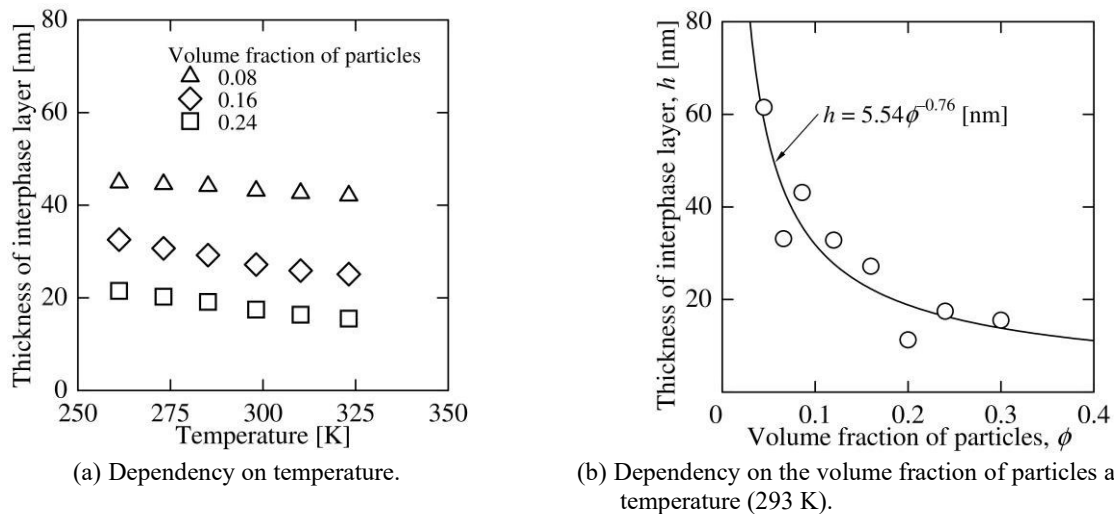


Fig. 4 Average thicknesses of interphase layers.

5.2 Young’s modulus

One of the most important properties for rubber composites is flexibility, meaning low-elasticity behavior. This behavior can be characterized by the slope of the stress-strain curve, Young’s modulus and its applicable strain region, and the proportional limit strain in the curve. The stress-strain curves were thus approximated linearly from their origins by the least-squares method. For the approximated lines whose the coefficient of determination in the least-squares method was 0.99, the range of the lines were defined as the linear low-elasticity deformation regions. The slopes and maximum strains in these regions were evaluated as the Young’s moduli and proportional limit strains, respectively, in the stress-strain curves of the composites.

The Young’s moduli of the nano- and micro-composites can be predicted from Eq. (1) by substituting the apparent volume fractions for the composites and the measured properties of the neat rubber: Young’s modulus, 3.90 MPa, and Poisson’s ratio, 0.5. Figure 5 shows the experimental Young’s moduli of the micro- and nano-particles plotted as triangles and the analytical result of Eq. (1) as a solid line. The relation between the moduli of the micro- and nano-composites, and the apparent volume fractions agreed with the analytical result. Thus, the presence of the interphase layer around the

nano-particles must be considered in evaluating the Young's moduli of nano-composites by the mixture law. Note, however, that the interphase layer did not affect the Young's moduli of the composites in the glassy state, because they agreed with the results of Eq. (1) for the actual volume fraction of the particles (Adachi et al., 2008, 2011, 2018).

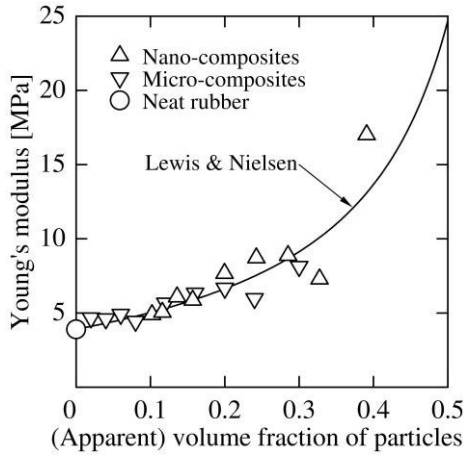


Fig. 5 Young's moduli.

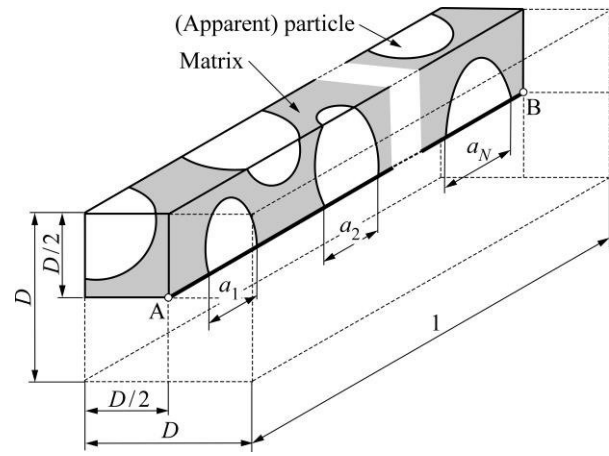


Fig. 6 Analytical model of composite.

5.3 Proportional limit strain

Next, the proportional limit strains of the rubber composites were analyzed to predict their low-elasticity behavior. The analysis used the composite model shown in Fig. 6. In the model, particles with diameter D are randomly and three-dimensionally distributed in a matrix space with a certain volume fraction of micro-particles ϕ or apparent volume fraction of nanoparticles ϕ' . The line between points A and B is an arbitrary line with unit length. Because the number of particles on the line A-B, denoted as N , corresponds to the number in a cubic region with height D , width D and unit length, N can be evaluated as

$$N = \frac{\phi' D^2}{v}, \quad (4)$$

where $v (= \pi D^3 / 6)$ is the volume of a particle. The total length of the rubber matrix region along line A-B, denoted as L_M , can then be expressed as follows:

$$L_M = 1 - \sum_{n=1}^N a_n = 1 - N a_m, \quad (5)$$

where a_n is the length of each particle on line A-B, and a_m is the mean particle length given by

$$a_m = \frac{2}{D} \int_{-D/2}^{D/2} \sqrt{\left(\frac{D}{2}\right)^2 - r^2} dr = \frac{\pi D}{4}.$$

Assuming that only the matrix rubber deforms in the composite, because the deformation of particles with a high elastic modulus is negligibly small, the logarithmic strain ε in the composite can be determined as

$$\varepsilon = \ln(\Delta L_M + 1), \quad (6)$$

where ΔL_M is the extension of the matrix rubber along the line A-B. The extension is calculated from the strain of the matrix rubber, ε_M , as follows:

$$\Delta L_M = L_M \{ \exp(\varepsilon_M) - 1 \}.$$

When the strain of the matrix reaches the proportional limit strain ε_0 of the neat rubber, the strain of the composite (Eq. (6)) also arrives at its proportional limit strain, ε_ϕ . Then, ε_ϕ is finally evaluated by substituting Eqs. (4) and (5) into Eq. (6):

$$\varepsilon_\phi = \ln \left| \frac{\exp(\varepsilon_0) + \frac{\phi'}{2} \{1 - \exp(\varepsilon_0)\}}{1} \right| \quad (7)$$

The proportional limit strain of the composite was thus evaluated from the measured proportional limit strain of the neat rubber, 0.23, and the volume fraction or apparent volume fraction of the particles. The critical volume fraction of particles for $\varepsilon_\phi = 0$ was evaluated as ϕ or $\phi' = 2/3 (= 0.67)$ from Eq. (7). This approximately coincided with the maximum fraction of randomly or irregularly packed spheres, 0.64 (Scott and Kilgour, 1969; Berryman, 1983; Song et al., 2008), and it is close to the maximum fraction of regularly packed spheres, 0.74. Thus, Eq. (7) is clarified to be valid theoretically.

The proportional limit strains of the composites were identified experimentally as the strain ranges to which the approximated lines for determining the Young's moduli could be applied. Figure 7 shows the relations between the proportional limit strains and the apparent volume fractions for the micro- and nano-particles plotted as triangles, with the result of Eq. (7) drawn as a solid line.

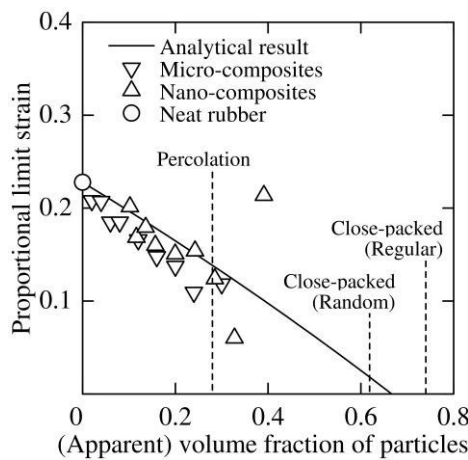


Fig. 7 Relations between proportional limit strains and (apparent) volume fractions of composites.

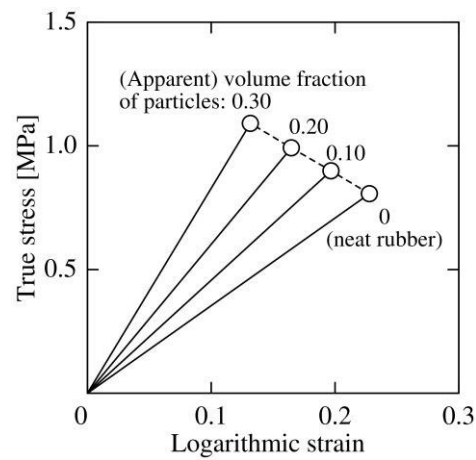


Fig. 8 Analytical stress-strain curves in the linear elastic region.

As seen in Fig. 7, the proportional limit strains were dependent on the apparent volume fractions regardless of the particle size, so the interphase layer around the nano-particles affected the proportional limit strains. The result of Eq. (7) approximately in agreed with the experimental results. Above a volume fraction of approximately 0.3, however, the experimental results varied drastically and deviated from the analytical result. This fraction of 0.3 coincides with the threshold of percolation phenomena for spheres distributed in a three-dimensional region which is 0.29 (Christian and Robert, 2001). Thus, it is clear that the proportional limit strain of a rubber composite can be analyzed with Eq. (7) as long as particle percolation phenomena do not occur in the rubber matrix.

Therefore, the stress-strain curves in the low-elasticity region for a rubber composite can be analyzed with Eqs. (1) and (7). Accordingly, Fig. 8 shows some analytical results. Hence, the stress-strain curve of a rubber composite filled with nano- and micro-particles can be designed in the region surrounded by the solid lines, which are the stress-strain curves of neat rubber and a composite with an apparent volume fraction of 0.3, and the broken line connecting the proportional strain limits.

6. Conclusion

A combination of experimental data and theoretical analysis was used to investigate the linear elastic behaviour of silicone rubber composites that were filled with nano- and micro-silica particles. A matrix rubber interphase layer was created to encase the nano-particles. Rather than temperature, the experimental results showed that the volume percentage of nano-particles determined the interphase layer thickness. It seemed as if the nano-particles and the interphase layer were one and the same, which is how the composite's nano-particles behaved. So, within the linear elastic area of a recorded tensile stress-strain relation, the Young's modulus of the rubber composite might be predicted by using Lewis and Nielsen's mixing law with the apparent volume fraction. The composite's proportional limit strain was determined.

in theory, via the use of a model with a randomly distributed set of particles across three dimensions. By comparing the calculated limit strain with the observed data, we were able to determine that it was true for particle percolation scenarios where the apparent volume fraction was less than 0.3. Analysis of the composites' Young's moduli and proportional limit strains revealed, in the linear elastic area, stress-strain relations.

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References

- Adachi, T., Imai, Y. and Higuchi, M., Fracture energy of nano- and micro-silica particle-filled epoxy composites, *International Journal of Theoretical and Applied Multiscale Mechanics*, Vol.2 (2011), pp.82–94.
- Adachi, T., Osaki, M., Araki, W. and Kwon, S. C., Fracture energy of nano- and micro-silica particle-filled epoxy composites, *Acta Materialia*, Vol.56 (2008), pp.2101–2109.
- Adachi, T., Yamada, Y. and Ishii, Y., Interphase-layer effect on deformation of silicone rubber filled with nano-silica particles, *Journal of Applied Polymer Science*, Vol.135 (2018), p.45880.
- Aranguen, M. I., Mora, E., Macosko, C. W., and Saam, J., Rheological and mechanical properties of filled rubber: silica-silicone, *Rubber Chemistry and Technology*, Vol.67 (1994), pp.820–833.
- Bergström, J. S. and Boyce, M. C., Mechanical behavior of particle filled elastomers, *Rubber Chemistry and Technology*, Vol.72 (1999), pp.633–656.
- Berryman, J. D., Random close packing of hard spheres and disks, *Physical Review A*, Vol.27 (1983), pp.1053–1061.
- Brinke, J. W. ten, Debnath, S. C., Reuvekamp, L. A. E. M. and Noordermeer, J. W. M., Mechanistic aspects of the role of coupling agents in silica–rubber composites, *Composites Science and Technology*, Vol.63 (2003), pp.1165–1174.
- Camenzind, A., Schweizer, T., Sztucki, M. and Pratsinis, S.E., Structure & strength of silica-PDMS nanocomposites, *Polymer*, Vol.51 (2010), pp.1796–804.
- Christian, D. L. and Robert, M. Z., Precise determination of the critical percolation threshold for the three-dimensional “Swiss cheese” model using a growth algorithm, *Journal of Chemical Physics*, Vol.114 (2001), pp.3659–3661.
- Edwards, D. C., Polymer-filler interactions in rubber reinforcement, *Journal of Materials Science*, Vol.25 (1990), pp.4175–4785.
- Fu, S. Y., Feng, X. Q., Lauke, B. and Mai, Y. W., Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites, *Composites Part B: Engineering*, Vol.39 (2008), pp.933–961.
- Galanti, A. V. and Sperling, L. H., Morphology and structure of silica agglomerates in silica -reinforced silicone rubber, *Journal of Applied Polymer Science*, Vol.14 (1970), pp.2785–2796.
- Gauthier, C., Reynaud, E., Vassoille, R. and Ladouce-Stelandre, L., Analysis of the non-linear viscoelastic behaviour of silica filled styrene butadiene rubber, *Polymer*, Vol.45 (2004), pp.2761–2771.
- Ge, X., Li, M. C. and Cho, U. R., Novel one-step synthesis of acrylonitrile butadiene rubber/bentonite nanocomposites with (3-Mercaptopropyl) trimethoxysilane as a compatilizer, *Polymer Composites*, Vol.36 (2015), pp.1693–1702.
- Guth, E., Theory of filler reinforcement, *Journal of Applied Physics*, Vol.16 (1945), pp.20–25.
- Hashin, Z. and Shtrikman, S., A variational approach to the theory of the elastic behaviour of multiphase materials, *Journal of the Mechanics and Physics of Solids*, Vol.11 (1963), pp.127–140.
- Jordan, J., Jacob, K. I., Tannenbaum, R., Sharat, M. A. and Jasiuk, I., Experimental trends in polymer nanocomposites– a review, *Materials Science and Engineering: A*, Vol.393 (2005), pp.1–11.
- Kerner, E.H., The elastic and thermo-elastic properties of composite media, *Proceedings of the Physical Society. Section B*, Vol.69 (1956), pp.808–813.
- Kwon, S.C., Adachi, T., Araki, W. and Yamaji, A., Thermo-viscoelastic properties of silica particulate-reinforced epoxy composites: Considered in terms of the particle packing model, *Acta Materialia*, Vol.54 (2006), pp.3369–3374.
- Lewis, T. B. and Nielsen, L. E., Dynamic mechanical properties of particulate-filled composites, *Journal of Applied*

- Polymer Science, Vol.14 (1970), pp.1449–1471.
- Li, M.-C. and Cho, R., Effectiveness of coupling agents in the poly (methyl methacrylate)-modified starch/styrene-butadiene rubber interfaces, *Materials Letters*, Vol.92 (2013), pp.132–135.
- Mei, H., Chen, G., Zhu, Q., Dong, P., Zhao, D. and Raza, W.A., Improving properties of silicone rubber composites using macromolecular silane coupling agent (MMSCA), *Journal of Applied Polymer Science*, Vol.133 (2016), pp.43415.
- Mori, T. and Tanaka, K., Average stress in matrix and average elastic energy of materials with misfitting inclusions, *Acta Metallurgica*, Vol.21 (1973), pp.571–574.
- Nielsen, L. E. and Landel, R. F., *Mechanical Properties of Polymers and Composite*, 2nd ed. (1994), p.377–378, Marcel Dekker.
- Patwardhan, S. V., Taori, V.P., Hassan, M., Agashe, N. R., Franklin, J. E., Beaucage, G., Mark, J. E. and Clarson, S. J., An investigation of the properties of poly(dimethylsiloxane)-bioinspired silica hybrids, *European Polymer Journal*, Vol.42 (2006), pp.167–178.
- Salvi, A. M., Pucciariello, R., Guascito, M. R., Villani, V. and Intermite, L., Characterization of the interface in rubber/silica composite materials, *Surface and Interface Analysis*, Vol.33 (2002), pp.850–861.
- Scott, G. D. and Kilgour, D. M., The density of random close packing of spheres, *Journal of Physics D: Applied Physics*, Vol.2 (1969), pp. 863–866.
- Song, C., Wang, P. and Makse, H. A., A phase diagram for jammed matter, *Nature*, Vol.453 (2008), pp.629–632.
- Sternstein, S. S., Amanuel, S. and Shofner, M. L., Reinforcement mechanisms in nanofilled polymer melts and elastomers, *Rubber Chemistry and Technology*, Vol.83 (2010), pp.181–198.
- Umboh, M. K., Adachi, T., Nemoto, T., Higuchi, M. and Major, Z., Non-stoichiometric curing effect on fracture toughness of nanosilica particulate-reinforced epoxy composites, *Journal of Materials Science*, Vol.49 (2014), pp.7454–7461.
- Umboh, M. K., Adachi, T., Oishi, K., Higuchi, M. and Major, Z., Mechanical properties of nano-silica particulate-reinforced epoxy composites considered in terms of crosslinking effect in matrix resins, *Journal of Materials Science*, Vol.48 (2013), pp.5148–5156.
- Van Assche, G. and Van Mele, B., Interphase formation in model composites studied by micro-thermal analysis, *Polymer*, Vol.43 (2002), pp.4605–4610.
- Vollenberg, P. H. T. and Heikens, D., Particle size dependence of the Young's modulus of filled polymers: 1. Preliminary experiments, *Polymer*, Vol.30 (1989), pp.1656–1662.
- Vondráček, P. and Schätz, M., NH₃-modified swelling of silica-filled silicone rubber, *Journal of Applied Polymer Science*, Vol.23 (1979), pp.2681–2694.
- Wu, C. L., Zhang, M. Q., Rong, M. Z. and Friedrich, K., Silica nanoparticles filled polypropylene: effects of particle surface treatment, matrix ductility and particle species on mechanical performance of the composites, *Composites Science and Technology*, Vol.65 (2005), pp.635–645.
- Yan, F., Zhang, X., Liu, F., Li, X. and Zhang, Z., Adjusting the properties of silicone rubber filled with nanosilica by changing the surface organic groups of nanosilica. *Composites Part B: Engineering*, Vol.75 (2015), pp.47–52.
- Yatsuyanagi, F., Suzuki, N., Suzuki, M. and Kaidou, H., Effects of secondary structure of fillers on the mechanical properties of silica filled rubber systems, *Polymer*, Vol.42 (2001), pp.9523–9529.
- Zhang, C., Pal, K., Byeon, J.-U., Han, S.-M. and Kim, J. K., A study on mechanical and thermal properties of silicone rubber/EPDM damping materials, *Journal of Applied Polymer Science*, Vol.119 (2011), pp.2737–2741.
- Zhang, H., Zhang, Z., Friedrich, K. and Eger, C., Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content, *Acta Materialia*, Vol.54 (2006), pp.1833–1842.