

Establishment of Constitutive Model of Silicone Rubber Foams Based on Statistical Theory of Rubber Elasticity

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Abstract In this study, a constitutive model based on microscopic physical mechanism of silicone rubber foams was established. A theoretical statistical model of rubber elasticity considering the effect of dangling chains was modified to build this model. When a strain amplification factor (X) was introduced, the theoretical model could fit the tensile stress-strain data of mono- and bi-modal foam matrix well (Adj. R-Square = 0.9989, 0.9983). Parameters related to the polymer network, namely, average molecular weight (M_c) and volume fraction (ϕ) of chain segments between adjacent cross-linking points (network strands), were calculated by probabilistic method from the number-average molecular weight (M_n), vinyl content (w_{vi}) of the primary polysiloxanes and percent conversion (q) of vinyl groups. The primary and infinite strain amplification factors (X_0 , X_∞) and decay exponent (z), introduced by X and related to the nanoparticles, were obtained by fitting. Inspired by the fact that the actual strain of matrix was lower than that of the foams', we introduced another item, strain hysteresis item (H , related with the foam porosity and cell structure), into the statistical model as well. With the same above values of M_c , ϕ , X_0 and X_∞ , the model could also fit the compressive stress-strain data of mono- and bi-modal foams well (Adj. R-Square = 0.9948, 0.9985). Interestingly, the strain hysteresis items of the mono- and bi-modal foams almost completely coincided under all experimental strains, which may be attributed to the almost equal porosity and similar cell structure of the two foams. This constitutive model may connect the macroscopic stress-strain behaviour to the parameters of microscopic molecular structures, promisingly providing a basis for the performance improvement and optimization of silicone rubber foams.

Keywords Silicone rubber foams; Constitutive model; Statistical theory of rubber elasticity; Strain amplification factor; Strain hysteresis item

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INTRODUCTION

Silicone rubber foams are kinds of low density porous polymer materials formed by foaming process of silicone rubbers^[1–3]. Combining the advantages of silicone rubbers with foam materials^[4], silicone rubber foams exhibit excellent comprehensive performances and are widely used in electronics industry, chemical industry, aerospace, etc^[5, 6]. The stress-strain properties of silicone rubber foams are very important for keeping their functions. The mechanical properties of silicone rubber foams, especially the stress-strain properties and stress relaxation behavior, have been widely studied around the world^[7].

The nowadays cellular solids models could be divided into two categories: phenomenological models and micro-mechanical models. The phenomenological models, such as Rusch model^[8] and Massimiliano Avalor's model^[9], aim to give the best fit for experimental data, without direct relationship with the physics of the phenomenon. However, the micro-mechanical models, such as Gibson model^[10], are

based on the analysis of the deformation mechanisms of the micro-cell structure under loading.

Studying the mechanical properties of polymer matrix of silicone rubbers is an effective route to understand the stress-strain properties of silicone rubber foams. Mooney-Rivlin model, one of the widely used empirical constitutive models of rubbers, could fit the experimental data well. But, study on the viscoelastic behavior of silicone rubber from the microscopic view could definitely help to understand the silicone rubbers' viscoelasticity deeply, as well as providing a base for performances modification. The constitutive model based on microscopic mechanism could build a connection between the microscopic and the macroscopic stress^[11, 12].

Silicone rubber matrixes are essentially cross-linked polymer networks with SiO₂ nanoparticles. In the statistical theories of rubber elasticity, the elasticity of polymer networks originates from entropy change of the stretched cross-linked polymer networks^[13]. The main statistical models of rubber elasticity, which promote the microscopic understanding of rubber elasticity, include the "affine network model" (proposed by Flory), "phantom network model" (proposed by James and Guth), "tube model" (proposed by Edwards), and so on^[14]. However, the models mentioned above were mostly based on intact network,

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ignoring the influence of network defects, such as the dangling chains^[15]. Tsenoglou^[16] proposed that the dangling chains in the cross-linking polymer network could affect their stress-strain properties and stress relaxation. Through modification of classical affine network model, they obtained the constitutive model based on microscopic molecular network parameters. But unfortunately, they did not use their model to fit practical experimental data, and the decision of parameters in their model was not mentioned. The introduction of nanoparticles, such as carbon black and SiO₂, which help to improve the performance of silicone rubber greatly, causes severe difficulty in establishment of constitutive model of composite materials based on statistical theory^[17]. Considering the hydrodynamic reinforcement effect of nanoparticles, Manfred Klüppel^[18] introduced a hydrodynamic amplification factor into the constitutive model based on “tube model”, which could solve this problem well. However, all parameters in their model, including the molecular parameters, were decided by data fitting, which may introduce uncertainty. The influences of network defects, such as dangling chains, on the performance of rubber were not considered as well. For polymer foams, as far as we know, there are no constitutive models based on statistical theory being established yet because of the complex strain process of the foam materials.

Here, a constitutive model based on statistical theory was established by introducing a strain amplification factor and a strain hysteresis item into a statistical model of rubber elasticity considering the effect of dangling chains. Inspired by the works of J. E. Mark and Kenji Urayama *et al.*, this model was used to fit the stress-strain data of a mono-modal silicone rubber, as well as a bi-modal one. Some parameters related to the polymer networks, such as average molecular weight (M_c) of chain segments with both ends attached to the network (network strands) and volume fraction (ϕ) of network strands, were calculated using the molecular weight (M_c), vinyl content (w_{vi}) of the polysiloxane and percent conversion (q) of vinyl groups. The parameters related to the nanoparticles, such as primary strain amplification factor (X_0), infinite strain limits of the amplification factor (X_∞) and decay exponent (z), were obtained by fitting the tensile stress-strain data. All of the parameter values obtained above, as well as a strain hysteresis item associating with the foam porosity, were used in the following fitting of the compressive stress-strain data. The resulting fitting curves were in good agreement with the experimental data of both mono- and bi-modal silicone rubber composites. The constitutive model based on microscopic physical mechanism could become the bridge connecting the macroscopic stress-strain behaviour to the microscopic molecular structure parameters. And our work could promisingly provide a basis for the performance improvement and optimization of silicone rubber.

THEORY AND MODEL

Constitutive Model of Polymer Matrix

Christos Tsenoglou^[16] considered that there were two kinds of segments in rubber elastomers: the network strands with

both ends cross-linked and the dangling chains with only one end cross-linked (shown in Fig. 1).

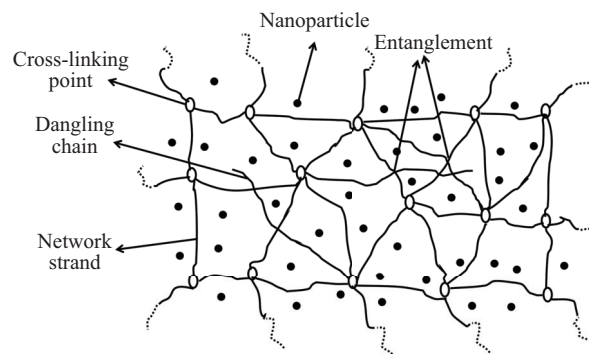


Fig. 1 Schematic representation of polymer cross-linking network

The authors considered that both kinds of segments would be stretched to the same strain when the elastomers were stretched to a certain strain. Based on the classical theory of rubber elasticity and the assumption that each network contributed independently to the stress, the constitutive model was proposed as follows (Eq. 1):

$$\tau_{ij} = (\tau_{ij})_S + (\tau_{ij})_D = 3k_B T (v_S N_S + v_D N_D) \left\langle \frac{r_i r_j}{N_e b^2} \right\rangle \quad (1)$$

where v_S and v_D represent the contributing population densities of strands and dangling ends, N_S and N_D the number steps per strand and dangling segment, i and j the particular components of the stress tensor ($i, j = 1, 2, 3$), r the end to end distance after stretched step of initial size r_0 , N_e the number of mers between entanglements and b the (bond) length of a monomer. But after the strain imposition, the two kinds of segments represent different behaviours. For the dangling chains, the free ends would retract to previous position and then the chains would relax through path fluctuations continuously. But for the network strands, they would keep the stretched state because both ends were fixed. But some of the entanglements would disappear because of the retraction of adjacent dangling chains. Thus, the authors obtain the following constitutive model of rubber elastomers under uniaxial stretching (Eq. 2):

$$\frac{\tau_{11} - \tau_{22}}{\lambda} = 3RT\rho \left\{ \frac{\phi}{M_c} + \frac{1}{M_e} \left[\phi + (1 - \phi) \frac{F(t)}{\alpha(\vec{E})} \right]^2 \right\} \alpha(\vec{E}) \{ H_{11}(\vec{E}) - H_{22}(\vec{E}) \} \quad (2)$$

where M_c is the molecular weight of elastically active strands, ϕ the volume fraction of elastically active strands, M_e the molecular weight between entanglements, α , H_{11} and H_{22} the functions of deformation gradient tensor $\vec{E}$, $F(t)$ the fraction of the original path still occupied by the chain (a decreasing function of time, $1 \geq F(t) \geq 0$). When under uniaxial stretched, the expressions are as follows:

$$\alpha(\vec{E}) = \frac{\lambda}{2} \left(1 + \frac{\ln(\lambda^{3/2} + (\lambda^3 - 1)^{1/2})}{\lambda^{3/2}(\lambda^3 - 1)^{1/2}} \right), 1 < \lambda < 6 \quad (3)$$

$$H_{11} - H_{22} = \frac{\lambda(2\lambda^3 + 1)}{4(\lambda^3 - 1)} \cdot \left(1 - \frac{4\lambda^3 - 1}{2\lambda^3 + 1} \cdot \frac{\ln(\lambda^{3/2} + (\lambda^3 - 1)^{1/2})}{\lambda^{3/2}(\lambda^3 - 1)^{1/2}} \right) \quad (4)$$

where λ is the extension ratio. When under uniaxial compression, the expressions are as follows^[19]:

$$\alpha(\vec{E}) = \frac{\lambda}{2} \left(1 + \frac{\sin^{-1}(1 - \lambda^3)^{1/2}}{\lambda^{3/2}(1 - \lambda^3)^{1/2}} \right) \quad (5)$$

$$H_{11} - H_{22} = \frac{\lambda(1 + 2\lambda^3)}{4(1 - \lambda^3)} \cdot \left(1 + \frac{1 - 4\lambda^3}{1 + 2\lambda^3} \cdot \frac{\sin^{-1}(1 - \lambda^3)^{1/2}}{\lambda^{3/2}(1 - \lambda^3)^{1/2}} \right) \quad (6)$$

where λ is the compression ratio. In this study, we consider the moment only after stretching or compression, so $F(t) = 1$.

Strain Amplification Factor X

For filler reinforced elastomer systems, Manfred Klüppel^[18] considered the hydrodynamic reinforcement effect of nanoparticles by introducing a strain amplification factor X , shown as follows:

$$\lambda = 1 + X\varepsilon \quad (7)$$

where λ and ε are strain rate and external deformation, respectively. Strain amplification factor X relates with the cluster size, nanoparticle size, interactions between nanoparticle and polymers. Eq. (7) could be approximately expressed as follows:

$$\lambda = 1 + X\varepsilon \approx 1 + (X_\infty + (X_0 - X_\infty)\exp(-z\varepsilon))\varepsilon \quad (8)$$

where X_0 and X_∞ are the primary and infinite strain limits of the amplification factors, respectively, and z gives the exponential decay factor. When Eq. (8) is inserted into Eqs. (3) and (4) or Eqs. (5) and (6), and then inserted into Eq. (2), the constitutive models of nanoparticles reinforced rubber elastomer under uniaxial extension or compression could be obtained.

Strain Hysteresis Item H

Now we discuss the deformation process of foam materials. For open cell foams under compression, the reacting force of foams mostly comes from the strain of foam matrix. As we could imagine, the matrix's strain would be less than the foam's because it is easier for the cells to deform than the matrix in most cases. Then the ideal deformation process of a cross section parallel to the compressive direction would be considered. As shown in Fig. 2, L , L_{c0} and L_{m0} give the primary total thickness of foam, cells and matrix, respectively. L , L_{c0} and L_{m0} will decrease gradually when the foam is compressed. ΔL , ΔL_c and ΔL_m represent the reduction of thickness of foam, cells, matrix, respectively. ε and ε_m give the strain of foam and matrix, respectively, and H is defined as the difference of them. H is expressed as Eq. (9).

$$H = \varepsilon - \varepsilon_m = \frac{\Delta L}{L_0} - \frac{\Delta L_m}{L_{m0}} = \frac{\Delta L_c + \Delta L_m}{L_{c0} + L_{m0}} - \frac{\Delta L_m}{L_{m0}} \quad (9)$$

Now we consider an ideal situation that the cells would be compressed firstly and then the base after the total compression

of cells. We divide the compression process of foams into two stages: before and after the total compression of cells. In the first stage ($0 \leq \Delta L_c \leq L_{c0}$, $\Delta L_m = 0$), H could be simply expressed as Eq. (10), increasing with the increase of ΔL (Fig. 2, left lower). But in the second stage ($\Delta L_c = L_{c0}$, $0 \leq \Delta L_m < L_{m0}$), H could be expressed as Eq. (11), decreasing with the increase of ΔL (Fig. 2, right lower). As a result, the difference of stain (H), increasing with the increase of total stain firstly and then decreasing, has a maximum. We could think of that the maximum and change rate of H may be related with the porosity, configuration and distribution of cells, and so on.

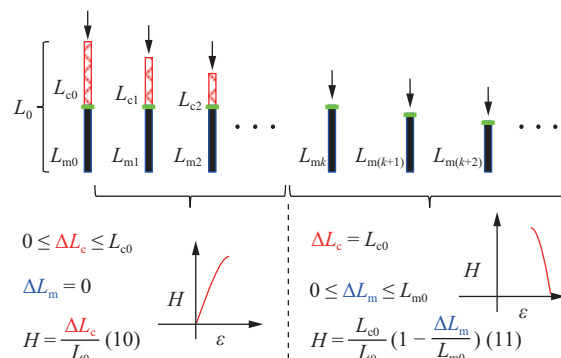


Fig. 2 Schematic representation of realistic compressive deformation process of open cell foams

Then, we propose an expression of H , shown as Eq. (12).

$$H = H_m - z_c \cdot \left(\frac{f - \varepsilon}{1 - \varepsilon} \right)^2 \quad (12)$$

where H_m gives the maximum of H , ε is the strain of foam, z_c is a factor related with configuration and distribution of cells, f is an item related with the original porosity. With this expression, H would increase firstly and then decrease, and the rate of change of H correlates with the residual porosity. Then for the foams under compression, Eq. (8) could be modified as follows:

$$\lambda = 1 + X\varepsilon_m \approx 1 + (X_\infty + (X_0 - X_\infty)\exp(-z\varepsilon_m))\varepsilon_m \quad (13)$$

where

$$\varepsilon_m = \varepsilon - H = \varepsilon - \left[H_m - z_c \cdot \left(\frac{f - \varepsilon}{1 - \varepsilon} \right)^2 \right] \quad (14)$$

Estimation of ϕ and M_c

For random cross-linking system, John G. Curro^[20] considered the generation probability ($P(n)$) for a dangling chain owing n cross-linkable points as Eq. (15):

$$P(n) = q(1 - q)^{n-1} \quad (15)$$

where q is the cross-linking probability of every cross-linkable point. Similarly, we consider that the cross-linking process of methyl vinyl silicone rubber was initiated by benzoyl peroxide (BPO) as random cross-linking process.

Divinyl-terminated methyl vinyl polysiloxane could be abstracted into a linear model owing N cross-linkable points, with M_i as the average molecular weight of segments between cross-linkable points, as shown in Fig. 3. N and M_i

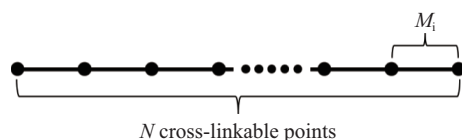


Fig. 3 Abstract model of divinyl-terminated methyl vinyl polysiloxane

could be calculated by Eqs. (16) and (17), respectively.

$$N = \frac{M w_{Vi}}{M_{Vi}} \quad (16)$$

$$M_i = \frac{M}{N-1} \quad (17)$$

where M , N , w_{Vi} , M_{Vi} represent the number average molecular weight of poly(methyl vinyl silicone), number of vinyl groups in every molecular, weight ratio of vinyl groups, molecular weight of vinyl group, respectively. The cross-linking process of poly(methyl vinyl silicone) initiated by BPO is in fact a process of free radical polymerization initiated by BPO, which could be considered as random cross-linking process of these N continuous cross-linkable points. The cross-linking probability (q) of these points could be similarly considered as the conversion rate of vinyl group. Of course, this approximation contains two hypotheses. One is the even distribution of vinyl groups in the methyl vinyl molecular and equal cross-linking probability (equal to the conversion of vinyl group) of every vinyl groups (ignoring the steric effect). The other is that only the vinyl groups could be cross-linked. In fact, some methyl points could be cross-linked in the process as well.

The probability ($P(n)$) for generating dangling chains owing n of continuous cross-linkable points is expressed as follows (Eq. 18):

$$P_d(n) = 2q(1-q)^{n-1} \quad (2 \leq n \leq N) \quad (18)$$

where q gives the cross-linking probability of vinyl groups. The factor 2 in Eq. (18) is because that dangling chains could generate from both ends of the molecular. Then the total molecular weight (M_d^{total}) of dangling chains could be calculated by the following expression (Eq. 19):

$$\begin{aligned} M_d^{\text{total}} &= M_i \cdot N_c \cdot \sum_{n=2}^N (n-1) P_d(n) \\ &= M_i \cdot N_c \cdot \sum_{n=2}^N (n-1) \cdot 2q(1-q)^{n-1} \end{aligned} \quad (19)$$

where N_c represents the total times of cross-linking process of vinyl groups.

The probability $P(n)$ for generating strand network chains owing n continuous cross-linkable points is expressed as follows (Eq. 20):

$$P_s(n) = (N-n+1)q^2(1-q)^{n-2} \quad (2 \leq n \leq N) \quad (20)$$

The factor $(N-n+1)$ indicates that there are $(N-n+1)$ cases for selecting n continuous points from N continuous points. The total molecular weight (M_c^{total}) of network strands can be calculated from the following expression (Eq. 21):

$$M_c^{\text{total}} = M_i \cdot N_c \cdot \sum_{n=2}^N (n-1) P_s(n) \quad (21)$$

The weight ratio (ϕ) of network strands can be calculated by Eq. (22):

$$\phi = \frac{M_c^{\text{total}}}{M_c^{\text{total}} + M_d^{\text{total}}} \quad (22)$$

The average molecular weight (M_c) of network strands can be calculated after normalization of the generated probabilities, as shown in Eq. (23).

$$M_c = M_i \cdot \sum_{n=2}^N (n-1) P_s(n) / \sum_{m=2}^N P_s(m) \quad (23)$$

EXPERIMENTAL

Materials and Reagents

All the commercially available reagents were used as received unless otherwise noted. Methyl vinyl polysiloxane (0.2 wt% of vinyl content) was purchased from Zhejiang Xin'an chemical industry co., Ltd., China. Methyl vinyl polysiloxanes (0.8 wt% and 1.3 wt% of vinyl content), fumed silica nanoparticles, urea (blowing agent) were provided by Institute of Chemical Materials, China Academy of Engineering Physics. The number-average molecular weights of the above three polysiloxanes were all about 3.2×10^5 g/mol. Benzoyl peroxide (BPO, vulcanized agent) and hydroxyl silicone oil (constitution controller) were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

Analyses

Tensile and compressive tests were both performed on a Universal Material Testing Machine. Tensile tests were performed at the rate of 500 mm/min according to ISO 37:2005. Compressive tests were performed at the rate of 0.5 mm/min.

Preparation of Silicone Rubber Foams

Two silicone rubber materials, namely, a mono-modal one (0.8 wt% of vinyl content) and a bi-modal one (0.8 wt% of average vinyl content)^[21] were prepared in this study. Because of very easy broken after little strain of silicone rubber matrix under compression and foams under stretched, we intend to obtain the parameter values from the tensile experiment data fitting of silicone rubber matrix, and then use most of them to fit the compressive experiment data of silicone rubber foams.

Methyl vinyl polysiloxane (100 phr), fumed silica (40 phr), and hydroxy silicone oil (constitution controller) were first put into an internal mixer (HAAKE, PolyLab OS-RheoDrive 7) to obtain a rubber compound. Then, the rubber compound, urea (blowing agent), BPO (vulcanized agent) were thoroughly mixed in the mixer. Next, the mixture was cast into moulds and cured under pressure by a plate vulcanizing press (Laboratory platen press, P300E) to form silicone rubber. Then the silicone rubber foam was obtained after the rubber washed with solvent.

RESULTS AND DISCUSSION

Silicone Rubber Foam Matrixes under Uniaxial Tension

Mono-modal silicone rubber nano-composites

Mono-modal silicone rubber nano-composites were made of mono-component polysiloxane with 0.8 wt% of vinyl content. The stress-strain data of mono-component silicone rubber are shown in Fig. 4. The parameter values of the unvulcanised silicone rubber molecular are shown in Table 1 with N and M_i calculated from Eqs. (16) and (17), respectively.

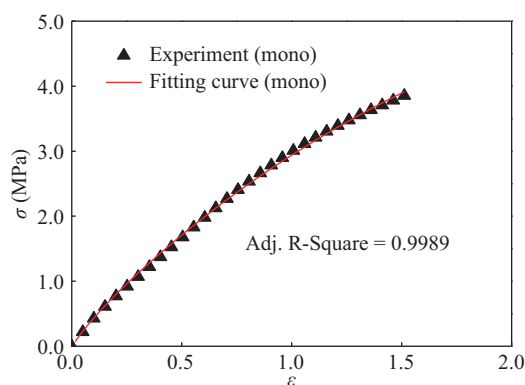


Fig. 4 Experimental stress-strain data and calculated and fitting curve of silicone rubber nano-composite of 0.8 wt% vinyl content under uniaxial tension

Table 1 Molecular parameters of polysiloxane with 0.8 wt% of vinyl content

M_n (g/mol)	w_{Vi} (%)	N	M_i (g/mol)
About 3.2×10^5	0.8	95	3410.98

In this study, we estimated the conversion of vinyl groups, namely, the cross-linking probability of vinyl groups, to be 0.9, a relatively reasonable value. Then the total molecular weight (M_d^{total} , M_c^{total}) of dangling chains and network strands could be calculated from Eqs. (19) and (21), respectively. The weight ratio (ϕ) and average molecular weight (M_c) could be calculated from Eqs. (22) and (23), respectively. The calculation results are listed in Table 2.

Table 2 Parameter values of cross-linking network of mono-modal silicone rubber with 0.8 wt% of vinyl content and hydrodynamic reinforcement of nanoparticle under uniaxial tension

M_d^{total} (g/mol)	M_c^{total} (g/mol)	ϕ	M_c (g/mol)
$757.99N_c$	$319873.7N_c$	0.9976	3785.44
ρ	X_0	X_∞	z
0.8286	2.61	1.18	0.31

Combining Eq. (8) with Eqs. (2)–(4), the stress-strain data of mono-component silicone rubber nano-composite could be fitted by the least square method. The fitting curve is shown in Fig. 4. The fitting results of X_0 , X_∞ , z are listed in Table 2 (the value of M_c (8100 g/mol) is obtained from reference^[22], $T = 293.15$ K).

As shown in Fig. 4, the equation, obtained by substituting Eq. (8) into Eqs. (3) and (4) and then into Eq. (2), could fit

the experimental tensile stress-strain data well with some estimated parameters (ϕ , M_c) and other parameters (X_0 , X_∞ , z) determined by fitting (Adj. R-Square = 0.9989).

Bi-modal silicone rubber foam matrix

Bi-modal silicone rubber foam matrix made of dual component polysiloxane with 0.8 wt% of average vinyl content (mixture of 0.2 wt% and 1.3 wt% ones) were designed to verify our viewpoint as well. The molecular parameters of the two kinds of polysiloxanes above are listed in Table 3. The weight ratios of the two components were about 45.5 wt% and 54.5 wt%, respectively.

Table 3 Molecular parameters of polysiloxane with 0.2 wt% and 1.3 wt% of vinyl content

M_n (g/mol)	w_{Vi} (%)	N	M_i (g/mol)
About 3.2×10^5	0.2	24	14094.62
About 3.2×10^5	1.3	154	2090.49

We also estimated the cross-linking probability of vinyl groups to be 0.9. Then the total molecular weight (M_d^{total} , M_c^{total}) of dangling chains and network strands could be calculated from Eqs. (19) and (21), respectively. The weight ratio (ϕ) and average molecular weight (M_c) could be calculated from Eqs. (22) and (23), respectively. The calculation results are listed in Table 4.

Table 4 Parameters of cross-linking network of bi-modal silicone rubber with 0.8 wt% of average vinyl content and hydrodynamic reinforcement of nanoparticle under uniaxial tension

w_{Vi} (%)	M_d^{total} (g/mol)	M_c^{total} (g/mol)	ϕ	ρ	M_c (g/mol)
0.2	$3132.14N_c$	$321044.05N_c$	0.9903	0.3441	15584.66
1.3	$464.55N_c$	$317290.10N_c$	0.9985	0.46	2321.07
X_0		X_∞		z	
2.22		1.18		0.30	

The stresses generated by the long and the short chains were added together based on independent network theory. Then the stress-strain data were fitted by least square method and the result is shown in Fig. 5. The fitting results of X_0 , X_∞ , z are listed in Table 4 (the same values assigned to M_c (8100 g/mol) and T (293.15 K)).

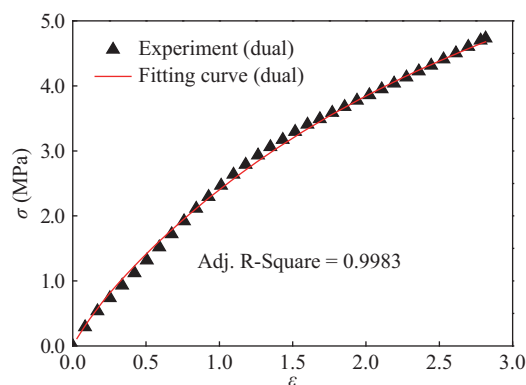


Fig. 5 Experimental stress-strain data and calculated and fitting curve of silicone rubber nano-composite of 0.8 wt% average vinyl content under uniaxial tension

Similarly, the equation, obtained by substituting Eq. (8) into Eqs. (3) and (4) and then into Eq. (2), also could fit the experimental stress-strain data well with some estimated parameters (ϕ , M_c) and other parameters (X_0 , X_∞ , z) determined by fitting, as shown in Fig. 5 (Adj. R-Square = 0.9983).

Note that the same values of X_∞ and z could fit the stress-strain data of mono- and bi-modal nanoparticle reinforced silicone rubber matrix well with the different values of X_0 . This could be reasonably explained from the microscopic mechanism as follows. The SiO₂ nanoparticles should have the same z and X_∞ because they came from the same batch. And because of the shorter network strands (coming from the polysiloxane with 1.3 wt% of vinyl content), the nanoparticle clusters were smaller in the bi-modal silicone rubber nano-composite than in the mono-modal one, causing the smaller value of X_0 . This fact could also support that our constitutive model based on microscopic mechanism has certain rationality.

Silicone Rubber Foams under Compression

Mono-modal silicone rubber foam

Mono-modal silicone rubber foam was made of the same mono-component polysiloxane with 0.8 wt% of vinyl content. The stress-strain data under uniaxial compression are shown in Fig. 6. The same parameter values of the unvulcanised silicone rubber molecular were used (shown in Table 1). The same parameter values of cross-linking network were also used (shown in Table 2). The same values were assigned to M_e (8100 g/mol) and T (293.15K).

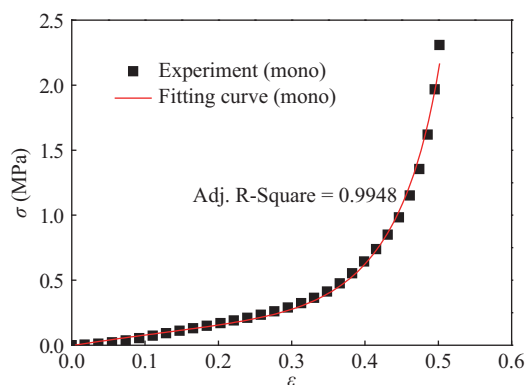


Fig. 6 Experimental stress-strain data and calculated and fitting curve of silicone rubber nano-composite of 0.8 wt% vinyl content under uniaxial compression

In order to fit the stress-strain data under uniaxial compression, a strain hysteresis item (H) with the expression shown in Eq. (12) was introduced. The fitting results are shown in Table 5 and Fig. 6. As shown in Fig. 6, the equation obtained by substituting Eq. (13) into Eqs. (5) and (6) and then into Eq. (2) could fit the experimental stress-strain data well (Adj. R-Square = 0.9948).

Bi-modal silicone rubber foam

Bi-modal silicone rubber foam made of the same dual component polysiloxanes with 0.8 wt% of average vinyl content (mixture of 0.2 wt% and 1.3 wt% ones) was prepared

Table 5 Parameter values of hydrodynamic reinforcement effect of nanoparticle and strain hysteresis item of mono-component silicone rubber foam under uniaxial compression

X_0	X_∞	z
2.61	1.18	0.1
H_m	f	ε
0.3388	1.6599	0.4514

to verify our viewpoint.

The same parameter values of the unvulcanised silicone rubber molecular and the cross-linking network were also used (shown in Tables 3 and 4, respectively). The same values were assigned to M_e (8100 g/mol) and T (293.15 K).

The fitting results are shown in Table 6 and Fig. 7. As shown in Fig. 7, the equation obtained by substituting Eq. (13) into Eqs. (5) and (6) and then into Eq. (2) also could fit the experimental stress-strain data well (Adj. R-Square = 0.9985) when a strain hysteresis item (H) was introduced.

Table 6 Parameter values of hydrodynamic reinforcement effect of nanoparticle and strain hysteresis item of bi-modal silicone rubber foam under uniaxial compression

X_0	X_∞	z
2.22	1.18	0.1
H_m	f	ε
0.3329	1.5861	0.4560

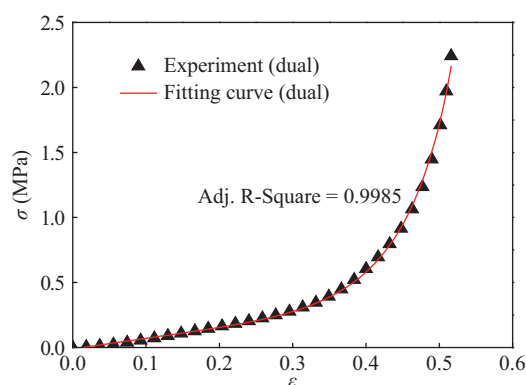


Fig. 7 Experimental stress-strain data and calculated and fitting curve of silicone rubber nano-composite of 0.8 wt% average vinyl content under uniaxial compression

Strain Hysteresis Item (H) of Silicone Rubber Foams under Compression

Now we focus on the strain hysteresis items (H) of the two silicone rubber foams under compression. The strain hysteresis items of the two foams under different strains are shown in Fig. 8. As we could see, both of the strain hysteresis items increase firstly and then fall, matching the above theoretical analysis of the item well.

Note that the strain hysteresis items of the two different foams almost completely coincided under all strains. As shown in the above theoretical analysis in the “Strain hysteresis item H ” subpart, the change rate of H correlates with the residual porosity of the foam and configuration and distribution of the cells and the maximum of H correlates with the porosity of the foam. The mono- and bi-modal foams used in our experiments were prepared with the same

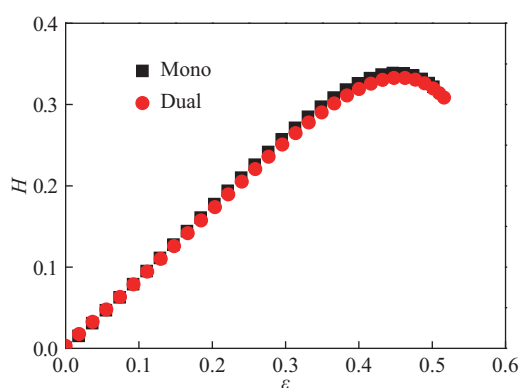


Fig. 8 Strain hysteresis item H of mono-modal (0.8 wt% vinyl content) and bi-modal (0.8 wt% average vinyl content) silicone rubber foams under uniaxial compression

process and the porosities of the foams were almost equal (0.526 and 0.534, respectively). And it is reasonable to believe that the cells in the two foams had similar configuration and distribution. So the items of the two foams should have similar value under all strains. In turn, this fact that the strain hysteresis items almost completely coincided proved the certain rationality of our theory.

CONCLUSIONS

In summary, a constitutive model based on microscopic physical mechanism was established by introducing a strain amplification factor and a strain hysteresis item into the statistical model of rubber elasticity considering the effect of dangling chains. Some parameters related to the polymer network, such as average molecular weight (M_c) and volume fraction (ϕ) of network strands, were calculated using the molecular weight (M_c), vinyl content (w_{vi}) of the polysiloxane and percent conversion (q) of vinyl groups. The primary strain amplification factor (X_0), infinite strain limits of the amplification factor (X_∞) and decay exponent (α), which are related to the nanoparticles, were obtained by fitting the tensile stress-strain data. All of the obtained parameter values above, as well as a strain hysteresis item associating with the foam porosity, were used in the following fitting of the compressive stress-strain data. The resulting fitting curves were in good agreement with the experimental data of both mono- and bi-modal foams. This constitutive model may become the bridge connecting the macroscopic stress-strain behaviour to the microscopic molecular structure parameters, promisingly provide a basis for the performance improvement and optimization of silicone rubber.

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