

On Micromechanical Behavior of Glassy Polymer Blended with Different Sized Rubber Particles

W. Lu^{1, 2}, Y. Tomita²

Summary

The effect of the size of rubber particles on the micromechanical behavior in glassy polymer matrix is investigated employing the homogenization method, together with a unit cell model containing irregularly distributed heterogeneous particles. It is clarified that the localized plastic zone only occurs between cavitated large particles and the noncavitating small particles merely change their shapes and conform to the propagation of the localized plastic zone without promoting plastic deformation in the matrix. The maximum mean stress in the matrix and the average normal stress on the noncavitating small particle mainly depend on the macroscopic triaxiality of the loading condition.

Introduction

In rubber-blended polymer, the onset of cavitation in multiple rubber particles relaxes the high triaxiality stress state and suppresses the formation of macroscopic crack in the polymer. As a result, large plastic deformation is substantially promoted compared with single-phase polymer [1]. It is also well known that the onset of cavitation is dependent on the size of particles and is inhibited in particles smaller than 200nm [2].

To clarify the size dependence of the cavitation behavior, the main objective of studies has been to determine the critical stress for the initiation of a void in rubber material. Because the cavitation process requires surface energy, van der Waals intermolecular force, in other words, surface tension, is taken into account for the bulk [3] and for rubber particle [4]. Moreover, as void nucleation develops via chain scission, the contribution of the tear energy of the molecular chain to the critical stress for the initiation of a void in the rubber particle is also considered [4]. On the other hand, to investigate the post-cavitation behavior in rubber-blended polymer, an axisymmetric unit cell model with a small void pre-existing inside the particle has been used [5]. Furthermore, employing a plane-strain unit cell model, the effects of stiffness, volume fraction and heterogeneity of the particle on the post-cavitation behavior under complex loading are also investigated [6]. The results indicate that regardless of the magnitude of the stiffness of the particle, the relationships of the average normal stress normalized by particle stiffness and the volumetric strain of particle are cast into a characteristic single line. However, since the typical value of initial stiffness of rubber material is 1MPa, the effect of the deformation constraint from a cavitated rubber particle on the plastic deformation in the matrix is negligible, and therefore plastic deformation in a porous material has been investigated [7]. Recently, a modified pre-existing small void model, in which the surface tension is assumed to act on the surface of the void [8], has been used to investigate the size dependence of the cavitation behavior.

¹Postdoctoral Fellow of Japan Society for the Promotion of Science

²Graduate School of Science and Technology, Kobe University, Kobe, 657-8501, JAPAN

It was clarified that the decrease in the size of particles causes the increase in the average normal stress on the interface and the suppression of cavitation.

To address the effect of the size of rubber particles on the micromechanical behavior of the polymer blend, in this study, we employ the homogenization method together with a unit cell model containing irregularly distributed heterogeneous particles. Assuming that cavitation occurs at the initial deformation stage in the case of large particles, we replace these particles with voids of the same size. Furthermore, small particles are assumed to deform without cavitation throughout the whole deformation process. A parametric study is performed to clarify the effect of particle size on the plastic deformation in the matrix under different loading conditions. Subsequently, the development of the maximum mean stress in the matrix and the average normal stress on noncavitating small particles are investigated.

Constitutive Equation

The complete constitutive equation for the rubber material employed in this investigation is derived based on the affine molecular chain network theory [9]. According to this theory, the deviatoric component of the principal stress b_i and principal stretch λ_i relation becomes [9]

$$b'_i = \frac{1}{3} C^R \sqrt{N} \frac{\lambda_i^2 - \lambda_c^2}{\lambda_c} L^{-1} \left(\frac{\lambda_c}{\sqrt{N}} \right), \quad (1)$$

$$L(x) = \coth x - \frac{1}{x}, \quad \lambda_c^2 = \frac{1}{3} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2),$$

where N is the average number of segments in a single molecular chain, $C^R = nk_B T$ is the shear modulus, n is the number of molecular chains per unit volume, k_B is Boltzmann's constant, T is the absolute temperature and L is the Langevin function.

The rate-type expression of the constitutive equation, which relates the rate of Kirchhoff stress \dot{S}_{ij} to strain rate $\dot{\epsilon}_{ij}$, becomes

$$\dot{S}_{ij} = (R_{ijkl} - F_{ijkl}) \dot{\epsilon}_{ij} - \dot{p} \delta_{ij}, \quad (2)$$

$$R_{ijkl} = \frac{1}{3} C^R \sqrt{N} \left[\left(\frac{\xi}{\sqrt{N}} - \frac{\beta_c}{\lambda_c} \right) \frac{A_{ij} A_{kl}}{A_{mm}} + \frac{\beta_c}{\lambda_c} (\delta_{ik} A_{jl} + A_{ik} \delta_{jl}) \right],$$

$$F_{ijkl} = \frac{1}{2} (\sigma_{lj} \delta_{ki} + \sigma_{kj} \delta_{li} + \sigma_{li} \delta_{kj} + \sigma_{ki} \delta_{lj}),$$

$$\xi_c = \frac{d}{dx} L^{-1}(x) \Big|_{x=\frac{\lambda_c}{\sqrt{N}}} = \frac{\beta_c^2}{1 - \beta_c^2 \text{csch}^2 \beta_c}, \quad \beta_c = \lambda_c / \sqrt{N}, \quad \dot{p} = -K \dot{\epsilon}_{mm},$$

where σ_{ij} , δ_{ij} and A_{ij} are the Cauchy stress tensor, Kronecker's delta and the left stretch tensor, respectively. To introduce the volume constant constraint to rubber material, we use the penalty method with the penalty parameter $K = 5000$.

The constitutive equation used to model the large strain plastic behavior of the polymer matrix is derived based on the nonaffine molecular chain network theory given in Ref. [10], which is a modified version of the eight-chain model [9] and which accounts for the change

of the number of entangled points, in other words, the average number of segments N in a single molecular chain. Here, we provide a brief explanation of the constitutive equation. The total strain rate is assumed to be decomposed into the elastic and plastic strain rates. The elastic strain rate is expressed by Hooke's law, and the plastic strain rate is modeled using the nonaffine eight-chain model [10]. The final constitutive equation that relates the rate of Kirchhoff stress \dot{S}_{ij} and strain rate $\dot{\epsilon}_{ij}$ becomes

$$\begin{aligned} \dot{S}_{ij} &= (D_{ijkl}^e - F_{ijkl}) \dot{\epsilon}_{ij} - P'_{ij}, \\ P'_{ij} &= D_{ijkl}^e \frac{\tilde{\sigma}'_{kl}}{\sqrt{2\tilde{\tau}}} \dot{\gamma}^p, \quad \tilde{\tau} = \left(\frac{1}{2} \tilde{\sigma}'_{ij} \tilde{\sigma}'_{ij} \right)^{1/2}, \quad \tilde{\sigma}'_{ij} = \sigma'_{ij} - B'_{ij}, \end{aligned} \quad (3)$$

where D_{ijkl}^e is the elastic stiffness tensor and σ_{ij} is the Cauchy stress. The shear strain rate $\dot{\gamma}^p$ in Eq. (3) is related to the applied shear stress $\tilde{\tau}$ as [11]

$$\dot{\gamma}^p = \dot{\gamma}_0 \exp \left\{ -\frac{A\tilde{s}}{T} \left[1 - \left(\frac{\tilde{\tau}}{\tilde{s}} \right)^{5/6} \right] \right\}, \quad (4)$$

where $\dot{\gamma}_0$ and A are constants, $\tilde{s} = s + \alpha p$ indicates shear strength [12], s is the shear strength that changes with plastic strain from the athermal shear strength $s_0 = 0.077\mu / (1 - \nu)$ to a stable value s_{ss} , p is the pressure, α is a pressure-dependent coefficient, μ is the elastic shear modulus and ν is Poisson's ratio. Since s depends on the strain rate, the evolution equation of s can be expressed as $\dot{s} = h[1 - (s/s_{ss})] \dot{\gamma}^p$ where h is the rate of resistance with respect to plastic strain. Furthermore, B'_{ij} in Eq. (3) is the deviatoric component of back stress, and the deviatoric component of principal back stress is given by an expression of the same type as Eq. (1) but as a function of the principal plastic stretches. However, we assume that elastic strains remain small, so that the back stresses can be evaluated based on the total stretches. Note that only the deviatoric components of back stress are needed in Eq. (3) so that the hydrostatic part is irrelevant. Full details may be found in Ref. [10].

Computational Model

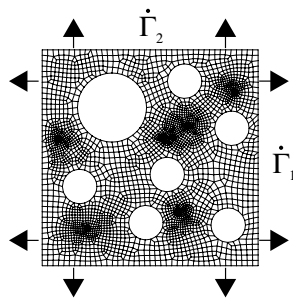


Figure 1: Computational model

Figure 1 illustrates the plane-strain unit cell model containing irregularly distributed heterogeneous particles. With this model, we employ the homogenization method and the finite element method to establish a computational tool. The particles are assumed to be circular cylinders of three sizes with the size ratio 1:5:10 among particles. Here, the size of the smallest particles (dark circle) is assumed to be 200nm, and these particles deform without cavitation throughout the whole deformation process while the others, sized as 1 μ m and 2 μ m, cavitate at the initial deformation stage and are replaced by voids of the same size.

With regard to the boundary condition of the unit cell, the macroscopic constant strain rate, $\dot{\Gamma}_2 = 1.0 \times 10^{-5}/s$, is applied on the unit cell and the macroscopic strain rate $\dot{\Gamma}_1$

is prescribed as different values to realize different macroscopic triaxiality of the loading condition. The material parameters for the rubber material employed are $N_0 = 16$, $n_0 = 1.0 \times 10^{26}$ and $T = 296K$. The volume fraction of particles is 20%, and the coherent boundary condition is assumed to apply to the particle-matrix interface. On the other hand, we use the same material parameters for the polycarbonate (PC) matrix as those used in Ref. [10].

Results and Discussions

Figure 2 indicates the macroscopic average stress and maximum mean stress in the matrix versus macroscopic equivalent strain relations, where macroscopic equivalent strain is defined as $\Gamma_e = \sqrt{(2/3)\dot{\Gamma}_i\dot{\Gamma}_i}$ and s_0 is the initial shear strength of matrix. Figure 3 indicates the distribution of the equivalent plastic strain rate and the high-mean-stress region (dotted line) in the matrix under the macroscopic strain rate ratio $\dot{\Gamma}_1/\dot{\Gamma}_2 = 0$, where $\dot{\epsilon}^p = \sqrt{(2/3)\dot{\epsilon}_{ij}^p\dot{\epsilon}_{ij}^p}$. At the early deformation stage ($\Gamma_e = 0.02$), the localized plastic zone only occurs between large particles, and the macroscopic stress decreases after the formation of a strong shear band at the upper part of the unit cell. In subsequent deformation stages, the shear band propagates along the surface of large particles and covers the area of noncavitating small particles and new shear bands onset between large particles at the lower part of the unit cell. Throughout the whole deformation process, the small particles merely change their shape and conform to the propagation of the localized plastic zone without promoting or suppressing the plastic deformation in the matrix. We also confirmed similar characteristics for the other macroscopic loading conditions, although different types of shear bands were observed. These results indicate that noncavitating small particles have negligible effect on the plastic deformation behavior in the matrix.

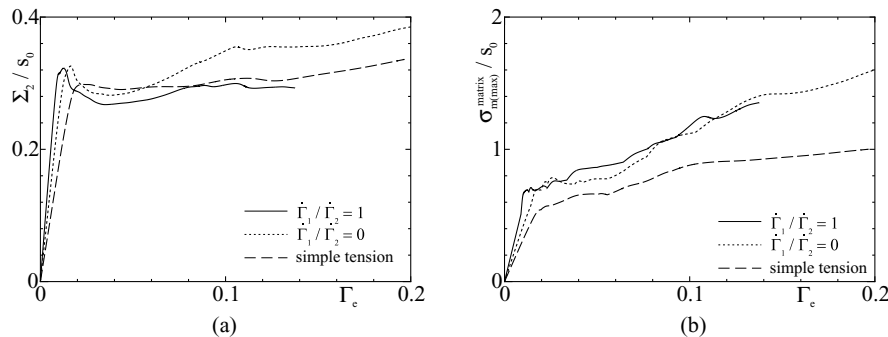


Figure 2: (a) Macroscopic average stress and (b) Maximum mean stress in matrix vs macroscopic equivalent strain

With regard to the maximum mean stress in the matrix, at the early deformation stage, the high-mean-stress region in the matrix is located near the inflection point of the inclination of the shear band or next to the equator of noncavitating small particles and the value of maximum mean stress increases when the macroscopic strain rate ratio increases. Similar results were reported for the case of cavitating particles in Ref. [6]. Therefore, we suggest

that the macroscopic triaxiality of the loading condition is the most important parameter in the evaluation of the maximum mean stress at an early deformation stage. At later deformation stages, as the stretch of the molecular chain along the surface of large particles increases, the maximum mean stress increases at the ligament between the large particles. These results confirmed that noncavitating small particles have insignificant effect on the maximum mean stress in the matrix.

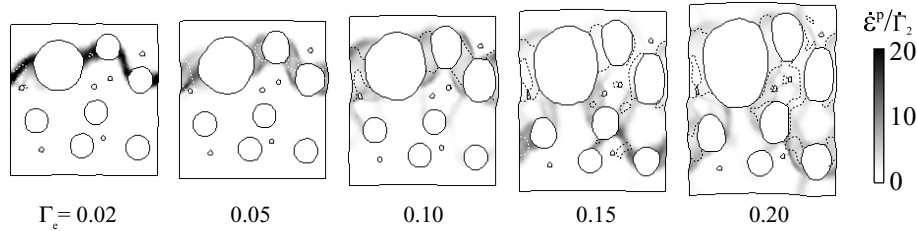


Figure 3: Equivalent plastic strain rate distribution and high mean stress regions in matrix (dotted line) for $\dot{\Gamma}_1/\dot{\Gamma}_2 = 0$

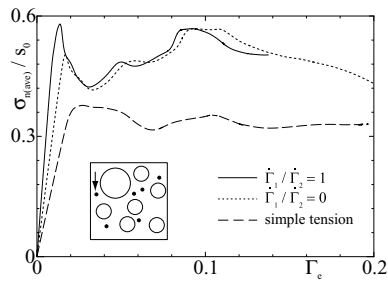


Figure 4: Average normal stress on the interface of noncavitating small particle (below the arrow) vs macroscopic equivalent strain

Figure 4 indicates the development of average normal stress on the interface of noncavitating small particles. Even though the shape of the particle changes from a circle to long and slender when the localized plastic zone passes through, the distribution of the normal stress along the interface remains almost uniform, which is attributable to the hydrostatic stress condition caused by the low stiffness of the rubber. Moreover, the average normal stress on the interface of noncavitating small particles at the early deformation stage increases when the macroscopic strain rate ratio increases, and then it decreases when localized deformation occurs in the matrix. At the subsequent deformation stages, the average normal stress reaches another peak when the localized plastic zone propagates to the particle, and it decreases when the plastic zone leaves the surface of that particle. These results indicate that the average value of the normal stress on noncavitating small particles also depends on the macroscopic triaxiality of the loading condition and that the onset of debonding may occur when the localized plastic zone propagates to the small particle.

Moreover, the results presented above suggest that large particles are beneficial for promoting plastic deformation in the matrix. To our knowledge, Bucknall had mentioned a similar result in Ref. [1], in his experimental study on the evaluation of the toughness of rubber-blended polymer. Therefore, we conclude that the model containing irregularly distributed heterogeneous particles can be used to clarify the toughening mechanism in rubber-blended polymer.

Conclusions

In this study, we employed the homogenization method together with a unit cell model containing irregularly distributed heterogeneous particles to investigate the effect of the size of rubber particles on the micromechanical behavior in glassy polymer matrix. The following is a summary of the results: (1) The localized plastic zone only occurs between large particles and the noncavitating small particles merely change their shapes and conform to the propagation of the localized plastic zone without promoting or suppressing the plastic deformation in the matrix. (2) The maximum mean stress in the matrix mainly depends on the macroscopic triaxiality of the loading condition, and the noncavitating small particles have insignificant effect on it. (3) The average normal stress on the noncavitating small particle also depends on the macroscopic triaxiality of the loading condition, and the onset of debonding may occur when the localized plastic zone propagates to the small particle.

Acknowledgment

Financial support from MEXT of Japan through Grant-in-Aid for Scientific Research and Grant-in-Aid for JSPS Fellows is gratefully acknowledged.

Reference

1. Bucknall, C.B. (1977): *Toughened Plastics*, Applied Science.
2. Fond, C. (2001): "Cavitation criterion for rubber materials: a review of void-growth models", *Journal of Polymer Science*, Vol.39, pp.2081-2096.
3. Gent, A.N., Tompkins, D.A. (1969): "Surface energy effects for small holes or particles in elastomers", *Journal of Polymer Science*, A2, Vol.7, pp.1483-1488.
4. Bucknall, C.B., Karpodinis, A., Zhang, X.C. (1994): "A model for particle cavitation in rubber-toughened plastics", *Journal of Material Science*, Vol.29, pp.3377-3383.
5. Steenbrink, A.C., Van der Giessen, E. (1999): "On cavitation, post-cavitation and yield in amorphous polymer-rubber blends", *Journal of the Mechanics and Physics of Solids*, Vol.47, pp.843-876.
6. Tomita, Y., Lu, W. (2002): "Computational characterization of micro- to macroscopic mechanical behavior and damage of polymer containing second-phase particles", *International Journal of Forming Processing*, Vol.5, pp.521-530.
7. Tomita, Y., Lu, W. (2002): "Characterization of micro- to macroscopic response of polymers containing voids under macroscopically uniform deformation", *International Journal of Solids and Structures*, Vol.39, pp.3409-3428.
8. Lu, W., Tomita, Y. (2003): "Numerical simulation of size dependent micromechanical behavior of rubber-blended polymer", USNCCM7 (Albuquerque, New Mexico, USA), Abstract.
9. Arruda, E.M., Boyce, M.C. (1993): "A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials", *Journal of the Mechanics and Physics of Solids*, Vol.41, pp.389-412.
10. Tomita, Y., Adachi, T., Tanaka, S. (1997): "Modelling and application of constitutive equation for glassy polymer based on nonaffine network theory", *European Journal of Mechanics, A/Solids*, Vol.16, pp.745-755.
11. Argon, A.S. (1973): "A theory for low-temperature plastic deformation of glassy polymers", *Philosophical Magazine*, Vol.28, pp.839-865.
12. Boyce, M.C., Parks, D.M., Argon, A.S. (1988): "Large inelastic deformation of glassy polymers, Part I: rate dependent constitutive mode", *Mechanics of Materials*, Vol.7, pp.15-33.