Modeling of the Effect of Rigid Fillers on the Stiffness of Rubbers

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ABSTRACT: The theories that predict the increase in the modulus of elastomers resulting from the presence of a rigid filler are typically derived from Einstein's viscosity law. For example, Guth and Gold used this approach to predict how the Young's modulus of an elastomer is related to the filler volume fraction. Hon et al. have shown using finite element microstructural models that stiffness predictions at small strains were also possible. Here, microstructural finite element models have been used to investigate the modulus of filled elastomer over a wider range of strains than has been possible previously. At larger strains, finite extensibility effects are significant and here an appropriate stored energy function proposed by Gent was adopted. In this work, the effect of spherical MT-type carbon-black filler behavior was considered. Different models were made and the results were then compared to experimental measurement of the stiffness taken from the literature. It is shown that the boundary conditions of the microstructural unit cell lie between the two extremes of free surfaces and planar surfaces. Also as the filler volume fraction increases then the number of filler particles required in the representative volume to predict the actual stiffness behavior also increases. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2572–2577, 2008

Key words: elastomers; fillers; modeling; modulus; rubber

INTRODUCTION

Elastomers deform to large strains under load and recover to their original shape upon unloading. Reinforcing rigid fillers such as carbon black are added to elastomers to increase the mechanical properties such as the modulus, strength, and wear resistance. The addition of these rigid fillers therefore increases the range of properties available for using elastomers in industrial applications.

A theory for the stiffening of elastomers by carbon-black fillers is based on Einstein's theory[1,2] for the increase in viscosity of a suspension due to the presence of spherical colloidal particles. The Einstein equation is given as

$$\eta = \eta_0(1 + 2.5\phi) \tag{1}$$

where η is the viscosity of suspension, η_0 is the viscosity of the incompressible fluid, and ϕ is the volume fraction of the spherical particles.

Guth and Gold[3] and Smallwood[4] adapted the viscosity law given in Eq. (1) to predict the modulus of an elastomer filled with rigid spherical particles and they included an additional term to account for the interaction of rigid fillers at larger filler volume fractions. They proposed that the increase in the modulus due to the incorporation of spherical rigid fillers was given by

$$E = E_0(1 + 2.5\phi + 14.1\phi^2), \tag{2}$$

where E is the modulus of the filled rubber, E_0 is the modulus of the unfilled rubber, and ϕ is the filler volume fraction. This relation also assumes that the carbon-black filler particles are spherical, well dispersed throughout the matrix, and that each is perfectly bonded to the rubber.

The prediction of the stiffness of filled rubber is well described at small strains below about 10% by the relationship derived by Guth and Gold[3] and Smallwood.[4] Hon et al.[5] have shown that these stiffness predictions at small strains were well represented using finite element microstructural models. For moderate strain of less than 100%, Kashani and Padovan[6] have shown that the mechanical properties of filled rubbers follow a spring in series model, similar to the one shown in Eq. (2). Further, the rubber matrix and rigid fillers are in state of uniform stress rather than state of uniform strain. However, at larger strains these existing theories cannot predict the stiffness accurately and the microstructural finite element approach has not been tried. Hence, the present work uses micro mechanical modeling to predict large strain behavior including a considera-

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tion of the finite extensibility effects for filled elastomers. A range of single rigid filler and four filler models in an elastomer matrix have been investigated. The precise boundary conditions applied to the model are important. Two extreme boundary conditions termed ''plane surface'' and ''free surface'' have been investigated. The behavior of unfilled elastomers is frequently modeled using Mooney stored energy function.[7] However, it is clear that the Mooney equation cannot represent the finite extensibility stiffening behavior at large strains. Therefore, in this work, a more appropriate function proposed by Gent[8] is used to predict the large strain behavior and the effects of finite extensibility.

This investigation provides insight into rigid filler reinforcement and the filler interaction mechanisms. This study considers Medium Thermal (MT) carbon-black filled rubber because of the large amount of experimental data available in the literature. In addition, the simple spherical shape typical of MT carbon-black with its random spatial distribution and low agglomeration is an ideal rigid filler to establish the reliability of the modeling technique.

MATERIAL CHARACTERIZATION

To simulate the rubber–filler interaction using FEA, the matrix elastomer behavior has to be characterized first. Elastomeric materials are commonly characterized using stored energy functions, W, which can be expressed as functions of strain invariants; thus,

$$W = f(I_1, I_2) \tag{3}$$

I_1 and I_2 are the first and second strain invariants, respectively. Rubber for the purpose of this work is assumed to be isotropic and incompressible in bulk. Mooney[7] derived a two-term stored energy which has the following form

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) \tag{4}$$

where C_1 and C_2 are material constants. The constants C_1 and C_2 used in this work were derived from the unfilled rubber stress versus strain measurements of Mullins and Tobin.[9] This was achieved by plotting the curve of reduced stress versus the inverse of extension ratio. The curve fitting was done so that the Mooney stored energy function represented the behavior of the unfilled elastomer accurately up to 50% strain as shown in Figure 1. The constants used in the Mooney SEF were C_1 = 0.1658 MPa and C_2 = 0.0598 MPa. Typically, the Mooney SEF reasonably represents the behavior of an unfilled elastomer up to 100% strain in simple extension, although the fit for a more general strain is less good.

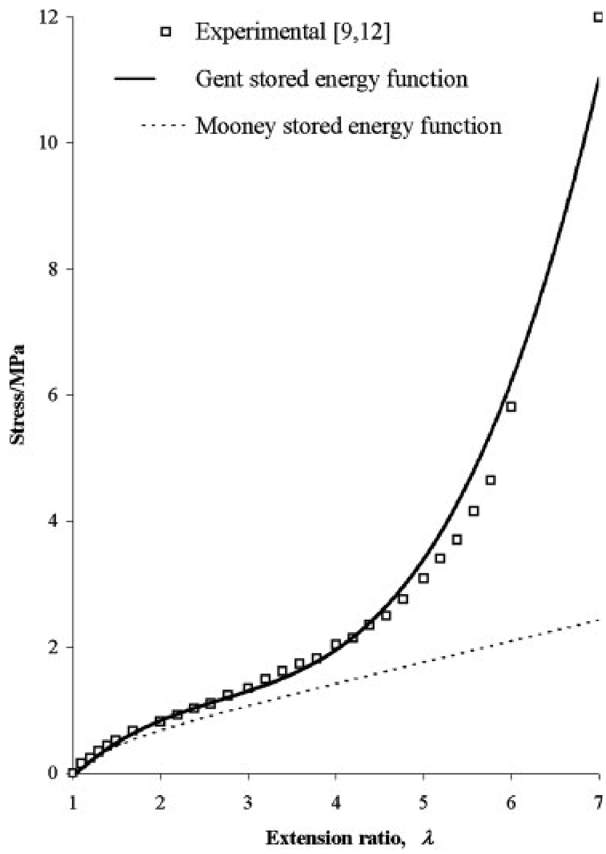

Figure 1 Comparisons of the experimental behavior of the unfilled rubber[9] with the stiffness fitted using the Mooney and the Gent stored energy functions.

Gent[8] derived a SEF from empirical considerations which has the form

$$W = -\frac{E}{6} I_m \ln\left[1 - \left(\frac{I_1}{I_m}\right)\right]. \tag{5}$$

In the above expression, E represents the low strain tensile modulus and I_m introduces a finite extensibility asymptote. Gent's SEF is applicable over large strains, gives a better fit at a higher extension ratio, and can be used in any deformation mode. This allows flexibility in terms of representing the behavior of an elastomer over a range of strains. In the present case, E was fitted to represent the small strain behavior accurately up to 50% strain as shown in Figure 1. The finite extensibility term was fitted to represent the behavior accurately at 600% strain. The constants used here were E = 1.29 MPa and I_m = 63.

As Mullins and Tobin's data[9] for unfilled rubber were not available at higher extension ratio, the fitting at higher extension ratio was carried out using data acquired on a nominally identical unfilled rubber examined by Harwood et al.[10] Figure 1

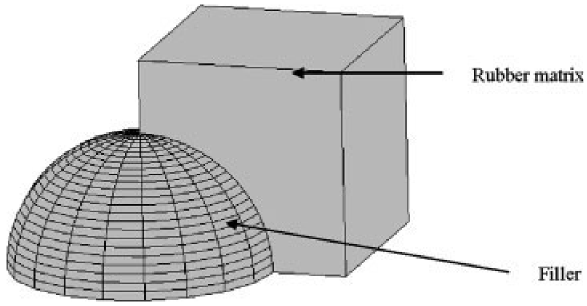

Figure 2 Finite element analysis representation of MT carbon-black filler embedded in rubber.

shows that Gent's SEF shows a significant and realistic upsweep at the higher extension ratios to represent the finite extensibility of the elastomeric network.

The Mooney SEF function is widely used in industry especially for tensile loading conditions. Its use here allows a comparison to be made between the geometric stiffening behavior and the material nonlinearity which the Gent equation would also be able to model at higher strains.

FINITE ELEMENT ANALYSIS

The filler particles, being much stiffer than the rubber, were modeled as rigid spheres. Typical models used in this work are shown in Figures 2 and 3. The single-particle model, which assumed an idealized packing array [Figs. 2 and 3(a)], exploited symmetry, so that only 1/8th of the rubber around a single rigid filler was modeled. The single rigid filler octant symmetry models are shown in Figures 2 and 3(a,b). The other models differed by either using an increased number of particles in the model [Fig. 3(c–e)] or altering the surface boundary conditions [Fig. 3(b,e)]. Different filler volume fractions can be created using similar models just with either the size of the filler(s) or the size of the unit cube altered slightly.

Two different types of boundary conditions were used for the plane sides of the unit cells. The first boundary condition assumed that all the surfaces are plane and remain plane. The second model assumed that some of the outer surfaces not in contact directly with the rigid filler particle were free to deform. The plane boundary conditions represent the interactions present in the bulk of the elastomers assuming that the fillers are evenly distributed with perfect packing and the free-surface conditions represent the behavior that is more typical close to the free surfaces of a filled rubber model.

Figure 3(c) shows a four rigid filler particle model with an irregular distribution of particles. The rubber was assumed to be perfectly bonded to the rigid filler. The four rigid filler particle model with free-surface boundary condition is shown in Figure 3(e). The two-symmetry plane model shown as the front and right-hand face in Figure 3(e) makes the four rigid filler particle model behave as if it was a 16 rigid filler particle model. The models were created using I-DEAS 9 preprocessor software and were analyzed using ABAQUS v6.4 software.

RESULTS AND DISCUSSION

Hon et al.[11] showed that whilst stiffness predictions at small strains were very good, the stiffness at large strains and at higher filler volume fractions was unrealistic for plane-surface models. This is because the constraints applied in these models, that all the surfaces remain plane, encounter a difficulty when the deformed width of the unit cube approaches the radius of the rigid filler. By examining such a cube in simple extension it is possible to deduce the limiting extension, λ_c, at which the rigid filler particles

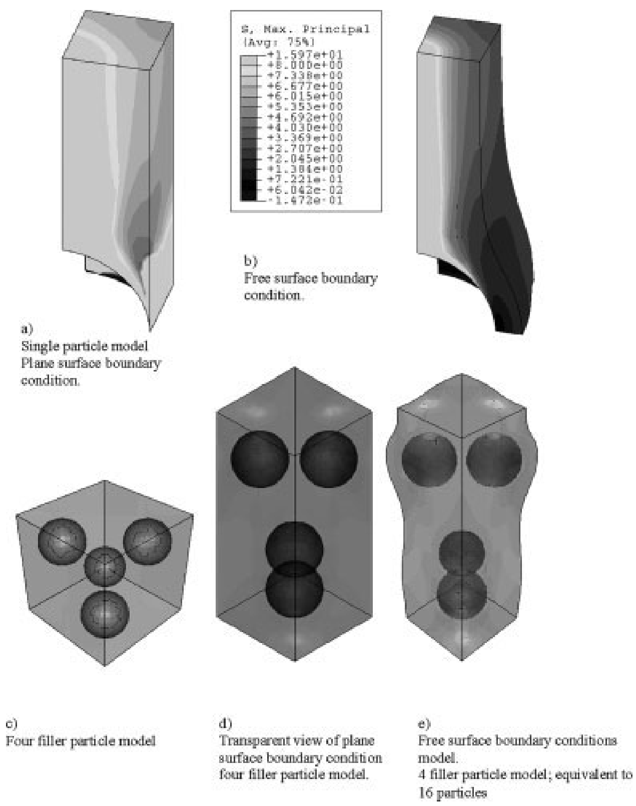

Figure 3 Three-dimensional models showing maximum principal stress contour plots at filler volume fraction of 13.8%. (a) Single-particle model plane-surface boundary condition. (b) Free-surface boundary condition. (c) Four filler particle model. (d) Transparent view of plane-surface boundary condition four filler particle model. (e) Free-surface boundary conditions model. Four filler particle symmetry model; equivalent to 16 particles.

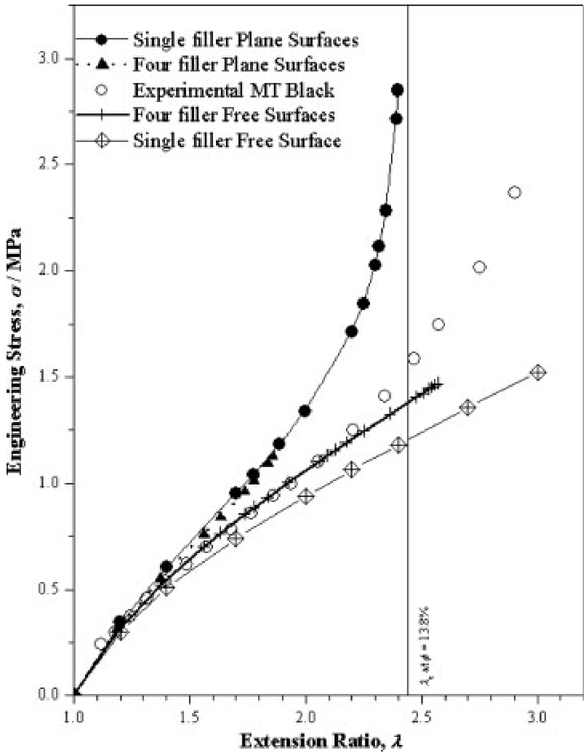

Figure 4 Engineering stress versus extension ratio for MT carbon-black filled rubber and models at 13.8% filler volume fraction. The limiting extension, λ_c, of the planar-surface single-particle model is shown as the asymptote (Mooney stored energy function).

touch for a given volume fraction of filler as

$$\lambda_c = \frac{1}{4}\left(\frac{4\pi}{3\phi}\right)^{2/3}. \quad (6)$$

The plane-surface asymptotes are shown in Figures 4 and 5 as solid vertical lines for volume fractions of 13.8% and 20.9%. These asymptotes were an artefact of these particular models which did not occur with a more realistic, random arrangement of the rigid filler particles. To remove this artificial stiffening an alternative single rigid filler unit cell boundary condition was introduced, where the two nonsymmetrical outer surfaces not in contact with the rigid filler particle, that is, the right and back surfaces as shown in Figure 3(b), were allowed to move freely. This boundary condition is termed the free-surface condition. Figure 3 shows the single rigid filler models and the four rigid filler models with a filler volume fraction of 13.8% displaying the maximum principal stress contour plots. The introduction of the free-surface boundary condition causes the models to have lower stress compared to the plane-surface model at equivalent global displacement. In a previous work by Hon et al.[8] and again here the Mooney SEF was initially used to represent the material behavior.

Figure 4 shows the experimental data obtained by Mullins and Tobin,[9] as well as the calculated values for both the single rigid filler and four rigid filler models with the plane-surface as well as the free-surface boundary conditions modeled using the Mooney SEF at a filler volume fraction of 13.8%. The limiting extension effects were clearly absent in the free-surface model. However, in comparison to the plane-surface model, the calculated stress–strain behavior for the single rigid filler model underestimated the experimental behavior even at lower extensions. It is proposed that this is due to two separate effects. Firstly, that the free-surface boundary condition only represents the behavior of fillers nearer to the edges of rubber which will have a softer stiffness response. In practice, at larger filler volume fractions the behavior will lie somewhere in between the two extremes of plane surface and free surface. Secondly, the Mooney SEF does not predict the finite extensibility behavior of the rubber. The free-surface four-particle model

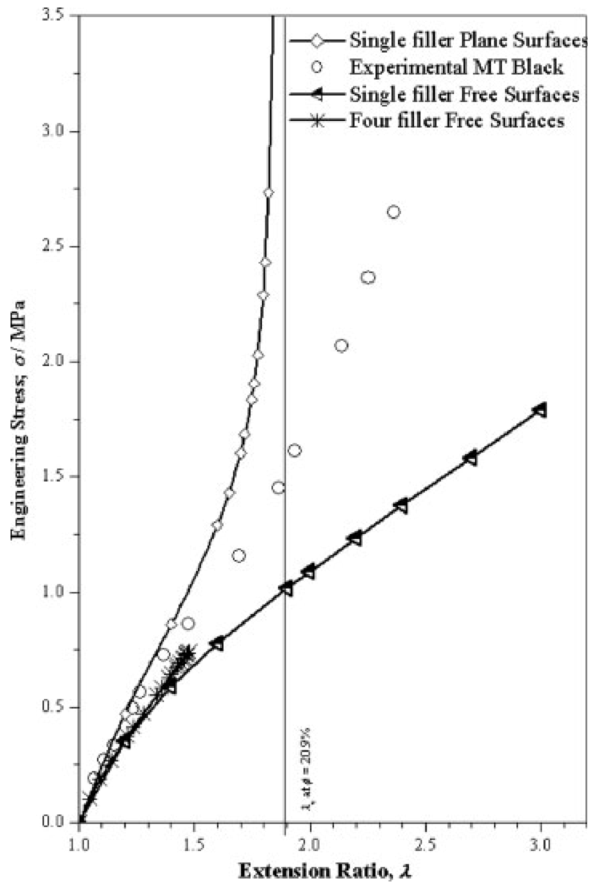

Figure 5 Engineering stress versus extension ratio for MT carbon-black filled rubber and models at 20.9% filler volume fraction. The limiting extension, λ_c, of the planar-surface single-particle model is shown as the asymptote (Mooney stored energy function).

shows a reasonable correlation with the experimental data over a wide range of extension ratios until the strains become large enough for finite extensibility effects to become significant.

Figure 5 is similar to Figure 4 but this time for a greater filler volume fraction of 20.9%. Again the plane-surface model overestimated the stiffening due to the limiting extension effect discussed previously. In this case the four rigid filler models had large local strains at relatively modest global strains. The free-surface model only extended to a strain of 50% before some elements became too distorted to allow the model to be extended further. Before this limit is reached though it is clear that the multiple rigid filler model is stiffer than the single rigid filler model. It is also apparent that the stiffness of both models is lower than the experimental data. It is proposed therefore that as the filler volume fraction increases, the significance of finite extensibility effect becomes greater as a result of strain amplification.[8]

The next approach was to introduce a stored energy function to model more realistically the finite extensibility effect. The function chosen was that proposed by Gent,[8] which was fitted to the literature data.[9] The stiffness was fitted to the small strain behavior as well as at an extension ratio of 7, as shown in Figure 1. The Gent function now produces an acceptable degree of fit to the measured stress versus strain data of the entire range of strains.

All the models that had been made earlier were reinvestigated with the material behavior described by this stored energy function. Figure 6 shows the results at a filler volume fraction of 13.8%. The free-surface single rigid filler model using Gent SEF follows the experimental observed behavior more closely than single rigid filler model based on Mooney SEF. The free-surface four rigid filler model using the Gent SEF now over predicts the stiffness when compared with experimental observed behavior. It is clear that the choice of SEF, boundary conditions, and the representative number of rigid fillers particles are all important when determining the appropriate model to represent the stiffness behavior.

Figure 7 compares the Gent SEF results at a filler volume of 20.9%. The single rigid filler model using Gent SEF shows a significant upsweep when compared with the model based on Mooney SEF. The single rigid filler free-surface models using Gent's SEF now shows a softer response than the experimentally observed behavior. The models that combined both the Gent SEF and the four rigid filler particles were not able to deform to sensible extensions as a result of very high local strain gradients and so they are not shown here. It is thought though that as the filler volume fraction is increased the significance of the filler–filler interaction becomes greater and

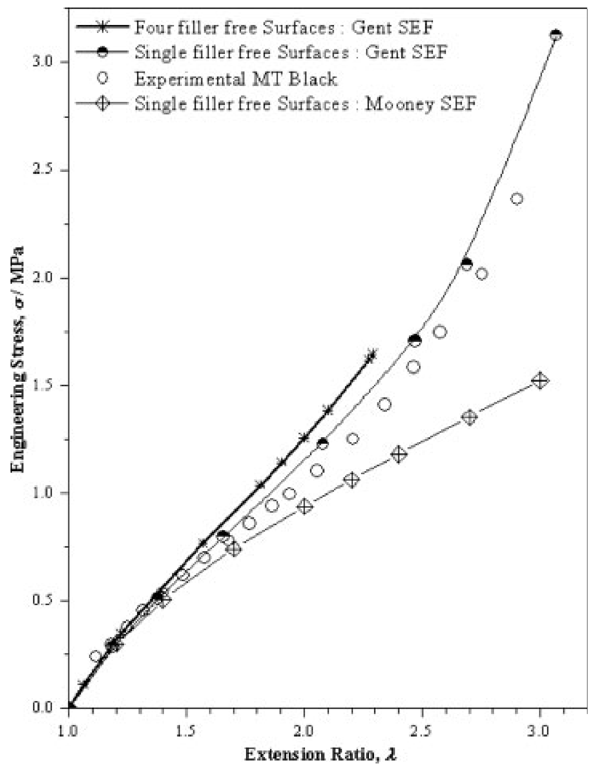

Figure 6 Engineering stress versus extension ratio for MT carbon-black filled rubber and models at 13.8% filler volume fraction.

hence the models that incorporate only a single particle will increasingly underestimate the stiffness.

It is clear, however, that to predict the behavior at higher filler volume fractions and at extension ratios higher than 2, it is essential that a more realistic SEF should be adopted.

Having undertaken this investigation a number of questions arise. Firstly, in all cases an increase in the number of particles in the representative volume at a specific volume fraction results in an increase in the predicted stiffness. Therefore, more than a single particle will be required to predict the behavior for a range of strains or volume fractions, but as yet it is unknown exactly what the required number of particles would be to determine the behavior of all MT carbon-black filled rubbers.

In the present case, the rigid filler was perfectly bonded to the interface; it is thought that this is the reason for the over prediction in the stiffness at a volume fraction of 13.8% for the multiple rigid filler particle model based on the Gent stored energy function. Dannenberg[12] suggested that at larger strains there is some slippage of the rubber over the rigid filler surface. Hence in future more appropriate boundary conditions at the filler–rubber interface could be investigated. This can be done by considering slippage at filler–rubber interface. Slippage at filler–rubber interface will allow rigid filler particle

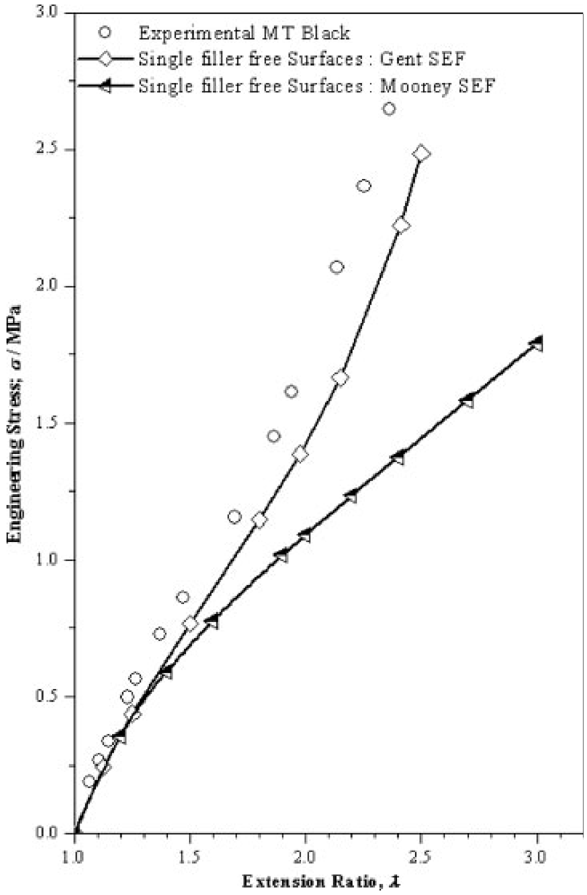

Figure 7 Engineering stress versus extension ratio for MT carbon-black filled rubber and models at 20.9% filler volume fraction.

to slide at an appropriate shear stress, causing a decrease in the stiffness and an increase in the internal viscosity. This model will overcome the limitation of perfectly bonded model presented here.

In addition, it is not clear as to how the precise location alters the filler interaction and affects the stiffness of the composite. The four rigid filler particle model shown in Figure 3(c) only reflected one specific spatial arrangement of particles in the elastomeric matrix. Hence, future models should also consider the effects of particle distribution. An ideal rigid filler rubber model would probably be made with a large number of filler particles randomly distributed in the elastomer matrix.

CONCLUSIONS

Previous work by Hon et al.[5,11] has shown that a single rigid filler (1/8th symmetry with perfect bonding) microstructural model using plane-surface boundary conditions was able to predict the behavior of a MT carbon-black filled rubber well at small strains. This work has shown that at larger strains the boundary conditions become more important, with a simple model either overestimating or underestimating the stiffness depending on the exact type of boundary condition used. A four rigid filler model was used here which improved the predictions of the stiffness behavior, but which still resulted in either an overestimation or an underestimation depending upon the exact boundary conditions adopted and stored energy function used. Strain amplification due to the presence of the rigid filler results in local strains being significantly higher than the globally applied strain; therefore, the Gent stored energy function is more appropriate. Future work should consider investigating what is the required number of rigid fillers in a representative volume to accurately model the behavior; this work should also consider the importance of the spatial arrangements, whereby effects such as filler clustering and occluded rubber may be expected to play a part. The precise nature of the interfacial boundary between the filler and rubber will impact the stiffness behavior significantly and hence a more appropriate model which also incorporates slippage should be considered.

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