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Sankalp Gour  
Maulana Azad National Institute of Technology Bhopal

Deepu Kumar Singh  
Maulana Azad National Institute of Technology Bhopal

Deepak Kumar (deepakkumaromre@manit.ac.in)  
Maulana Azad National Institute of Technology Bhopal

Vinod Yadav  
Maulana Azad National Institute of Technology Bhopal

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Constitutive modeling for the mechanical behavior of rubber with filler particles

SANKALP GOUR¹, DEEPU KUMAR SINGH¹, DEEPAK KUMAR¹* and VINOD YADAV¹

¹Department of Mechanical Engineering, Maulana Azad National Institute of Technology Bhopal, Madhya Pradesh, India-462003
e-mails: sankalpgour@gmail.com; deepukumarsingh1995@gmail.com; deepakkumaromre@manit.ac.in; vyadav@manit.ac.in

Abstract. The present study deals with the constitutive modeling for the mechanical behavior of rubber with filler particles. An analytical model is developed to predict the mechanical properties of rubber with added filler particles based on experimental observation. To develop the same, a continuum mechanics-based hyperelasticity theory is utilized. The model is validated with the experimental results of the chloroprene and nitrile butadiene rubbers filled with different volume fractions of carbon black and carbon nanoparticles, respectively. The findings of the model agree well with the experimental results. In general, the developed model will be helpful to the materialist community working in characterizing the material behavior of tires and other rubber-like materials.

Keywords. Continuum Mechanics, Constitutive modeling; Hyperelastic materials; Reinforced rubbers.

1 Introduction

In general, rubber is a long-chain polymer with minor impurities of other organic compounds. A polymer that exhibits rubber-like elasticity is also referred to as elastomer or sometimes rubber elastomer [1]. Polymeric materials have high availability and low raw material costs with a wide range of desirable properties. The most distinguished property of rubber elastomers is their ability to undergo large deformations under small stresses without considerable permanent deformation after removal of stress [2, 3]. They also possess energy absorption and excellent damping characteristics, resiliency, flexibility, long service life, ability to seal against moisture, heat, and pressure, and non-toxic properties. They can be easily molded into intricate shapes. These materials have been used in diverse applications such as vibration isolation, structural bearings, tires, biomechanics, gaskets, engine mounts, etc [4]. These materials obey the theory of hyperelastic or Green elastic materials. In such materials, the stress-strain relationship is defined as non-linearly elastic, isotropic, and incompressible [5, 6]. It is a type of constitutive model for ideally elastic material for which the stress-strain relationship derives from a strain energy density function [7, 8, 9].

Fillers play vital roles in transforming the desirable properties of polymers and decreasing the overall cost of their composites. Several researchers [10, 11, 12] have experimentally studied the mechanical behavior of rubber elastomer with different volume fractions of filler materials. They found that the mechanical properties of the rubber elastomers can be induced by varying the volume fraction, shape, and size of the filler particles. A further enhancement of the mechanical properties can also be acquired by the use of filler materials with higher aspect ratios, like short glass fibers [13, 14]. The dispersion of filler particles with dimensions in the nanometer level having very high aspect ratios and stiffness in a polymer matrix may result in even higher mechanical properties [15, 16, 17]. Such fillers include layered silicates and carbon nanotubes [18, 19]. In view of the constitutive modeling developments of the rubber elastomers with filler particles, Reichert [20] earlier proposed a double network-based model by writing the stress as a superposition of stresses of the individual networks to describe filled elastomers. Further, Farris [21] studied the influence of vacuole formation on the response and failure of filled elastomers. Furthermore, Berriot [22] modeled the filler-elastomer interaction based on the HNMR experiments on filled rubbers. In the recent developments, Leonard et al. [23] proposed a computational method to model the polydimethylsiloxane (PDMS) elastomer with prototypical added fillers. At last, Kluppel and Schramm [24] developed a tube model to study the stress softening of filled elastomers.

Finally, it is recognized that the theoretical understanding of filled elastomers has not been improved so much to the extent that now a connection can be made between the filler structures on larger length scales. In line with that, the present study aims to develop an analytical model to predict the mechanical properties of rubber elastomers with added filler particles based on experimental observation.

The organization of the paper in line with the current Section 1 is as follows. In Section 2, a constitutive model is developed to describe the nonlinear elastic response of the various particle-reinforced rubber elastomers. In Section 3, the analytical and experimental results are compared and analyzed. Finally, Section 4 concludes the article
2 Constitutive modeling

In this section, an analytical model for the mechanical behavior of rubber with filler particle is developed. To develop the same, a hyperelasticity theory is adopted.

2.1 Problem definition

Consider a rubber sample having the dimensions \((L_1, L_2, L_3)\) in the reference configuration \(\beta_0\) shown in Figure 1. A compressive force \(P\) is applied on the rubber sample to deform the same for the deformation analysis. The deformed rubber sample are now having the dimensions \((l_1, l_2, l_3)\) in the current configuration \(\beta\). The rubber sample is assumed to be incompressible, isotropic, and homogeneous. For a given deformation of an applied compressive force, the problem aims to derive an expression of the constitutive relationship between stress and deformation, including the volume fraction of filler particles following a classical continuum mechanics-based approach.

![Figure 1. Schematic diagram of a rubber sample with filler particles in undeformed and deformed configurations.](image)

2.2 Hyperelastic deformation

The domain occupied in a 3-D space by a rubber sample shown in Figure 1 may be represented as

\[
\beta_0 = \{x \in \mathbb{R}^3 : \frac{-L_1}{2} \leq x_1 \leq \frac{L_1}{2}, \frac{-L_2}{2} \leq x_2 \leq \frac{L_2}{2}, \frac{-L_3}{2} \leq x_3 \leq \frac{L_3}{2}\},
\]

\[
\beta = \{x \in \mathbb{R}^3 : \frac{-l_1}{2} \leq x_1 \leq \frac{l_1}{2}, \frac{-l_2}{2} \leq x_2 \leq \frac{l_2}{2}, \frac{-l_3}{2} \leq x_3 \leq \frac{l_3}{2}\},
\]

For a given reference \(\beta_0\) and current configuration \(\beta\) domains in the above equation (1), the stretches in the principal direction may be defined as

\[
\lambda_1 = \frac{l_1}{L_1}, \quad \lambda_2 = \frac{l_2}{L_2}, \quad \lambda_3 = \frac{l_3}{L_3}.
\]

On using the incompressibility constraint \(\lambda_1\lambda_2\lambda_3 = 1\), the principal stretches for an uniaxial compression of the rubber sample are given as

\[
\lambda_1 = \lambda, \quad \lambda_2 = \frac{1}{\sqrt{\lambda}}, \quad \lambda_3 = \frac{1}{\sqrt{\lambda}}.
\]

where \(\lambda\) denotes the stretch in the direction of applied load. The deformation gradient tensor \(F\) and the corresponding left-Cauchey green deformation tensor \(B = FF^T\) for an uniaxial compression of the rubber sample having the deformation domain (1) in terms of principal stretches are defined as

\[
F = \begin{bmatrix}
\lambda & 0 & 0 \\
0 & \frac{1}{\sqrt{\lambda}} & 0 \\
0 & 0 & \frac{1}{\sqrt{\lambda}}
\end{bmatrix}, \quad B = \begin{bmatrix}
\lambda^2 & 0 & 0 \\
0 & \frac{1}{\lambda} & 0 \\
0 & 0 & \frac{1}{\lambda}
\end{bmatrix}.
\]

2.3 Governing equations

To model the mechanical behavior of rubber with filler particles, we first require an energy density function that can capture the effect of filler content on the shear modulus of the rubber matrix. For the same, we use a strain energy density function in line with the literature [25, 26] which includes the volume fraction term of the filler particles. The expression of the strain energy density function is given as

\[
W = (1 - V_f)\frac{\mu}{2}(1 + 3.5V_f + 30V_f^2)(I_1 - 1),
\]

where \(V_f\), \(\mu\), and \(I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2\) are the volume fraction of the added filler particle in the rubber matrix, shear modulus, and the first invariant of the left-Cauchey green deformation tensor \(B\). From the theory of hyperelasticity [27, 28], the Cauchy stress tensor for a given strain energy density function \(W\) is expressed as

\[
S = -pI + 2\frac{\partial W}{\partial I_1}B - 2\frac{\partial W}{\partial I_2}B^{-1},
\]

where \(p\) is a Lagrange multiplier associated with the constraint of incompressibility and \(I_1, I_2\) are the first and second invariants of the left-Cauchey green deformation tensor \(B\).

On using the given filler particle volume dependent strain energy density function (5) in (6), the corresponding principal Cauchy stress components are obtained as

\[
S_{11} = -p + (1 - V_f)\mu(1 + 3.5V_f + 30V_f^2)\lambda^2,
\]

\[
S_{22} = -p + (1 - V_f)\mu(1 + 3.5V_f + 30V_f^2)\frac{1}{\lambda},
\]

\[
S_{33} = -p + (1 - V_f)\mu(1 + 3.5V_f + 30V_f^2)\frac{1}{\lambda}.
\]

2.4 Constitutive model

On applying uni-axial compression boundary conditions, i.e., \(S_{11} = \sigma, S_{22} = S_{33} = 0\) in (7), the Cauchy or true stress \(\sigma\) in the applied load direction is obtained as

\[
\sigma = (1 - V_f)\mu(1 + 3.5V_f + 30V_f^2)\left(\lambda^2 - \frac{1}{\lambda}\right).
\]

The above constitutive relation (8) represents a continuum mechanics-based analytical model to predict the experimentally observed mechanical behavior of the filler particles reinforced rubber elastomers.
3 Results and discussions

In this section, the constitutive model presented in Section 2 is compared and validated with the chloroprene and nitrile butadiene rubbers data filled with different volume fractions of carbon and carbon nanotube particles, respectively. It is also utilized in characterizing the mechanical behavior of the same.

3.1 Model validation with chloroprene rubber data filled with different percentages of carbon black

To check the validity of the proposed model (8) derived in section 2, we compare our theoretical findings with the experimental work performed by Bergstrom and Boyce [29].

Bergstrom and Boyce [29] performed several compression tests to study the stress-strain behavior of a chloroprene rubber at different volume fractions of N600 carbon black filler particles content. The testing was done on a computer controlled Instron servo-hydraulic uniaxial testing machine operating in strain control mode. The different ASTM-sized specimens were used and tested at room temperature. We analyze these experimental results [29] and obtain the same analytically by utilizing a constitutive model (8). To compare both analytical and experimental findings, we plot the Cauchy stress versus stretch data for a chloroprene rubber with varied N600 carbon black filler particles shown in Figure 2. Herein, the analytical results obtained from the model (8) agree well with experimental data [29].

By fitting the model (8) with experimental data [29] shown in Figure 2, we tabulate the shear modulus $\mu$ values in Table 1 at different percentages of carbon black filler particles added in a chloroprene rubber. In Table 1, increasing carbon black particles from 0 to 7%, 7 to 15%, and 15 to 25% lead to an increase in the shear modulus of the chloroprene rubber 48.48%, 17.34%, and 0.52%, respectively. As a consequence, it is found that the addition of the carbon particles in the rubber matrix increases the shear modulus up to a certain value. It is also seen from Figure 2 that the effects of the percentage of filler particle content are more pronounced at a high stretch as compared to a low stretch. The variation of Cauchy stress with the stretch is almost linear. However, the slope in each case of different specimen is almost flat.

The dependency of the proposed model (8) is highly desirable on the shear modulus of the specified rubber filled with carbon black filler particles.

Table 1. Shear modulus values for a chloroprene rubber at different percentages of added carbon black filler particles.

| Carbon Black Particles | Shear Modulus  |
|------------------------|----------------|
| 0 %                    | 330 kPa        |
| 7 %                    | 490 kPa        |
| 15 %                   | 575 kPa        |
| 25 %                   | 578 kPa        |

3.2 Model validation with nitrile butadiene rubber data filled with different percentages of carbon nano particle

To further assess the validity of the proposed model (8), we compare the analytical findings with the experimental work performed by Mahmoud et al. [30]. Mahmoud et al. [30] experimentally characterized the mechanical behavior of the nitrile butadiene rubber (NBR) by adding carbon nanoparticles (CNPs). The nanocomposites were in the form of strips as per the ASTM D 412-8a standards. The testing was done on a computer controlled material testing machine (AMETEK, USA) connected by a digital force gauge (Hunter Spring AC-CU Force II, 0.01-Nresolutions) to estimate the forces. We re-analyze these experimental results [30] and obtain the same analytically by utilizing a constitutive model (8). To make a comparison between the analytical and experimental findings, we plot the Cauchy stress versus stretch data for a nitrile butadiene rubber filled with different levels of carbon nanoparticles shown in Figure 3. Herein, the analytical results obtained from the model (8) qualitatively go with experimental data [30].

Following the procedure of estimation the shear modulus $\mu$ as mentioned earlier, we tabulate the corresponding values in Table 2 at different percentages of carbon nanoparticles filled in a nitrile butadiene rubber. In Table 2, increasing carbon nanoparticles from 0 to 0.7% and 0.7 to 1.3% lead to an increase in the shear modulus of the nitrile butadiene rubber 203% and 66.67%, respectively. Further, the carbon nanoparticles volume percentage is increased from 2 to 2.6% and 2.6 to 3.3%; the values of the shear modulus of the nitrile butadiene rubber increase by 39.58% and 7.46%, respectively. It is interesting to observe that with increasing the carbon nanoparticles from 0 to 3.3% in the nitrile butadiene rubber, the shear modulus is jumped by 1354%.
theoretically. On the other hand, it is also observed that the rate of increase in shear modulus is low with increasing the percentage of carbon nanoparticles in the nitrile butadiene rubber. Hence, the combined effect of increasing the carbon nanoparticles along with the shear modulus is studied underpin. It is seen from Figure 3 that with increasing the carbon nanoparticles, the Cauchy stress–stretch curves become steeper. This may be due to an increase in the shear modulus of the rubber matrix. Also, the stretch abilities of the rubber are reduced significantly in line with the experimental data [30]. Hence, the proposed model (8) can predict the stress–strain or stress–stretch behavior of any filler particles-reinforced rubber.

![Figure 3. Validation of the model (8) with Mahmoud et al. experimental data [30] for a nitrile butadiene rubber (NBR) filled with different levels of carbon nanoparticles (CNPs).](image)

**Table 2.** Shear modulus values for a nitrile butadiene rubber (NBR) at different percentages of added carbon nanoparticles (CNPs).

| Carbon Nano Particles | Shear Modulus  |
|-----------------------|----------------|
| 0 %                   | 495 kPa        |
| 0.7 %                 | 1500 kPa       |
| 1.3 %                 | 2500 kPa       |
| 2 %                   | 4800 kPa       |
| 2.6 %                 | 6700 kPa       |
| 3.3 %                 | 7200 kPa       |

4 Concluding remarks

In this paper, an experimentally validated analytical model is presented for the finite deformation of the filler particles-induced rubber elastomers subjected to a stretch in an applied load direction. An explicit expression of the Cauchy or true stress is driven by connecting the volume fraction of the added filler particles, shear modulus, and stretch for a given deformation in the direction of the applied load. As a result, it has been observed that the enhanced mechanical properties of rubber elastomer can be attainable by doping filler particles. This may help the materialist community working in characterizing the material behavior of tires and other rubber-like materials.

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Figures

Figure 1

Schematic diagram of a rubber sample with filler particles in undeformed and deformed configurations.

Figure 2

Validation of the model (8) with Bergstrom and Boyce experimental data [29] for a chloroprene rubber filled with different levels of N600 carbon black.
Validation of the model (8) with Mahmoud et al. experimental data [30] for a nitrile butadiene rubber (NBR) filled with different levels of carbon nanoparticles (CNPs).