Constitutive modelling of elastomer/graphene platelet nanocomposites

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Abstract. Elastomers are used in a wide variety of structural and engineering applications. They exhibit a nonlinear elastic stress-strain behaviour known as hyperelasticity which is generally described by hyperelastic strain energy functions. The question raised in the current study was; which model can accurately describe and predict the actual behaviour of the elastomer nanocomposites. The tensile data were used to fit the various elastomeric material models available in MSC.MARC finite element analysis package. The relative percentage error was calculated to determine the goodness of fit in order to select the best model. Numerical results showed that the third order deformation model was the best among the various material models since giving a maximum relative error of fit was 2.7% at small and large strains. To verify the effectiveness of third order deformation model, FE simulations for tensile test was carried out. The results showed that the third order model is sufficiently enough to regenerate the experimental data for uniaxial test and efficiently capture the hyperelastic behavior as good as the experiments.

1. Introduction
In recent years, rubber products as engineering materials have been used in many industries such as seals, vehicles tires, hydraulic hoses, and engine mountings. These materials usually exhibit very large strains, with a strongly non-linear stress–strain relation. The wide range of application of hyperelastic materials justifies a high research interest in their characterization through experimental techniques and in the study of accurate constitutive models able to characterize their particular behaviour [1]–[3]. As an important type of polymer material, rubber (also called elastomer) is widely used in industry due to its reversible and high deformability. The introduction of computers in structural analysis using finite element analysis (FEA) allows computer simulation of how a part will respond to loads and forces in its application environment. In other words, it is used to predict the effectiveness of design concepts of elastomeric components. This is mainly because elastomeric components exhibit large deformations, nonlinear stress-strain relationships during load, viscoelastic processes such as heat dissipation and time-dependent behaviour, and nearly incompressible characteristics during deformation [4]–[7]. A stored energy function can define rubber materials as hyperelastic material. The coefficients of these functions should be determined by shear test, biaxial, and uniaxial data.
The biggest problem in characterising the mechanical behaviour of rubber materials is how to determine the proper strain energy function and material model that provides a good fit with available experimental data. In this study, different material models groups, such as Mooney-Rivlin, Principle of stretch and Micromechanical models for incompressible isotropic hyperelastic materials were used to model and capture the hyper-elastic mechanical properties of SBR with different percentage of graphene platelets. The relative percentage error was calculated to determine the goodness of data fit to select the best model that can accurately reproduce the uniaxial tensile test data.

2. Experimental procedures

2.1. Material
The styrene butadiene rubber (SBR, 1502 styrene content 23.5% with a Mooney viscosity of ML (1+4)) at 100 °C =52). The rubber was reinforced with different graphene platelets (GnPs) to prepare samples for tensile tests.

2.2. Experimental work
Compounding GnPs into styrene butadiene rubber was done by a laboratory size open two-roll mill machine at room temperature. The volume ratio of GnPs in composites were 0, 2.4, 5, 10.5 and 16.7 vol.%. The tensile dumb-bell samples of neat SBR and its nanocomposites were die cut to record stress-strain graphs using Instron 5567 tensile machine with 2 kN load cell. The tensile test was accomplished according to ASTM D 412 standard [8]. The sample preparations and experimental procedure details follow a similar process as in Ref. [9].

2.3. Hyperelastic material models for elastomers
The non-linear behaviour of rubber requires specific constitutive material formulations, namely hyperelastic material models. In most commercial finite element (FE) softwares package such as MSC. Nastran, MSC. Marc, Abaqus, Ansys, etc., there are different forms of strain energy density functions \( W \) may characterise elastomeric materials. Generally, hyperelastic models are described by strain energy function density (\( W \)) which is formulated as a function depending on different magnitudes associated with the strain field and the material constants. Usually:

\[
W = W (\lambda_1, \lambda_2, \lambda_3) = W (I_1, I_2, I_3)
\]

where \( \lambda_1, \lambda_2, \lambda_3 \) are principal stretches, and \( I_1, I_2, I_3 \) are the invariants of the green deformation tensor. The strain invariants \( I_1, I_2 \) and \( I_3 \) in terms of the principal stretch ratios, \( \lambda_1, \lambda_2, \) and \( \lambda_3 \) are defined as:

\[
I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \quad I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \quad I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2
\]

where the stretch ratios are defined as:

\[
\lambda_i = \left( \frac{L_i + \Delta L_i}{L_i} \right) = 1 + \epsilon_i \quad ; i = 1, 2, 3
\]

where \( \epsilon_i = \Delta L_i / L_i \) is the engineering strain. In the case of perfectly incompressible materials, the third invariant equals one, i.e. \( I_3 = 1 \).

Three different hyperelastic models were studied to obtain a constitutive material model for elastomer material, and their formulation are described.

A) Mooney-Rivlin model [10], [11]
\[
W = C_{10} (I_1 - 3) + C_{01} (I_2 - 3)
\] (4)

where \( C_{10} \) and \( C_{01} \) are the material constants.
1. Neo-Hookean model [12]

\[ W = \frac{1}{2} G (I_1 - 3) = \frac{1}{2} G (\lambda_1^2 + \lambda_2^2 + \lambda_3^2) - 3 \] (5)

2. Two term Mooney - Rivlin energy function

\[ W = C_{10} (I_1 - 3) + C_{01} (I_2 - 3) \] (6)

where \( C_{10} \) and \( C_{01} \) are the material constants

3. Three term Mooney - Rivlin energy function

\[ W = C_{10} (I_1 - 3) + C_{01} (I_2 - 3) + C_{11} (I_1 - 3) (I_2 - 3) \] (7)

where \( C_{10}, C_{01}, \) and \( C_{11} \) are material constants

4. The Signorini model

\[ W = C_{10} (I_1 - 3) + C_{01} (I_2 - 3) + C_{20} (I_1 - 3)^2 \] (8)

5. Second order invariant

\[ W = C_{10} (I_1 - 3) + C_{01} (I_2 - 3) + C_{11} (I_1 - 3) (I_2 - 3) + C_{20} (I_1 - 3)^2 \] (9)

6. Third order deformation (or James-Green-Simpson):

\[ W = C_{10} (I_1 - 3) + C_{01} (I_2 - 3) + C_{11} (I_1 - 3) (I_2 - 3) + C_{20} (I_1 - 3)^2 + C_{30} (I_1 - 3)^3 \] (10)

7. Yeoh model [13]

\[ W = C_{10} (I_1 - 3) + C_{20} (I_1 - 3)^2 + C_{30} (I_1 - 3)^3 \] (11)

B) Principle of stretch models

1. Ogden model [14]

\[ W = \sum_{n=1}^{N} \frac{\mu_n}{\alpha_n} [ \frac{1}{3} (\lambda_1^{\alpha_n} + \lambda_2^{\alpha_n} + \lambda_3^{\alpha_n}) - 3 ] + 4.5K (J^3 - 1)^2 \] (12)

Usually, the number of terms taken into account in the Ogden models is \( N = 4 \). Where \( \mu_n \) and \( \alpha_n \) are material constants, \( K \) is the initial bulk modulus, and \( J \) is the volumetric ratio defined by \( J = \lambda_1 \lambda_2 \lambda_3 \).

2. Foam

\[ W = \sum_{n=1}^{N} \frac{\mu_n}{\alpha_n} [ \frac{1}{3} (\lambda_1^{\alpha_n} + \lambda_2^{\alpha_n} + \lambda_3^{\alpha_n}) - 3 ] + \sum_{n=1}^{N} \frac{\mu_n}{\beta_n} [ 1 - J^{\beta_n} ] \] (13)

where \( \mu_n, \alpha_n, \) and \( \beta_n \) are material constants.

C) Micromechanical models

1. Arruda-Boyce model [15]

\[ W = \mu \sum_{i=1}^{N} \frac{C_i}{\lambda_i} \left( I_1^i - 3^i \right) + \frac{1}{D} \left[ \left( J \right)^{2-1} - \ln J \right] \] (14)

where \( C_i \) and \( \lambda_i \) are material constants, \( \mu \) is the initial shear modulus and \( D \) is a material constant related to the bulk modulus.

\[ C_1 = \frac{1}{2}, C_2 = \frac{1}{20}, C_3 = \frac{11}{1050} \]
3. Results & discussion

3.1. Data fitting with different rubber material models
Figure 1. (a) – (c) presented, the result of data fitting with different rubber material models used in the present study. It is clear that the third order deformation model, Figure 1. (b), gave the best curve fitting if it compared with the other models. Moony3 and second order invariant models are shown in Figure 1(a) and (b) gave the second best fit after the third order model. The goodness of fit for the remaining hyperelastic models, Figure 1. (a)–(c) were invariably poor regarding the relative errors of the least square fitting of uniaxial data with these material models, as it will be explained in Figure 2. Therefore, the third order deformation model was chosen to represent the hyperelastic behaviour of the rubber nano-composite material hereafter in this paper because the relative error does not exceed 3%.

3.2. Effect of the ratio of GnPs % on the values of relative error of fitting
Figure 2 shows the variation of percentage relative error values with GnPs% for various material models. As shown in Figure 2, the lowest relative error value was observed with third order deformation model for all GnPs%. Arruda-Boyce model gave the worst fit since the relative error can reach 7%. The value of relative error in all material models increased with the increasing GnPs %. This trend was expected to happen because the stress-strain curves showed a marginal increase with
GnPs%. Figure 3 illustrates the variation of the material constants C10, C01, C11, C20 and C30 of third order deformation model with increasing of GnPs %. The material constants, C20 and C30, slightly affected by GnPs% whereas, C11 and C01 showed a continuous increase with %GnPs especially after 5% GnPs. On the contrary, C10 showed a decreasing trend with the addition of GnPs. The reason for this variation may attribute to the mathematical nature of the third order deformation model which is a polynomial hyperelastic model based on the statistical thermodynamics of cross-linked polymer chains [9-10]. These material constants are empirically determined, and therefore it is difficult to link directly or indirectly their variations to material anisotropy and inhomogeneity of the samples.

**Figure 2.** Percentage of relative error of fit for the various material models versus GnPs%.

**Figure 3.** The variation of the material constants for third order deformation model versus GnPs %.

### 3.3. Comparison between FE-simulation and experimental data

#### 3.3.1. The force/displacement curve.

Figure 4 shows a comparison between experiments and FE prediction for load/displacement response of uniaxial tensile test at different GnPs%. The effect of graphene platelets content, GnPs%, on the response of the uniaxial tensile test was simulated utilising the material constants obtained from the third order deformation model. It is seen that even addition of small values of GnPs% affected the measured stiffness. An increase in the percentage of GnPs% rubber is getting stiffer and the force-displacement response was higher. The differences between measured and predicted force-displacement response became significant at 16.7% GnPs. However, these differences could be eliminated if enough data was available and the material constants were derived from the combined test data. Material constants derived from the synthetic biaxial data provided a better prediction of rubber behaviour in both tension and simple shear modes [16], [17]. From the engineering point of view, differences between experimental and FE results, in Figure 4, even at high GnPs% are acceptable since the maximum relative error did not exceed 7%. The third order deformation model is sufficiently robust enough to regenerate the experimental data for the uniaxial test.
3.3.2. Uniaxial tensile strength.

Figure 4 shows a comparison between experimental and FE-predictions of uniaxial tensile strength at various GnPs%. In general, the trend of experimental results and FE-simulations are the same up to 10.5 %GnPs after that a slight difference was observed when GnPs% increased. The reason may be attributed the relative error of fit that increased significantly at GnPs value greater than 10.5 % (see Figure11). For GnPs% values less than 10%, the relative error of fit for third order deformation model was below 1% whereas it reached about 3% at 16.7% GnPs. Regardless of differences between experimental and FE-predictions of tensile strength, still the maximum prediction error did not exceed 4 % even at high GnPs values.

Figure 5. A comparison between experimental and FE-predictions of uniaxial tensile strength at different GnPs%.
4. Conclusion
The aim of this paper was to determine the best material model that representing the tensile behaviour of styrene-butadiene rubber (SBR) at a different volume fraction of graphene platelets (GnPs). To verify that, different hyperelastic material models have been studied in order to obtain the material constants of each model. The relative percentage error has been calculated to judge their goodness of fit and conclude which of them best represents the actual behavior of the rubber nanocomposites. In view of the obtained results, it concluded that the third order deformation model is the best one to regenerate tensile tests of SBR/GnPs samples since the relative errors did not research 2.7 %. Biaxial testing data are needed to minimize the relative error and provide a better prediction of rubber behaviour especially for rubber nano-composites contains GnPs greater than 10.5 vol. %.

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