Mechanics of Materials 106 (2017) 44–57

Contents lists available at ScienceDirect

Mechanics of Materials

journal homepage: www.elsevier.com/locate/mechmat

An experimental and numerical study on the volume change of particle-filled elastomers in various loading modes

Arne Ilseng[a,b,*], Bjørn H. Skallerud[a], Arild H. Clausen[a]

[a] Department of Structural Engineering, Norwegian University of Science and Technology, 7491, Trondheim, Norway
[b] Aker Solutions AS, 3408 Tranby, Norway

ARTICLE INFO

Article history:
Received 2 September 2016
Revised 5 January 2017
Available online 12 January 2017

Keywords:
Particle-filled elastomers
Volume change
In situ SEM
Single-particle model

ABSTRACT

Laboratory tests show that there is a pronounced difference in the volumetric response between uniaxial tension and confined axial compression loading for commercial particle-filled hydrogenated nitrile butadiene rubber (HNBR) and fluoroelastomer (FKM) compounds. In uniaxial tension (UT), a volume increase of 5% and 20% for the HNBR and FKM respectively was present for a hydrostatic stress of less than 6 MPa, in addition, both compounds showed a clear hysteresis loop in the hydrostatic stress - volume ratio space. For confined axial compression (CAC) tests, on the other hand, the materials reached a 6–7% volume change for a hydrostatic stress of 140 MPa, and an elastic behavior was seen. This loading mode dependence of the volumetric response has severe implications for the constitutive representation of the materials. It is demonstrated that existing elastomer models, whereof many assume incompressible volumetric response, are unable to capture the behavior in both loading modes. To gain an increased understanding of the macroscopically obtained results, a tension in situ scanning electron microscopy study was performed. Matrix–particle debonding was observed to occur at the external surface of the materials, rendering a possible explanation for the loading mode dependent volumetric behavior. Finite element simulations of a single-particle model, incorporating a cylinder of matrix material with a spherical particle in its center, showed that the observed debonding can explain the experimental response of the materials in a qualitative manner.

1. Introduction

Constitutive models commonly applied to predict the visco-hyperelastic response of elastomers in finite element simulations assume a nearly isochoric behavior independent of loading mode (Bergström and Boyce, 1998; Miehe and Göktepe, 2005; Ayoub et al., 2014). Based on available experimental data in uniaxial tension (UT) (Ilseng et al., 2016) and confined axial compression (CAC) (Ilseng et al., 2015), there are clear indications that this approach can be inaccurate for certain elastomers. It appears that the materials can exhibit a considerable increase of volume in UT, while the response in CAC is much stiffer with respect to volume change, yet there is a finite bulk modulus also in this loading case. However, before embarking on the task of developing constitutive models with improved correspondence to experimental observations, an enhanced understanding of the underlying mechanisms causing the loading mode dependent volume behavior should be provided.

Early work on elastomers (e.g. Treloar, 1943; Mooney, 1940; Rivlin, 1948) mainly dealt with the behavior of unfilled elastomer gums, for which the assumption of constant volume got accepted as the standard. However, raw gum elastomers have limited industrial application, and filler particles are normally added to the blend of industrial materials (Ciesielski, 1999). These fillers improve mechanical properties like stiffness and strength, but may also alter the volumetric behavior of the compounds.

Gent and Park (1984) and Cho et al. (1987) illustrated the possible effect that stiff particles can have on the volumetric response of elastomers by testing samples of a transparent elastomer matrix with spherical or cylindrical glass inclusions in uniaxial tension. They differentiated the observed response between two failure mechanisms; cavitation, i.e. the occurrence of voids in the material due to stress concentrations near the stiff inclusions; and decohesion, i.e. rupture of the cohesive zone between the inclusion and the matrix material. The failure process was initiated by the occurrence of small voids close to the stiff inclusion, which during deformation grew and coalesced to form larger cavities. As these cavities increased in size, they eventually led to decohesion between the filler particle and the surrounding elastomer

* Corresponding author at: Department of Structural Engineering, Norwegian University of Science and Technology, 7491, Trondheim, Norway.
E-mail address: arne.ilseng@ntnu.no (A. Ilseng).

http://dx.doi.org/10.1016/j.mechmat.2017.01.007
0167-6636/

matrix. For experiments involving large hydrostatic stresses, Gent and Lindley (1959) also found cavitation to occur in unfilled elastomers. This was attributed to pre-existing defects, experiencing unbounded growth when the hydrostatic tension stress exceeded a critical value. Such cavitation under high triaxiality stress states has later been studied further by different authors, e.g. Dorfmann (2003), Bayraktar et al. (2008), Lopez-Pamies et al. (2011). It is clear that the stress/deformation level where voids would start to grow and the number of voids that would initiate prior to particle decohesion are strongly dependent on properties like the fracture strength of the matrix material, the size and shape of the particles, and the cohesive strength between the matrix and its filler particles. In any event, a process of cavitation and decohesion would lead to a macroscopic volume growth of the material.

For the early research on the volumetric behavior of elastomers, the most accessible method for measuring global volume changes accompanying deformation was through dilatometry tests (Holt and McPherson, 1936; Jones and Yiengst, 1941; Shuttleworth, 1968; Penn, 1970). However, the progress of modern measuring techniques has simplified the evaluation of volume changes accompanying deformation significantly through the development of optical methods, like digital image correlation (DIC). Using DIC, Le Cam and Toussaint (2008) looked at the competition between volume increase due to void growth and volume decrease due to crystallization in natural rubber loaded in tension. They measured the volume change using DIC at one surface and assuming an isotropic material behavior. The results showed significantly larger volume growth for particle-filled natural rubber than for unfilled natural rubber. Due to crystallization, they observed a larger volume during loading compared with unloading. Le Cam and Toussaint (2009) also found a significant volume change in filled styrene-butadiene (SBR) dog-bone shaped specimens using a similar set-up. de Crevoisier et al. (2012) measured volume growth during cyclic loading of a filled SBR specimen using DIC at two perpendicular surfaces of a dog-bone-shaped specimen. They found the material to behave slightly anisotropic and to display a relatively small volume change. They also reported that the volume change in each deformation cycle started when the longitudinal deformation exceeded the previously obtained maximum deformation. Cantournet et al. (2014) recently studied the volume increase of a particle-filled natural rubber under various loading conditions. They measured the volume change occurring under uniaxial tension by use of a video traction system at one surface and the assumption of isotropic material behavior. The increase in volume was explained by cavitation and decohesion, and this phenomenon was studied using in situ scanning electron microscopy (SEM). They found that for loading at low stress triaxiality, volume growth occurred near ZnO particles, while no debonding could be observed between the elastomer matrix and carbon black particles. For a loading situation of large stress triaxialities, on the other hand, volume growth was seen to be dominated by matrix rupture rather than matrix-particle debonding.

Unit cell simulations are often used to explain globally observed results by studying mechanisms occurring at the scale of the material constituents. Such models have been extensively employed to study ductile fracture in metallic materials, e.g. Needleman (1972), Tvergaard (1981), Faleskog et al. (1998), Dæhli et al. (2016) and to some extent to study the behavior of particle-filled polymeric materials (Steenbrink et al., 1997; Cheng and Guo, 2007; Ognedal et al., 2014; Bergström and Boyce, 1999). Steenbrink et al. (1997) and Cheng and Guo (2007) looked at the effect of empty voids in glassy polymers by use of axisymmetric cell analyses. Ognedal et al. (2014) studied decohesion and volume growth in a mineral-filled PVC using a 3D model to resemble a polymer matrix with spherical particles. For the study of elastomers, Bergström and Boyce (1999) looked at how shape, dimension, and stiffness of carbon black particles altered the resulting equilibrium behavior on the macro scale.

Although the matrix-particle debonding effect in elastomers is experimentally documented in the literature, the implications this have for the macroscopic mechanical response has gained limited attention. In this paper, commercial hydrogenated nitrile butadiene rubber (HNBR) and fluoroelastomer (FKM) materials commonly applied for sealing applications in the oil and gas industry are tested in UT and CAC to investigate the difference in volumetric behavior. To examine the source of the volume growth observed in the UT experiments, an in situ SEM study of tensioned specimens was performed. A single-particle model was then used to see if the behavior observed in the macroscopic experiments could be explained based on micromechanical effects. No study could be found in the literature neither dealing with the volumetric behavior of HNBR and FKM elastomers nor debonding or cavitation around particles in such materials. In addition, to the best of the authors' knowledge, single-particle models have not yet been used to study the loading mode dependent volume behavior of particle-filled elastomeric materials.

The paper is organized as follows: The set-up and results for the UT and CAC macroscopic experiments are presented in the following section. Implications of the findings for constitutive modeling of particle-filled elastomers are discussed in Section 3. In Section 4, the set-up and results of the in situ SEM study on the materials are given, while Section 5 studies a single-particle model to explain the macroscopic experimental results in a qualitative manner. In the final section, a summary and some concluding remarks are given.

Table 1
Tested materials, their geometries and properties.

Material	Geometry	Density	Temperature range	Hardness
HNBR	ISO 37 - Type 1	1.29 g/cm^3	−35 to 150 °C	86 shore A
FKM	ISO 37 - Type 2	1.77 g/cm^3	−40 to 200 °C	89 IRHD

2. Macroscopic experiments

2.1. Uniaxial tension

2.1.1. Set-up

For the UT tests, one HNBR and one FKM compound commonly used for sealing applications in the oil and gas industry were delivered from two different suppliers as 2 mm thick dog-bone shaped tension specimens with dimensions in line with ISO37 Type 1 and Type 2 respectively (ISO, 2011). The gauge length of the Type 1 specimens applied for HNBR is 33 mm, while the corresponding length of the Type 2 FKM samples is 25 mm. The specimens were cut from 2 mm thick mats produced by a rolling process. The two materials, their dumbbell geometry, the measured pre-testing density, and the temperature range and hardness values given in the materials data sheets are listed in Table 1. According to the suppliers, the lower bound of the temperature range indicates the temperature for which the materials have fully transitioned into the glassy region.

The specimens were tested using an Instron 5944 testing machine with a 2 kN load cell. The deformation cycle addressed herein exposed the test samples to a maximum machine displacement of 40 mm followed by an immediate unloading until zero force was measured by the load cell. A deformation rate of 1 mm/s was used during both loading and unloading which corresponds to a nominal strain rate of 0.03 s^{-1} for the HNBR material and 0.04 s^{-1} for the FKM.

While the force level F was measured by the load cell of the machine, optical means were used to determine the local deforma-