Polymer 54 (2013) 1190–1196

Contents lists available at SciVerse ScienceDirect

Polymer

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

Necking in fumed silica filled poly(dimethylsiloxane) and the resulting mechanical properties of the necked material

Oluwaseyi Ogebule, Grigori A. Medvedev, James M. Caruthers*

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA

ARTICLE INFO

Article history:
Received 12 November 2012
Received in revised form
19 December 2012
Accepted 22 December 2012
Available online 31 December 2012

Keywords:
Necking
Fumed silica
Poly(dimethylsiloxane)

ABSTRACT

Necking is a well known phenomenon in uniaxial extension of filled and unfilled semi-crystalline polymers as well as amorphous polymers below their glass transition temperature; however, necking has not been observed for elastomers. For the first time necking is observed for a lightly cross-linked poly(dimethylsiloxane) elastomer filled with 30 phr or more of high surface area ($\geq$300 m^2/g) fumed silica. A series of linear and nonlinear mechanical properties of the necked material were studied including (i) linear and nonlinear dynamic shear analysis including the Payne effect, (ii) uniaxial tension experiments including the Mullins effect, (iii) tensile strength, and (iv) tear resistance via the 'trouser' test. The tensile strength of the necked material was found to be significantly higher than that for non-neck forming systems. The observed necking behavior is consistent with deformation induced aggregate breakage.

1. Introduction

Filled elastomer systems are engineering materials with enhanced mechanical properties, including higher modulus, improved tensile strength, and greater tear resistance as compared to the unfilled elastomer. The nonlinear mechanical behavior of filled elastomers is quite complex exhibiting (i) stress–strain behavior with stress softening in cyclic uniaxial and shear deformations (i.e. the Mullins effect) [1–4], (ii) dynamic modulus that depends upon the strain amplitude and loading history (i.e. the Payne effect) [1,2,5,6], and (iii) a variety of other nonlinear effects [1,2]. A number of mechanisms have been proposed to explain these effects as well as the primary effect of filler reinforcement [1–3,5–13]; however, a fundamental understanding remains incomplete. There have been numerous studies of the large deformation behavior of filled elastomers including fumed silica in PDMS systems [13–23], where the review articles by Diani et al. [3] and Heinrich et al. [9] contain extensive references to papers where the properties of polymer and filler were varied and the resulting mechanical response investigated.

The work in this communication is part of a larger study of the mechanical properties of silica filled poly(dimethylsiloxane), PDMS, elastomer systems, where the time-dependent, nonlinear mechanical behavior is being investigated as a function of the composition of the filled elastomers. In the course of this study, an unanticipated necking phenomenon was observed for specific fumed silica filled PDMS systems. The resulting mechanical properties and the composition requirement for necking in these elastomer systems are the focus of this communication. Although there have been numerous studies of the nonlinear mechanical properties of PDMS filled with both carbon black and fumed silica particulates [13,16,18–23], to the best of our knowledge this is the first time that necking has been reported for silica filled PDMS or, more generally, for any unfilled or filled elastomer system. As will be discussed in this paper, the conditions for necking are (i) a high filler surface area (which is equivalent to small primary particles), (ii) filler aggregates with high structure and (iii) strong bonding between the filler surface and the polymer. We believe that this specific set of compositional requirement has not been met in previous studies of particulate elastomer systems.

In this paper we will report on fumed silica filled elastomers that can exhibit necking, including the nonlinear stress–strain behavior, dynamic mechanical response, tensile strength, and tear resistance of these filled elastomers. The paper is organized as follows: In the Experimental Section the filled elastomer synthesis and the mechanical testing setups are described. In the Results Section the formation of a neck as the filled elastomer is subjected to uniaxial tension test is presented as well as the mechanical characterization of the necked material. Finally, in the Discussion section a possible mechanism responsible for the necking behavior will be proposed.

* Corresponding author. Tel.: +1 765 494 6625.
E-mail address: caruther@ecn.purdue.edu (J.M. Caruthers).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.12.065

2. Experimental

The elastomer was trimethylsiloxy-terminated PDMS (DMS-T72, Gelest Inc) with a kinematic viscosity of 2 million cSt and a weight average molecular weight of greater than 500,000 g/mol as reported by the manufacturer. Evonik, Inc provided hydrophilic, pyrogenic fumed silica with varying surface areas as given in Table 1, where the surface of the fumed silica is hydroxylated and consequently interacts with the PDMS primarily via hydrogen bonds. The surface area of the hydrophilic silica ranges from 50 to 380 m^2/g. The PDMS was cured using dicumyl peroxide (DCP) at 1 phr (parts of DCP per 100 parts by weight of rubber).

The PDMS and silica were mixed in a Brabender internal mixer for 10 min followed by several passes through a two-roll mill for an additional 10 min, during which time the DCP was added. The mixture was then molded in a hot press (Carver Inc.) at 170 °C under a pressure of 15,000lbs for 90 min to produce a square sheet (100 mm × 100 mm × 3 mm) of the silica filled PDMS. Test specimens were then cut from this sheet. Various compositions of fumed silica filled PDMS elastomers test specimens were manufactured using this procedure.

Room temperature tensile tests were performed at a constant extension rate of 50 mm/min (i.e. a strain rate of approximately 0.01 s^{-1}), using an Instron 5567 testing instrument with a ±1000 N load cell. The axial strains were determined using an Instron Advanced Video extensometer unless specified otherwise. This setup was also used to measure the (i) tensile strength and (ii) tear resistance using the trouser test geometry. The standard sample dimensions for the tensile testing were 60mm × 4.4mm × 2.5mm, and the dimensions for preparing the 'necked' samples were 57 mm × 19.6 mm × 3.3 mm. The stresses reported are engineering stresses and the strains reported in % are $(l/l_o - 1) \times 100\%$.

Dynamic experiments were performed using a Dyanstat dynamic mechanical tester using a double shear sandwich test fixture. Payne experiments at strain amplitudes from 0.01 to 10% were carried out at room temperature at a constant frequency of 1 Hz. The sample dimensions for the Dynastat shear testing are 15 mm × 15 mm × 3 mm.

3. Results

Stress–strain curves in uniaxial extension are shown in Fig. 1 for PDMS filled with 40 phr of particulate silica for four different surface area fumed silica. The OX50 and A150 filled systems exhibit the well known stress–strain behavior of highly filled elastomers. Specifically, upon the first loading the stress–strain curve exhibits a tangent modulus that decreases from the initial value up through moderate deformations; subsequently, the modulus begins to exhibit strain hardening at large deformations. Upon unloading of the OX50 and A150 filled materials, there is a dramatic decrease in the stress, where the tangent modulus of the unloading curve can be an order-of-magnitude greater than the modulus just prior to unloading. The difference between the loading and unloading

Table 1
Properties of untreated fumed silica.

Silica	Surface area (m^2/g)	Ave. particle size (nm)
OX50	50	40
A90	90	20
A150	150	14
A200	200	12
A300	300	7
A300SP	300	7
A380	380	–

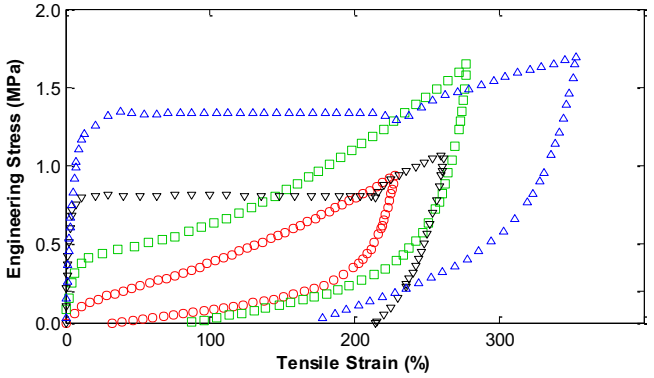

Fig. 1. Stress–strain behavior for various surface area 40 phr fumed silica filled PDMS elastomers systems. OX50 – circles; A150 – squares; A300 – down triangles; A380 – up triangles.

stress–strain curves results in considerable hysteresis, and upon unloading to zero stress there is a significant 'permanent' set in the material, where most of the 'permanent' set can be recovered upon resting for sufficient time in the load free state. The deformation of the OX50 and A150 test specimens is spatially uniform. In contrast to the stress–strain behavior exhibited by the OX50 and A150 filled systems, both the A300 and A380 filled PDMS exhibit a pronounced decrease in local cross-section area when subjected to uniaxial tension, which gradually extended to the entire specimen length between the grips, i.e. a neck is formed and propagates. The stress–strain response for the A300 and A380 filled PDMS systems is characterized by three distinct regions: (i) an initial region of rapidly rising stress, (ii) a region where the axial force (or equivalently the engineering stress) is constant until the necking reaches the grips and (iii) a region where stress increases again corresponding to further deformation of the necked material. A specimen that undergoes necking does not recover its original shape upon resting in the load free state even when the material is allowed to relax for several days at 100 °C. For the A380 filled PDMS material, the strains in Fig. 1 were measured using the crosshead displacement as the video extensometer failed after the necking started; consequently, the post necking portion for A380 stress–strain curve may also include necking that is continuing to occur within the gripped parts of the specimen. Neck formation was only observed for fumed silica filled PDMS with particulates having 300 or 380 m^2/g specific surface area. The role of the degree of cross-linking was also investigated, where 35 phr A380 filled PDMS materials cured with 0.5 phr DCP and 2 phr DCP were also prepared. The 0.5 phr DCP specimen exhibited brittle failure prior to any necking and the 2 phr DCP specimen did exhibit necking which was much less pronounced than the one in the case of the 1 phr DCP sample (see Supplementary information for details).

The stress–strain behavior of the necked material is shown in Fig. 2 for a 35 phr A380 filled PDMS specimen, where the primary question is if any more necking on top of the original necking occurs. The procedure for testing of the necked material in uniaxial deformation involved: (i) releasing the original specimen that underwent necking from the grips, (ii) cutting a new test specimen from the neck region, and (iii) re-gripping this specimen in the Instron test instrument. The strain in the necked material shown in Fig. 2 is defined as $\varepsilon = \Delta l/l_o$, where Δl is the change in length and l_o is the initial specimen length, which is new for each specimen. The stress–strain curve of the virgin material (solid line) has a characteristic flat region corresponding to neck formation and growth similar to the one seen in Fig. 1. The stress–strain curve of the specimen cut from the necked portion of the original sample does not have a flat region as shown in Fig. 2 (circles). When this specimen is released and re-