Available online at www.sciencedirect.com
ScienceDirect
Polymer Degradation and Stability 92 (2007) 2011–2015
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

On the degradation and stability of high abrasion furnace black (HAF)/acrylonitrile butadiene rubber (NBR) and high abrasion furnace black (HAF)/graphite/acrylonitrile butadiene rubber (NBR) under cyclic stress–strain

Waleed E. Mahmoud*, S.A. Mansour, M. Hafez, M.A. Salam

Suez Canal University, Faculty of Science, Physics Department, Ismailia, Egypt

Received 19 June 2007; received in revised form 28 July 2007; accepted 1 August 2007
Available online 15 August 2007

Abstract

Acrylonitrile butadiene rubber (NBR) compounds filled with 40 phr of high abrasion furnace black (HAF) and HAF (20 phr)/graphite (20 phr) were experimentally investigated. The stress–strain curves of the composites were studied, which are described by applying Ogden's model. The effect of cyclic fatigue and hysteresis was also examined. The dissipation energy that indicates the vibration damping capacity for all samples was determined. A continuum damage model is used to investigate the fatigue damage behavior for elastomers. Experiments on the cyclic fatigue of a carbon-filled NBR rubber and carbon/graphite filled NBR rubber were conducted to determine the relation between the number of cyclic fatigue and the strain amplitude. The results indicate that the theoretical formula for the number of cyclic fatigue as a function of the strain amplitude, derived from the damage model, can describe experimental data for the prepared samples very well.

Keywords: Cyclic stress–strain; Graphite; Ogden model; Mahmoud model

1. Introduction

Carbon fillers are regularly employed in the production of polymer composites to enhance electrical conductivity and mechanical properties, as well as to maintain light weight and corrosion resistance. Conductive carbon fillers of current commercial relevance include carbon black, graphite and carbon fiber, which differ greatly in both structure and form. When a rubber component filled with carbon black is under loading, the rubber matrix around carbon black is strained more than the rest. If a large or repeated force is applied under strain control and then unloaded, subsequent extension to the same strain requires a lower force. Further cycling results in continued softening at a progressively slower rate and a steady state may be reached. This softening phenomenon is an important indication of the amount of energy that the material can continue to absorb. This is generally known as the Mullins' effect [1], especially when considering rubbers. This softening affects the electrical as well as the mechanical properties of rubber samples. The present work represents a comparison study for the effect of cyclic stress–strain on the microstructure of rubber loaded carbon black (40 phr) and rubber loaded carbon black (20 phr) and graphite (20 phr), specially when those samples are used as a mechanical sensor.

2. Experimental

2.1. Materials and processing

Acrylonitrile butadiene rubber (NBR) (density 0.98 g/cm^3 and acrylonitrile content 32%) was used as polymer matrix.

* Corresponding author. Tel.:+2 016 2277227.
E-mail address: w_e_mahmoud@yahoo.com (W.E. Mahmoud).

0141-3910/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2007.08.005

High abrasion furnace (HAF) carbon black (29 nm particle size diameter, dibutyl phthalate absorption number (DBPA) 121 $cm^3/100$ g and 45 m^2/g surface area), graphite (40 nm particle size diameter and density 2.1 g/cm^3) were used as reinforcing fillers. Other compounding ingredients like zinc oxide and stearic acid (activators), dibenz thiazyl disulphide (MBTS) semi-ultra accelerator (vulcanization time 30 min at temperature 150 °C), phenyl-β-naphthyl-amine (PBN) antioxidant (melting point 105 °C), dioctyl phthalate (DOP) plasticizer and sulfur (vulcanizing agent) were used. These materials were supplied by Bayer Company (Germany) and used as received. These materials were compounded according to the recipe listed in Table 1.

For the compounding a home made two-roll mixing mill (length 0.3 m, radius 0.15 m, speed of slow roll 18 rpm and gear ratio 1.4) was used. The mixing occurred for 40 min at a temperature of 25 °C. The compounded rubbers were compression molded into cylinders of 1×10^{-4} m^2 area and 0.01 m in height. The vulcanization was conducted under a heating press (KARL KOLB, Germany) at a pressure of $P = 0.40$ MPa. The optimum conditions of temperature and time were $T = 150$ °C and $t = 30$ min. The vulcanized samples were shelf aged for 48 h before test. The mixing time and vulcanization conditions were fixed for all samples.

2.2. Mechanical measurements

The stress–strain behavior in case of uniaxial extension was measured at room temperature by using a material tester (AMETEK, USA), which was connected by a digital force gage (Hunter Spring ACCU Force II, 0.01 N resolutions, USA) to measure stress forces. The force gage was interfaced with computer to record the obtained data. The stress–strain behavior was measured at a strain rate of 0.1/s.

3. Results

3.1. Stress–strain behavior and strain energy density

Fig. 1 depicts the stress–strain curves for carbon black (40 phr) dispersed in the NBR matrix and carbon black (20 phr)/graphite (20 phr) dispersed in the NBR matrix. The stress–strain curves were fitted by the Ogden model [2], Eq. (1), and plotted in Fig. 1.

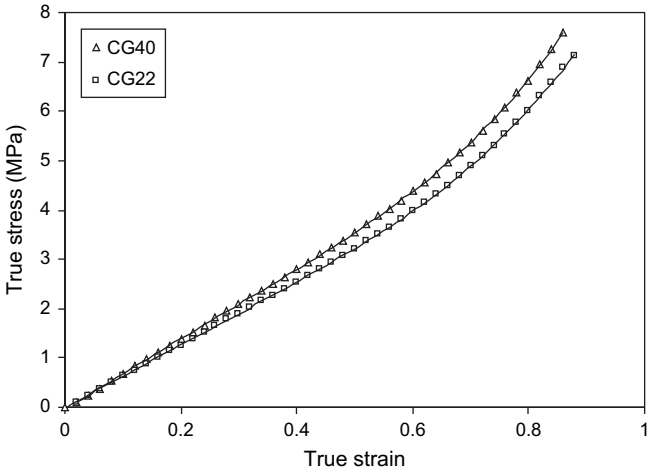

Fig. 1. True stress vs. true strain for the prepared samples. The solid line represents the data fitting by Ogden equation.

$$\sigma_w = \frac{\partial W}{\partial \lambda} = \frac{2\mu_1}{\alpha_1}\left(\lambda_w^{\alpha_1 - 1} + \lambda_w^{-\left(\frac{\alpha_1}{2}+1\right)}\right) = \frac{2\mu_1}{\alpha_1}\left([1+\varepsilon]^{\alpha_1 - 1} + [1+\varepsilon]^{-\left(\frac{\alpha_1}{2}+1\right)}\right) \quad (1)$$

where σ_w is the uniaxial stress, ε is the strain in the loading direction, λ_w is the stretch in loading dimension, μ_1 represents the shear modulus and α_1 is a material parameter depending on the host polymer. These two parameters can be determined by fitting experimental stress–strain curve. It was found that the fitting parameters μ_1 and α_1 are 2.07 MPa and 2.4 for sample CG_{40} and 2.05 MPa and 2.4 for sample CG_{22}, respectively.

The energy absorbed per unit volume (W) in deforming the rubber composites to a strain ε is simply the area under the stress–strain curve and can be written as [3]

$$W = \oint \sigma(\varepsilon)\mathrm{d}\varepsilon \quad (2)$$

where $\sigma(\varepsilon)$ is the stress as a function of the strain. Obviously, the higher the stress–strain curve, the higher the energy absorption capacity. As shown in Fig. 1, the energy absorbed by sample CG_{40} was 3.12 MJ/m^3 at 88% strain, while that absorbed by sample CG_{22} was only around 2.74 MJ/m^3.

3.2. Cyclic loading and unloading and energy dissipation

Fig. 2a and b show the experimental true stress–true strain behavior during the cyclic loading–unloading tests with $\varepsilon_{max} = 0.88$ for the prepared samples CG_{40} and CG_{22}. Several features are observed. First, the cyclic stress–strain curves for sample CG_{40} are displaced by a large rate from the first cycle compared with sample CG_{22}. This means that the softening behavior for sample CG_{40} is greater than that observed in

Table 1
Ingredients of the investigated NBR rubber composites

Sample ingredients (phr)[a]	CG_{40}	CG_{22}
NBR	100	100
Stearic acid	2	2
Zinc oxide	5	5
FEF	**40**	**20**
Graphite	–	**20**
DOP	10	10
MBTS	2	2
PBN	1	1
Sulfur	2.5	2.5

[a] Part per hundred parts of rubber by weight.