Composites: Part B 60 (2014) 555–560

Contents lists available at ScienceDirect

Composites: Part B

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

Structural modelling and stiffness of filled elastomers

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ARTICLE INFO

Article history:
Received 23 January 2013
Accepted 3 January 2014
Available online 9 January 2014

Keywords:
A. Particle-reinforcement
B. Microstructures
C. Computational modelling
Atomic force microscopy

ABSTRACT

A realistic model of spatial arrangement of fillers in the rubber matrix is developed. The structural parameters of the model such as the distribution of filler sizes, the fractal characteristics of clusters (agglomerates) and the presence of large dense particles (micropellets) are taken from the AFM-images of carbon black filled styrene–butadiene vulcanizates. A descriptor of filler distribution in the matrix, namely an index of heterogeneity, is proposed. The analysis of stiffness of synthesized 3D-structures allows us to determine the minimal representative size of the constructed systems and to judge the validity of various model simplifications (e.g., fillers of equal size or random arrangement, lack of micropellets, etc.).

1. Introduction

The addition of active fillers to a rubber matrix leads to significant reinforcement of composites. It is manifested as an increase in toughness, durability of elastomers and leads to a longer service life, whereas their elasticity and ability to multiple reversible deformations caused by stretching remain unchanged. This is mainly due to strong interphase physicochemical interactions proceeding in the composite. Filled elastomers are heterogeneous materials. A continuous filler network is formed in the material by the branches of fractal clusters even at a relatively low filler volume fraction of ~12%.

Literature surveys show that most authors use in their studies the percolation or kinetic models of filler networks [1]. According to the percolation theory, the composite structure is formed by the incorporation of filler units (particles or aggregates) into the arbitrarily chosen cells of a spatial network. The major parameter of the model is the fraction of occupied cells (percolation exponent). When this value exceeds the percolation threshold, the continuous structure of clusters emerges. Significant contributions and accomplishments based on this theory were made by Kraus' [2], Kantor and Webman [3], Lin (a Links-Nodes-Blobs model) [4], etc. The concepts of the percolation theory are successfully used to describe the mechanical behaviour of highly filled rubbers at small strains, but the percolation exponent cannot be determined experimentally. Moreover, the structures arranged by the cells of uniform network consist of large and loose clusters.

Kinetic models are based on the assumption that the filler inclusions fluctuate around their middle position in the matrix until they stick to others. When the filler fraction exceeds some critical value, a continuous network of clusters is formed. A further increase in the filler concentration causes a reduction of cluster sizes (based on the percolation theory, the cluster is growing) [5,6].

In all these cases, the parameters of the models are chosen by fitting or from the general theory of composites with periodic or aggregated structures and the research usually limited to the study of the small volumes of the material or interactions in a single cluster then obtained results are extrapolated to the whole composite. However, below we will show that the non-uniform size of inclusions and heterogeneous arrangement in the matrix lead to high fluctuation of stiffness in small structural volumes.

There are a lot of publications devoted to the study of the mechanical and fracture mechanical properties of particle reinforced composites. A detailed review of the literature on this topic can be found in recent article by Fu et al. [7]. The accurate knowledge of the local structure is decisive for the understanding of the material behaviour. More geometrical information is required to model their behaviour related to the arrangement of filler inclusions in fractal agglomerates. The present work focuses on the solution of this problem. The first stage of our investigation involves the calculation of the stiffness of the structure as a function of parameters of the model.

To predict the macroscopic response of the composite under loading, the model should reflect the peculiarities of the microstructure and demonstrate the interactions between neighbour

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http://dx.doi.org/10.1016/j.compositesb.2014.01.002

inclusions. The modern computers make possible to directly model a representative volume of the filler network under some external loading. A starting point for such simulations must be information about filler geometry and arrangement in the polymer matrix. The new methods of analysis of atomic force microscope (AFM) images of filled rubbers developed recently [8,9] allowed us to determine the filler geometry and parameters of clusters. This paper focuses on a method for computer synthesis and analysis of spatial filler networks. Input parameters for the model are taken from the structural analysis of AFM-images of filled styrene–butadiene rubbers (SBR).

In this paper we investigated the stiffness of the modelled structures as a function of the filler fraction, size of representative volume, random or cluster filler arrangement, and size of inclusions. Much attention is paid to the estimation of a minimal reliable size of the structure (mesoscale) to ensure that consideration is given to a typical representative volume element.

2. Material and methods

In order to obtain input parameters for the model, SBR filled with carbon black (CB) N222 were prepared as follows. The mixing process consisted of two steps. First, a certain amount of SBR and 2 phr of stearic acid and 3 phr of zinc oxide were mixed for 5 min at 140 °C. The content of CB of 10, 30 and 50 phr (grams of carbon black per 100 g. of polymer) corresponds to the volume fractions of 0.04, 0.13 and 0.21, respectively. Mixing time at this stage was 180 s. The additional sample with 50 phr of filler prepared using increased mixing time – 360 s. Then, the obtained SBR compound was mixed with 1.5 phr of sulphur and 1.0 phr of two types of accelerator (N-tert-butyl-2-benzothiazolesulphenamide and N,N′-diphenyl guanidine) at 80 °C using a two-roll mixing mill. The obtained rubber was vulcanized in a press mould at 170 °C for 12 min. All these four samples will be further labelled as SBR/10, SBR/30, SBR/50 and SBR/50_t.

Experiments for the structural investigation were carried out with an AFM *Bruker Icon*. The surfaces of the materials were prepared with cryo-ultramicrotome *Leica UC7* at −90 °C. For each specimen, several AFM-images of the size 20 × 20 μm with resolution in *xy*-plane 1280 × 1280 were obtained. The images were further analyzed using our algorithms developed in *Matlab*. Example of AFM-image of SBR/30 compound is presented in Fig. 1a.

Examination of the AFM-images reveals that the surface of the filled rubber sample is rough and has a lot of local minima and maxima. Thus, one can suppose that the inhomogeneous surface of the filled rubber is the visible part of the filler dispersed in a rubber compound. In further analysis, the algorithm of image segmentation developed in previous works was used [9].

The algorithm involves next steps. Step 1: Find any local maxima of the surface under study (vertices of future segments). Step 2: Examine the contour lines around the obtained maxima and determine the boundaries of segments. Hence, the continuous relief was divided into the separate segments (Fig. 1b). Step 3: Identification structural parameters and of fractal clusters (Fig. 1c).

Examination of the sizes and shapes of segments allowed us to define two types of inclusions in the polymer: (1) micropellets – segments of size (300 nm and compactness $\geqslant$0.85; (2) filler aggregates – for the rest of segments. Compactness is an area-perimeter ratio with respect to the circle, for which this value is equal to unity.

The importance of separation of rigid inclusions as aggregates and micropellets can be explained as follows. It was experimentally observed that there are cracks in the vicinity of large inclusions on the surfaces of stretched filled rubber. We suppose that such micropellets are not CB but zinc oxide or dust particles with weak interaction with polymer. Other micropellets could not show detachment of polymer during elongation of material. However, in stretched state the shape of such inclusions changes only slightly [9]. We assume that these are unbroken carbon black granules. Concentration of the filler in such form reduces their contact area with the polymer.

In the following we introduce several notations: (1) fraction of micropellets φ_{PEL}: ratio between the area of segments detected as micropellets and the total area of segments. (2) Average size (diameter) and area of aggregates d_{AG}, A_{AG}; and average size of micropellets d_{PEL} (area of micropellets is not used in this study).

To quantify the filler distribution (non-spherical objects of different sizes) in the observed areas (Fig. 1b), the heterogeneity index, J, is introduced. This value indicates the size s of the window, where the filler arrangement is assumed to be homogeneous and can be calculated as: the sufficient number m of squares with side s are chosen in the examined image, and $J(s)$ is defined as

$$J(s) = 0.5\lfloor \min_{i=1\ldots m}(\phi_i(s)) + \max_{i=1\ldots m}(\phi_i(s))\rfloor/\phi^*, \quad (1)$$

where $\phi_i(s)$ is the fraction of filler segments in the ith square sxs; ϕ^* is the fraction of filler segments in the entire image.

The closer the value of $J(s)$ is to unity, the more homogeneous the distribution of the filler throughout the material. The value of s^*, from which $J(s)$ substantially deviates from unity, can be regarded as a critical scale (mesoscopic scale); for any scale $s \geqslant s^*$, the filler distribution can be considered as homogeneous.

The segmented surfaces (Fig. 1b) are not homogeneous. It is seen that these surfaces have high filler concentration regions connected by branches, i.e., the visible parts of spatial secondary structures (agglomerates or clusters). The number of primary structures (aggregates), N, is related to the size (average diameter) of clusters, d_{CL}, by the fractal distribution law as

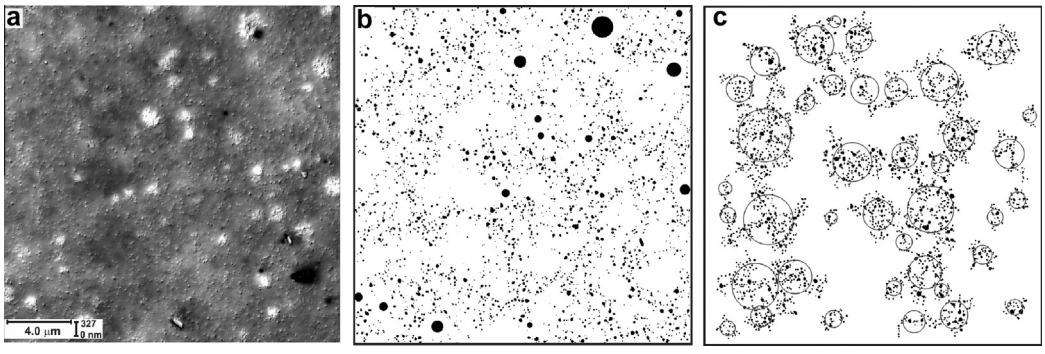

Fig. 1. Height AFM-image of the surface of SBR/30 (a); result of segmentation (b); detected clusters with corresponding sizes (c).