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Image analysis of the microstructure of magnetorheological elastomers

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Abstract The results presented refer to the structure analysis of magnetorheological elastomers (MREs), based on ferromagnetic particles in a polyurethane matrix. The influence of the volume fraction of the ferromagnetic particles on their arrangement in relation to the external magnetic field was investigated. The amount of carbonyl iron particles, of the average size 6–9 μm, varied from 1.5 to 33 vol.%. Scanning electron microscopy was used to observe magnetorheological elastomer microstructures. Image analysis has been applied to describe the microstructures. From author's previous studies it is known that the microstructure anisotropy has significant effect on the properties of magnetorheological elastomers. Two different techniques of image analysis: skeleton by influence zone method and linear covariance function were used to reveal the anisotropy in particle arrangements. These methods allowed quantitative microstructure description. The results show that particle arrangement changes with their volume fraction. The analyses confirm particle chain networks in composites with higher iron content. Differences in particles arrangement for samples prepared under diverse conditions were also clearly shown.

Introduction

Magnetorheological elastomers (MREs) are solid analogues of magnetorheological fluids (MRFs). These two consist of micrometer-sized magnetically permeable particles in a non-magnetic matrix. Magnetorheological elastomers are considered smart materials, since their properties can be reversibly changed and controlled by the application of an external magnetic field.

The ferromagnetic particles in MRE as in the MRF arrange themselves in the direction of the magnetic field [1–3]. The advantage of MRE over MRF is that ferrous particles in the former do not undergo the sedimentation. Also, to obtain similar properties the amount of the particle filler can be lower in MREs. As a result, the weight of sensing and actuating devices based on MREs is lower. Interest in MREs has increased recently in view of applications in variable-stiffness devices, adaptive structures in aerospace, automotive, civil and electrical engineering systems [4].

Different elastomers and magnetic particles can be used for fabrication of MREs [5, 6]. A strong external magnetic field is applied during the polymer curing process. The field induces dipole moments within the particles, which relax into minimum energy states. Particle chains with collinear dipole moments are formed and curing of the polymeric host material locks the chains in place [7, 8]. The particles can form separate chains, three-dimensional structures consisting of individual chains, or more complex structures, in which particles have multiple interaction points [9]. The obtained microstructures determine the magnetorheological properties of the composites.

It was found in the previous studies that fabrication conditions strongly influence on the microstructure and in the consequence on the magnetic, mechanical and rheological properties of MREs [10–12]. The aim of the present study was to quantify images of the microstructures of MREs to describe the anisotropy of particles arrangement as a function of the particles volume fraction, and the

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magnetic field applied during curing. To the author's knowledge such data has not been so far published.

Materials and methods

Soft polyurethanes (PU) were used as the matrix of magnetorheological elastomers. The substrates for PU synthesis were polyether polyol VORALUX® HF 505, 14922 polyol and isocyanate compound HB 6013, supplied by Dow Chemical Company. Mixing of substrates via mechanical stirring and curing process were conducted at room temperature. The PU obtained in this study was characterized by low values of the density (1.03 g/cm^3), viscosity before curing (ca. 1,600 mPa · s), hardness (below 10° ShA) and Young's modulus (below 0.1 MPa). Relatively low viscosity during the processing of the MRE makes the arrangement of the particles into chains relatively easy. Low stiffness of PU matrix renders the composites attractive rheological properties.

As a ferromagnetic filler, for the MREs fabrication, carbonyl-iron powder with particles size from 6 to 9 μm, produced by Fluka, was used. The amount of the carbonyl iron particles was equal to 1.5, 11.5, 18, 25 and 33 vol.%, respectively. The samples were subjected to a magnetic field of 0.3 T during curing to align iron particle into chains. Some samples were also cured using magnetic field strength of 0.1 T to verify the influence of a magnetic field strength on the anisotropy of particles arrangement. Microstructure observations were carried out on brittle fracture surfaces of MREs using scanning electron microscope.

Image analysis

Prior to quantitative analysis the image processing was performed. The original scanning electron microscope images (example see Fig. 1a) were transformed into binary (example see Fig. 1b), which depicted isolated iron particles (black) in the matrix (white). These binary images were subjected to image analyses.

The aim of the image analysis was to quantify spatial arrangement of the iron particles. Two methods were used to this end. The first method is based on the computer-aided technique of image processing known as SKIZ (skeleton by influence zone) [13]. This method generates granular structures, such as those shown in Fig. 1c. The 'grains' surrounding particles define the influence zones, i.e. sets of points whose distance from this particle is smaller than the distance from any other particle. The structure thus generated is subjected to a standard quantitative analysis, in which the distributions of grain sizes

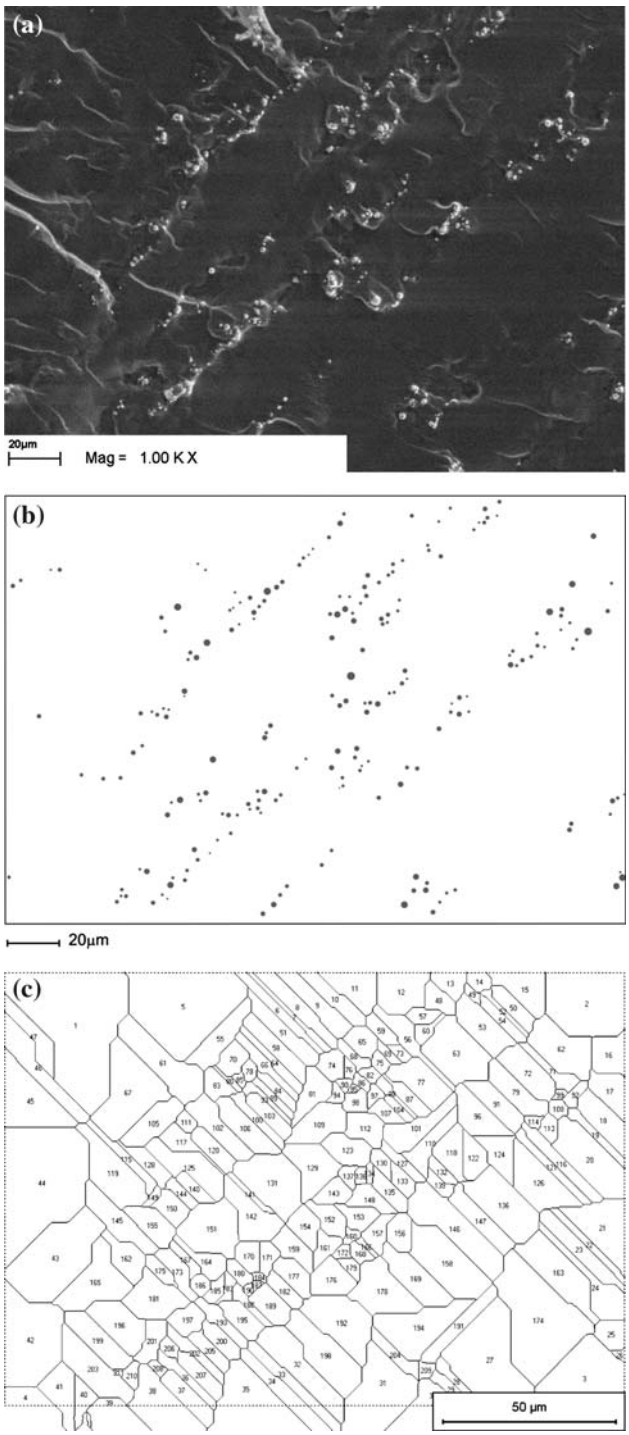

Fig. 1 An example of **a** original SEM image of brittle fracture surface (11.5 vol.% Fe), **b** its binary image, **c** image after SKIZ transformation

(influence zones) are determined. For each distribution obtained, we can determine several statistical values for equivalent diameters of the zones, such as the average, $E(d_2)$, standard deviation, $SD(d_2)$, variation coefficient, $CV(d_2) = SD(d_2)/E(d_2)$, etc.

The method described above is sensitive to clustering of particles. Dispersion of the area influence zones of the cluster-type structures is higher than in the structure with a random particle distribution. Distributions with $CV(d_2)$ below 0.5 were considered as typical of uniform particle spatial distribution. For $CV(d_2)$ above 0.5 the iron particles system was classified as cluster-type. This method has been applied to compare the anisotropy level for different samples and relate it to their properties. Five images for each type of sample were analysed.

The second method, used in these studies is based on the linear covariance function, defined as the average probability that both the plane P and the plane shifted by vector h intersect a given particle [14]. This method is sensitive to ordering of particles in the space.

In the case of a periodic structure, the linear covariance function has the form of a sequence of systematically repeated peaks. The spacing between the peaks corresponds to the spacing between the particle centres. With the uniform or cluster-type structure, the number of peaks decreases, and for the random structure the first peak which is directly related to the particle size can be observed. The covariance is very often determined along two directions: horizontal and vertical, and the directional covariance function is denoted as $C(x)$ and $C(y)$. This method has been used to determine the characteristic dimensions in different MRE microstructures like spacing between particle chains. The analysis has been performed on typical microstructures.

Results and discussion

Scanning electron microscope images shown in Fig. 2 exhibit the influence of particles volume fraction on the MREs microstructure. The lower fractions (1.5 and 11.5 vol.%) under the magnetic field lead to the formation of chains consisting of iron particles, which are very well visible in scanning electron microscope images (Figs. 1a and 2a). The spaces between individual particle chains seem to be bigger for the lower content of particles. Higher particles volume fraction (33 vol.%) results in more complex particles arrangement, typical of isotropic three-dimensional network of particles. Such a microstructure is caused by the magnetic dipoles, interacting under the magnetic field [15].

The existence of structural anisotropy for the samples with 1.5–25 vol.% Fe was confirmed by magnetic measurements carried out in the direction parallel and perpendicular to particles chains. An example of hysteresis loops, showing the magnetic anisotropy, obtained using Lake Shore Vibrating Sample Magnetometer is shown in Fig. 3. For the sample with 33 vol.% Fe hysteresis loops obtained in the direction parallel and perpendicular were overlapped.

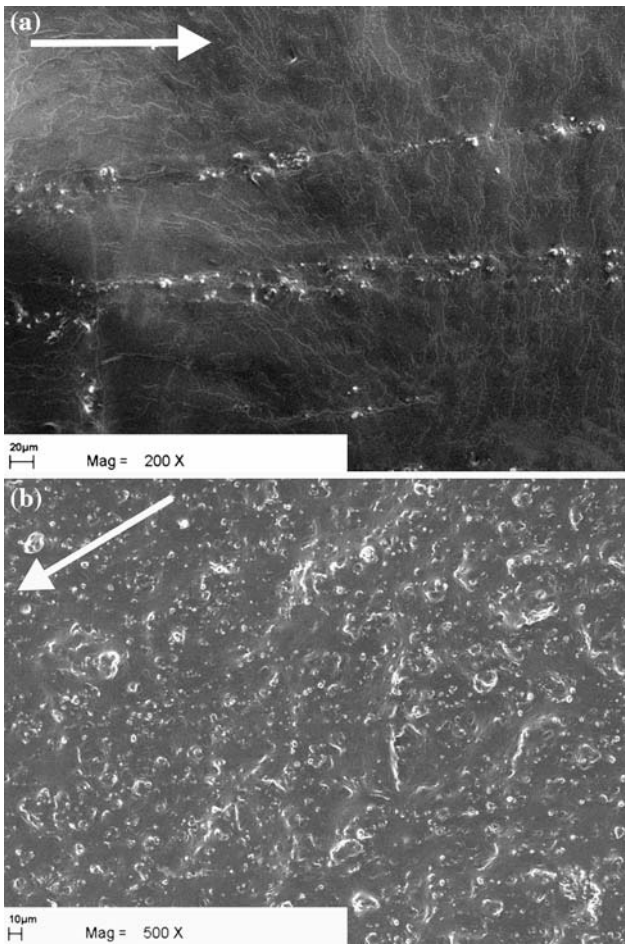

Fig. 2 SEM images of MREs with carbonyl-iron particles cured under magnetic field of 0.3 T: **a** 1.5 vol.%, **b** 33 vol.%. White *arrows* indicate magnetic field direction

The influence of particles volume fraction on the anisotropy of their arrangement has been quantified by image analysis. First SKIZ method was used, based on the computer-aided technique of image processing. The obtained values of variation coefficient, $CV(d_2)$ as a function of particles volume fraction is shown in Fig. 4.

The results indicate relatively high-uniformity of spatial distribution of particles. The highest $CV(d_2)$ value has been obtained for samples with the lowest amount of particles. The value of $CV(d_2)$ decreases with increasing particles volume fraction up to 18 vol.% Fe. This means that for lower volume fractions the non-uniformity of their arrangement is the highest. Clusters highly elongated are formed. For 1.5 and 11.5 vol.% Fe, chains of particles were observed in SEM images. The distance between chains decreases with the increase of particles volume fraction. For particles volume fraction in the range from 18 to 33 vol.%, the particle chains are close to each other, and finally for the highest volume fraction of particles an isotropic network is

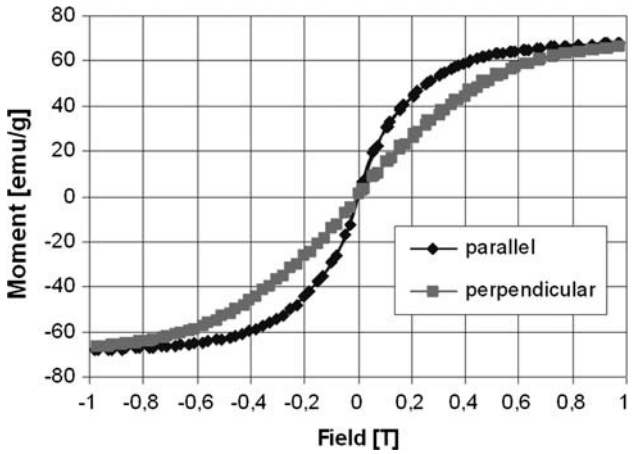

Fig. 3 Magnetic properties of MREs with 11.5 vol.% Fe, cured under magnetic field strength of 0.3 T

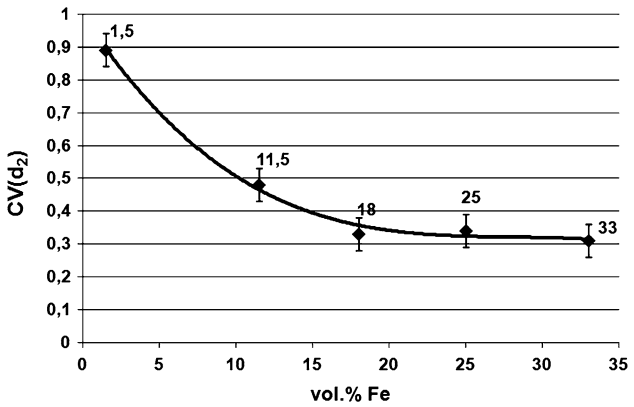

Fig. 4 CV(d_2) for different volume fraction of carbonyl-iron particles

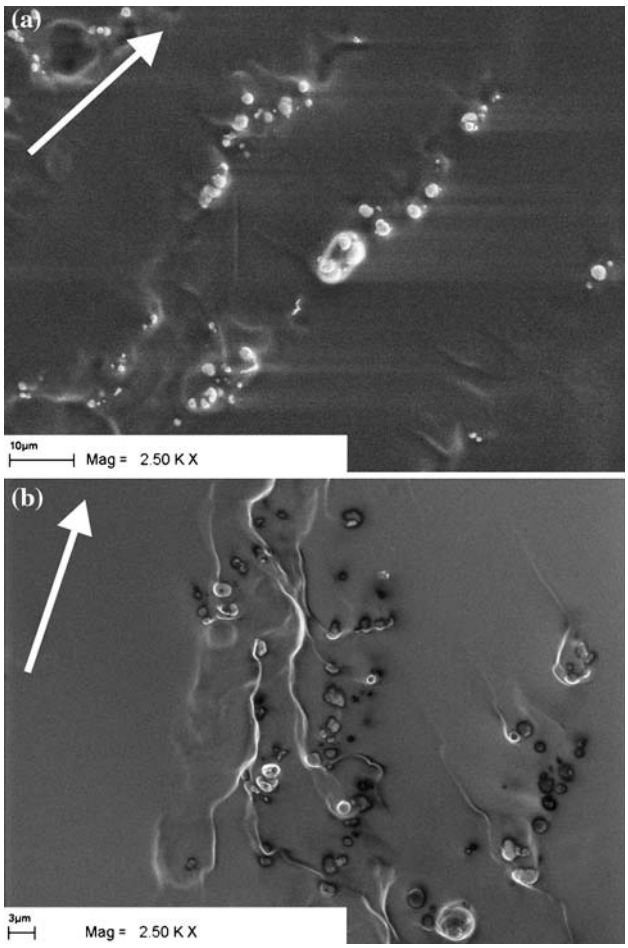

Fig. 5 SEM images of MRE with 11.5 vol.% of carbonyl-iron particles, cured under magnetic field of: **a** 0.1 T, **b** 0.3 T. White *arrows* indicate magnetic field direction

formed. This results also in a decrease of magnetic anisotropy for the MRE with 33 vol.% [11].

The effect of magnetic field strength on the MRE microstructure was also studied. The application of the 0.3 T magnetic field during curing leads to formation of wider particles chains, consisting of higher amount of particles. Spaces between chains are higher, as shown in Fig. 5.

By image analysis, it was confirmed that CV(d_2) depends on the magnetic field strength used during composite curing (see Fig. 6). Higher magnetic field leads to the higher non-uniformity of particles arrangement.

The covariance method was applied in two directions: parallel and perpendicular to the direction of the magnetic field used during curing. The obtained covariograms show changes in the particles distribution along the directions parallel and perpendicular to the direction of iron particle chains. Also the mean distance between particle chains can be measured between peaks. $C(y)$ curves correspond to the direction perpendicular to the particle chains and $C(x)$ to

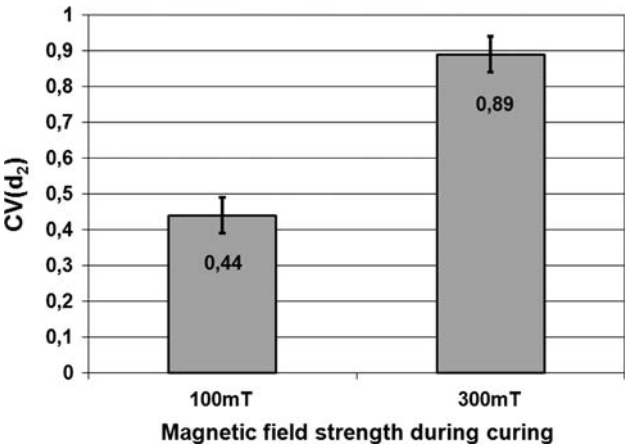

Fig. 6 CV(d_2) for samples with 1.5 vol.% Fe cured under different magnetic field strength

the parallel. Examples of covariograms for MREs containing different volume fraction of iron particles are given in Fig. 7.

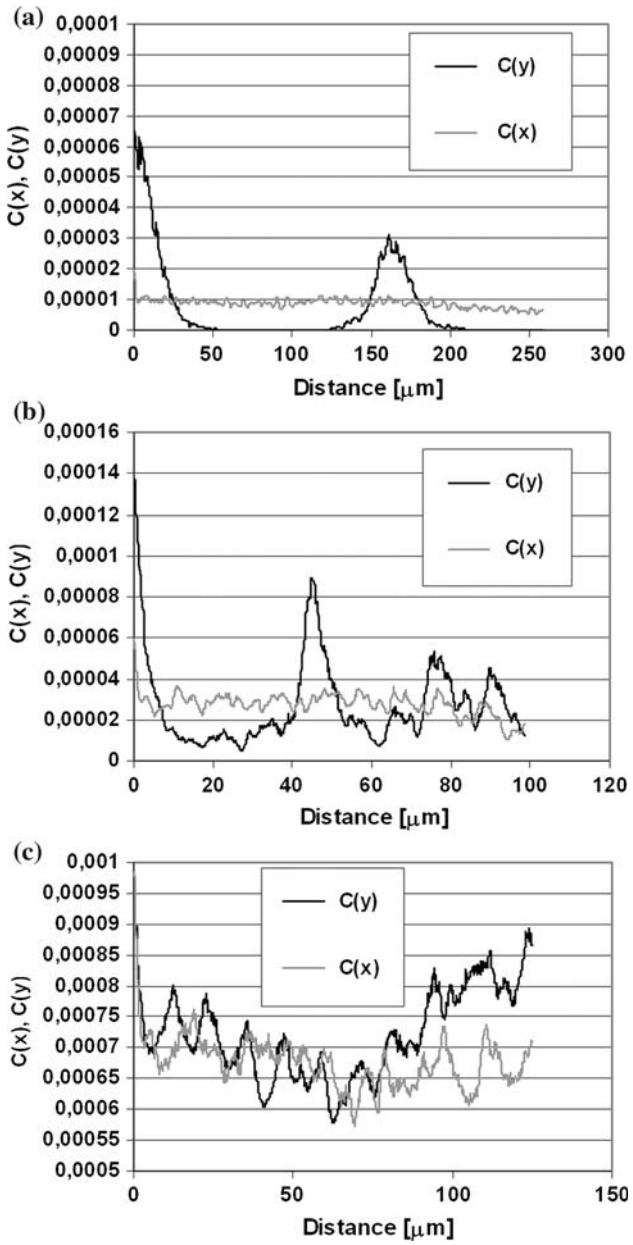

Fig. 7 Covariograms for samples with **a** 1.5, **b** 11.5, **c** 33 vol.% of Fe

For the samples with 33 vol.% of particles the microstructure resembles a network of parallel and perpendicular chains with mean distance between chains at about 15 μm.

In the case of the periodic structure, the linear covariance function has the form of a sequence of systematically repeated peaks. The spacing between the peaks corresponds to the spacing between the particle centres. With the uniform or cluster-type structure, the number of peaks decreases and for the random structure the first peak which is directly related to the particle size can be observed. Mean distances between particle chains have been calculated from selected covariograms for composites with 1.5, 11.5 and 33 vol.% of Fe (see Fig. 8). For 33 vol.% of Fe,

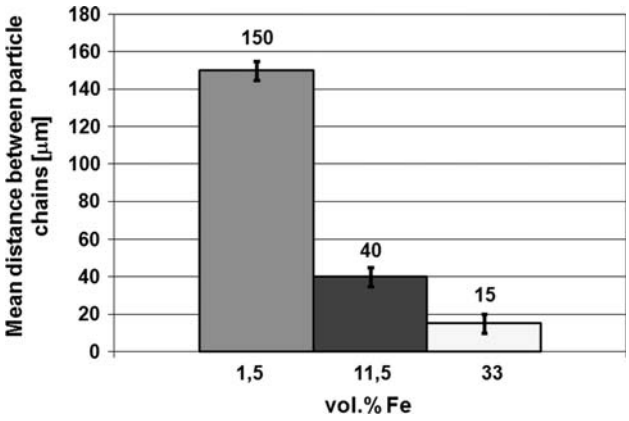

Fig. 8 Mean distance between particle chains for different particle amounts

the distance of 15 μm between chains corresponds with the 6–9 μm particle size.

Summary

Image analysis has been applied to describe the arrangement of particles in magnetorheological elastomers. Two different techniques of image analysis were employed: SKIZ method and linear covariance. This makes it possible to reveal the existence of non-homogeneity of particles arrangement anisotropy, which strongly influences the properties of composites. The results show that particle arrangement changes with the amount of the particles. The analysis results confirmed the existence of particle chain networks in composites with higher iron volume fraction. In the opposite, for lower particles volume fractions clusters highly elongated are observed. The applied methods enabled to determine characteristic distances between particle chains for different volume fractions. Differences in particles arrangement for samples prepared under diverse conditions were also clearly shown. The applied methods of image analysis are very promising, effective and provide useful description of the magnetorheological elastomers microstructure, which will be helpful in description of MREs microstructure-property relationships.

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