Polymer 147 (2018) 95–107

Contents lists available at ScienceDirect

Polymer

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

Dynamic-mechanical behaviour of anisotropic magneto-sensitive elastomers

Dmytro Ivaneyko [a, b], Vladimir Toshchevikov [a, c, *], Marina Saphiannikova [a]

[a] Leibniz-Institut für Polymerforschung e. V., Hohe Strasse 6, 01069, Dresden, Germany
[b] Institute of Applied Physics, Technische Universität Dresden, 01062 Dresden, Germany
[c] Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi prospect, 31, 199004, Saint-Petersburg, Russia

ARTICLE INFO

Article history:
Received 27 December 2017
Received in revised form
18 April 2018
Accepted 21 April 2018
Available online 27 April 2018

Keywords:
Magneto-sensitive elastomers
Structural anisotropy
Dynamic moduli
Microscopic theory

ABSTRACT

The low-frequency dynamics of magneto-sensitive elastomers (MSEs) with chain-like and plane-like distributions of magnetic particles is studied under a uniform magnetic field. In this study we continue our previous work [Ivaneyko D. et al., Soft Matter, 2015, 11, 7627–7638], in which a coarse-grained cubic network model was proposed for description of the dynamic-mechanical behaviour of isotropic MSEs. Presently, to describe the dynamics of MSEs with anisotropic particle distributions, we use a tetragonal lattice model, in which average distances between neighbouring particles along and perpendicular to the symmetry axis of an MSE may differ. Effects of the elastic network and magnetic interactions between the magnetic particles on the dynamics are taken into account. Application of the magnetic field **H** along the symmetry axis of MSE leads to a strong anisotropy of the dynamic storage G' and loss G'' moduli, which depend on the geometry of the applied shear strain with respect to **H**. The change of dynamic moduli under the magnetic field is more pronounced for MSEs with anisotropic particle distributions as compared to isotropic MSEs. G' and G'' can change up to several orders of magnitude in agreement with recent experiments.

1. Introduction

Investigation of the dynamic-mechanical properties of cross-linked elastomers remains an important task, since these polymer materials in many practical applications are influenced by time-dependent loadings. Mechanical response of an elastic material to the dynamic loadings is known to be determined by superposition of specific types of motions in a broad length scale stretching from short-scale segmental motions to long-range collective motions of large polymeric fragments [1,2]. The present article is devoted to the dynamics of magneto-sensitive elastomers (MSEs) with included magnetic particles, whose molecular mobility and the dynamic-mechanical response can be controlled by an external magnetic field. The authors devote this article to Yulii Ya. Gotlib, who was a world's leading expert in the field of the dynamics of complex polymer network structures.

Dynamics of cross-linked elastomers in the viscoelastic state at temperatures $T > T_g$ is defined by the entropic elasticity of polymer chains [1,2]. The molecular mobility of this type can be described in a good approximation by the classical Rouse model, which represents a one-dimensional string of the viscous beads connected by the (entropic) springs. To describe the dynamics of a three-dimensional network structure, a regular cubic network model built from the Rouse chains was suggested by Yulii Ya. Gotlib as early as in 1981 [3]. It was shown that the dynamics of a network structure can be represented as a superposition of intra-chain and collective inter-chain relaxation processes [3–5]. At times shorter than the maximal relaxation time of the chains between network junctions the interactions between cross-linked chains can be neglected and the network dynamics is defined by the intra-chain modes of separate Rouse chains. At longer times the relaxation processes in polymer chains are completed and the network dynamics is well reproduced by a coarse-grained network built from the single springs, which determine total entropic elasticity of the chains between network junctions.

In the series of further works of Yulii Ya. Gotlib the cubic network model was modified and successfully employed to study the dynamics of complex network structures: heterogeneous

* Corresponding author. Leibniz-Institut für Polymerforschung e. V., Hohe Strasse 6, 01069, Dresden, Germany.
E-mail address: toshchevikov@ipfdd.de (V. Toshchevikov).

https://doi.org/10.1016/j.polymer.2018.04.057
0032-3861/

networks with a variable degree of cross-linking [6], polymer networks with included rodlike particles [7–9] and with large viscous inclusions [10,11], etc. Introducing an anisotropy into the cubic network model, the dynamics of liquid crystalline elastomers [12,13] and polymer networks under a static tensile force [14] were studied theoretically. Successful application of the cubic network model and its modifications to describe the dynamics of polymer networks opens up the possibility to use this model for further studying the dynamics of complex network structures. In the present paper we would like to demonstrate how the approach, based on a regular network model, can be applied to study the dynamics of magneto-sensitive elastomers.

Magneto-sensitive elastomers establish a special class of smart materials, which are able to change their shape and mechanical behaviour under external magnetic field [15–18]. These perspective functional materials can be used for design of functionally integrated structures in sensors, robotics and actuators [18–20]. MSEs typically consist of micron-sized magnetizable particles (e.g. carbonyl iron) dispersed within a non-magnetic elastomeric matrix. The spatial distribution of magnetic particles in MSEs can be either isotropic or anisotropic, depending on whether they have been aligned by an applied magnetic field before the cross-linking of the polymer. Depending on the magnetic properties of the particles, their shape, size and spatial distribution, the MSEs can exhibit different mechanical behaviour.

There are a lot of experimental works [21–24] and theoretical studies [25–33], devoted to mechanical properties of MSEs in the equilibrium (static) state. On the other hand, a very important topic is the dynamic-mechanical behaviour of MSEs, since in various technical applications these materials can be influenced by the oscillating mechanical loading [23,34–36]. For instance, MSEs are widely used in development of adaptive tuned vibration and dynamic absorbers [37,38], as well as in development of dampers for seismic protection [39] and vibration isolators [40].

A number of experimental works [17,35,41–50] study the influence of the external magnetic field on the frequency dependences of the storage G' and loss G'' shear dynamic moduli. It is shown that the values of G' and G'' at a given frequency depend on the magnitude of the external magnetic field, the volume fraction and spatial distribution of the magnetic particles and the degree of cross-linking of an elastomeric matrix [42,51,52]. In particular, the shear dynamic moduli have been measured for isotropic and anisotropic MSEs with different types of matrix, size of the particles and different magnitude of the external magnetic field. It was shown that in both isotropic and anisotropic MSEs the moduli increase with the increase of applied magnetic field, and this increase is more pronounced in MSEs with anisotropically distributed particles in the process of manufacture.

Although the dynamic-mechanical behaviour of MSEs was extensively studied experimentally [17,35,41–52], this behaviour is understood not so deep from a theoretical point of view. The vibration dynamics of MSE samples of different size in a homogeneous magnetic field was analysed using continuum-mechanics approach [53–56]. Recently, the fractional rheological model was applied to model the constitutive behavior of MSEs [57]. A satisfactory description of the low-frequency dynamic behavior in magnetic field was found for the samples with restructuring magnetic filler [57]. On the microscopic level, we can mention only our recent theoretical work devoted to the dynamic moduli of isotropic MSEs [58]. In this study to describe the isotropic particle distribution, we used a microscopic model based on the simple cubic lattice. Anisotropic particle distributions within a polymer matrix were as well considered by us explicitly but with the aim to calculate the static Young's and shear moduli [29,59,60]. However, recent experiments show that the dynamic-mechanical behaviour is also very sensitive to the anisotropy of particle distribution [49,61–63].

The main purpose of present work is to study the influence of anisotropic distribution of magnetic particles on the dynamic-mechanical behaviour of MSEs under external magnetic field. In particular, the influence of the chain-like and plane-like distributions on the storage and loss moduli is investigated theoretically in a low-frequency regime under a uniform external magnetic field.

2. Coarse-grained network model of anisotropic MSEs

Let us consider an anisotropic MSE, in which the magnetic particles are embedded within a non-magnetic polymer matrix, see Fig. 1a. In the absence of an external magnetic field, the average distances between neighbouring particles along the x-, y- and z-axes are $\langle r_x\rangle$, $\langle r_y\rangle$ and $\langle r_z\rangle$, respectively. We assume that the distance $\langle r_x\rangle$ may differ from the distances $\langle r_y\rangle$ and $\langle r_z\rangle$: $\langle r_x\rangle \neq \langle r_y\rangle = \langle r_z\rangle$. Under such assumption, the x-axis becomes the axis of symmetry of an anisotropic MSE.

To describe axially symmetric anisotropic spatial distributions of magnetic particles, we will use a tetragonal lattice model, introduced by us earlier to calculate the static Young's and shear moduli [29], see Fig. 1b. The edges of the cell in this lattice are taken equal to $a_\parallel = \langle r_x\rangle$ and $a_\perp = \langle r_y\rangle = \langle r_z\rangle$. The size of the cell is related to the volume fraction of the particles, ϕ, as follows:

$$\phi = \frac{\upsilon}{a_\parallel a_\perp^2}, \tag{1}$$

where υ is the volume of one magnetic particle. The anisotropy of particle distribution can be characterized by a scalar parameter

$$\alpha = \frac{a_\parallel}{a_\perp}, \tag{2}$$

whereby $\alpha = 1$ for the isotropic distribution of magnetic particles, $\alpha < 1$ for the chain-like distribution and $\alpha > 1$ for the plane-like distribution. Note that the chains lie along the axis of symmetry x, whereas the planes are perpendicular to it.

Similar to our previous study [58], in this work we focus on the low-frequency viscoelastic behaviour of MSEs at scales longer than the distance between neighbouring particles. In this low-frequency regime fast relaxation motions of polymer chains inside each rectangular network domain containing a single magnetic particle are completed. Hence, each such domain behaves like a single viscoelastic object and a coarse-grained network model can be introduced to describe the long-scale dynamics of the network, as it was shown in a series of works of Yulii Ya. Gotlib [3–5]. The friction coefficient ζ of a junction in the coarse-grained network model describes the dissipative effects, which appear under displacement of the centres of mass of the domains on the long scales, see Fig. 1b. To describe the elastic (entropic) losses in the MSE under displacement of the domains with respect to each other, we introduce Hookean springs between the neighbouring domains. These springs are characterized by two elasticity constants $K_\parallel$ and $K_\perp$ for the neighbouring domains in the directions parallel and perpendicular to the axis of symmetry in the anisotropic MSE, see Fig. 1b.

In refs. [4–6, 10–12] it was shown that the dynamics of polymer networks of different structures on long scales is well reproduced by a coarse-grained network model with appropriately chosen effective friction coefficients and elastic constants, as described above. Successful application of the coarse-grained cubic network model to describe the dynamics of polymer networks with rigid embedded particles [7–11] as well as ordered networks [12–14],