Towards a theory of mechanical properties of ferrogels.

Effect of chain-like aggregates.

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Abstract

The paper deals with theoretical study of deformation of a ferrogel filled by magnetizable particles united in the chain-like aggregates. The sample is placed in a magentic field parallel to the chains. Uniaxil elongation of the sample along the field is studied. Analyis shows that interaction of the particles in the chains and rupture of the chains by the elastic forces lead to non linear dependence of the macroscopical stress on the elongation strain. The theoretical results are in principle agreement with known experimental study of the ferrogels deformation.

Key words: *Ferrogels; Chains; Deformation*

1. Introduction

Magnetic polymers, ferrogels and ferroelastomers, consist of the nano-or micron sized magnetic particles imbedded in a polymer matrix. Combination of rich set of physical properties of the polymer materials with the high reaction on magnetic field makes these smart systems very attractive for many industrial and bio-medical applications [1].

One of the interesting, from the scientific point of view, and valuable, from the viewpoint of practical applications, features of ferrogels is their ability to change mechanical properties and behavior under the action of external magnetic field. Magnetic field induces either elongation or contraction of the composites in the field direction (see discussion of this problem in [1]) and significantly changes mechanical properties of these systems. These magnetomechanic effects are especially strong in the systems with internal heterogeneous structures (chains, columns, etc.) formed by the particles [2-4]. Usually these aggregates are created by using magnetic field, at

the stage of the polymer matrix curing, when it is liquid. Polymerization of the matrix fixes the internal structures in the composites (see, for example, [2,4-8]).

For example, experiments [2] demonstrate significant increase, under the field action, of the elastic stress σ at a given uniaxial strain ε in magnetic elastomers with the chain-like aggregates. The dependence of σ on ε, measured in [2], was non linear, with especially fast increase of σ at small ε. Effect of the field H on the stress in the same systems with homogeneous and isotropic spatial distribution of the particles was rather negligible; in the isotropic composites [2] the stress linearly depended on the strain. It is interesting to note that non monotonic, *N*-like shape of dependence of the difference $\delta\sigma=\sigma(H)-\sigma(0)$ on the tensile strain ε in the composites with the chains was detected in [2].

The non linear relation between σ and ε in soft ferrogels, placed in magnetic field, has been observed in experiments [3]. This non-linearity was induced by formation, under the field action, of heterogeneous chain-like structures in the gel. Without magnetic field the composites demonstrated the linear dependence of σ on ε. Under the action of quite moderate magnetic field (1-3 kOe) the elastic stress increased, at least, several times as compared with the case of zero field.

The non-linear relation between the shear stress and shear strain in magnetic elastomers with the anisotropic structures has been observed in experiments [4].

Therefore one can conclude that appearance of the anisotropic heterogeneous aggregates in magnetic polymers significantly enhances mechanical properties of these composites and produces the non linear dependence of the mechanical stress σ on the deformation ε.

The aim of this work is theoretical study of the stress-strain dependence in ferrogels with the chain-like aggregates. To be specific, we focus on the modeling of the uniaxial deformation of the sample in the chains direction. We suppose that the chains have been created, as in [2,4-8], by the application of external magnetic field at the stage of the gel curing. That is why the chains have the same direction, parallel to the field of polymerization. As in experiments [2,3], the actual field **H** is imposed in the direction of the chains.

2. Mathematical model and results

The rheological properties of ferrogels depend on the properties of carrier polymer matrix; on concentration of the imbedded particles; on the law of their magnetization and magnetic interaction; on the length of the chains and details of the particles dispositions in these aggregates. For the maximal simplification of the physical analysis and transparency of the mathematical part of the problem, we will use the following approximations.

First, we will estimate magnetic force of the particle interaction in the dipole-dipole approximation. It is supposed that magnetic moment of the particle is not changed by the chain deformation.

Note that the similar approximation of the dipole-dipole interaction between the particles in the chains has been used successfully in the theory of rheological properties of suspensions [9,10] and polymer composites [11-13] of magnetizable particles. Possible ways of generalization of this approximation are discussed in the Conclusion.

Secondly, we will use the linear stress-strain relation for the polymer matrix. Physically this means that only small deformations of the matrix are considered. It should be noted the mechanical non-linear effects in the composites with the chains have been detected in the region of ε corresponding to the linear law of deformation of the pure matrix [2,3]. We will neglect fluctuations of the chains shape and suppose that centers of all particles in the chain are situated on a straight line parallel to the applied field **H**; all particles in the chain are in physical contacts with their nearest neighbors. This means that the gel was cured under the action of very strong magnetic field. We will suppose also that all chains consist of an identical number of particles; this number is determined by the features of the matrix curing. The length of the chain, like in experiments [2-4], is less than the size of the composite, i.e. the chains do not percolate the sample. The infinite chains, percolating the sample, are considered in ref.[14].

Diameter of the particle is supposed much more than the characteristic size of the gel cell, therefore, with respect to the particles, the gel can be considered as a continuous media. Taking into account that the typical size of the cells in synthetic gels is about several nanometers, for the micron-sized magnetizable particles this condition is well justified. Next, we will neglect any interactions between the chains. This approximation is based on the results of [15] which show that, in formation of macroscopic properties of the composites, effects inside the chains play dominate role as compared with effects of the interchain interaction. The considered model of the chain is illustrated in Fig.1.

We will study deformation of a single chain under the assumption that the composite experiences uniaxial deformation in the chain direction. For definiteness we will suppose that the chain consists of an odd number of the particle. Obviously, this assumption is not of principle for the physical analysis.

We will denote the mean vector of a material point displacement in the composite as $\boldsymbol{u}$.

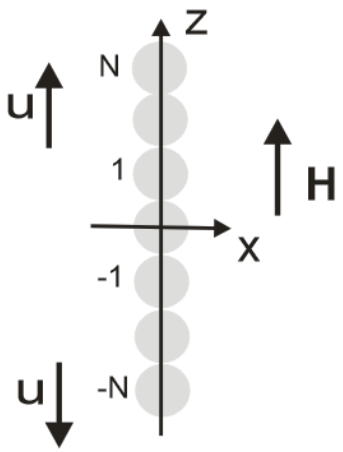

Fig.1. Illustration of the chain model

In the coordinate system, shown in Fig.1, the vector ***u*** of the mean composite displacement (i.e. displacement at the infinitive distance from the chain), can be presented as: $u_z=\varepsilon z$. The other components of ***u*** do not play a role in the framework of this model that is why we omit them here.

Let the total number of the particles in the chain be $2N+1$; n be number of a particle in the chain, starting from the central one, which number is 0. In the framework of the used approximations, equations of stationary displacement of the particles in the chain can be presented in the following form:

$$\beta(\varepsilon z_n - u_n) + \kappa\left[\frac{1}{(d+u_{n+1}-u_n)^4} - \frac{1}{(d+u_n-u_{n-1})^4}\right] + f_{n+1,n} - f_{n,n-1} = 0 \text{ , } -N<n<N \quad (1)$$

$$\beta(\varepsilon z_N - u_N) - \kappa\left[\frac{1}{(d+u_N-u_{N-1})^4}\right] - f_{N,N-1} = 0,$$

$$\beta(\varepsilon z_{-N} - u_{-N}) - \kappa\left[\frac{1}{(d+u_{-N}-u_{-N+1})^4}\right] - f_{-N,-N+1} = 0$$

$$u_0 = 0$$

$$\kappa = \mu_0\frac{3m^2}{2\pi}$$

Here $z_n = nd$ is the initial, before deformation, coordinate of the n-th particle, d is the particle diameter, u_n is the vector of displacement of the n-th particle, m is the particle magnetic moment, $f_{n.l}$ is the force of elastic interaction between the n-th and l-th particles, μ_0 is the vacuum magnetic permeability. The first terms in the left side of equations (1) mean the elastic forces, which act on the n-th particle, due to the fact that its displacement u_n is not equal to the

displacement $u = \varepsilon z_n$ of the matrix far from the chain at the level of the particle. This force is similar to the classical Stocks force, which acts on a particle in a Newtonian liquid when velocity of the particle differs from the liquid velocity. In the order of magnitude $\beta \sim G_0 d$, where G_0 is elastic modulus of the matrix. The second terms in (1) present the difference of the forces of magnetic attraction of the *n*-th particle to the (*n*+1)-th and (*n*-1)-th ones respectively.

Obviously, the function f_{nl} depends on the relative disposition of the particles. That is why we can present:

$$f_{l+1,l} = f(u_{l+1} - u_l) \tag{2}$$

We determine the function f by using the linear law of elasticity for the situation when the distance *r* between the particles centers is more than the particle diameter *d* and taking into account strong repulsion, which resists to the particles interpenetration when *r*<*d*:

$$f(x) = \begin{matrix} G_1 x, when\ x > 0 \\ -\infty, when\ x < 0 \end{matrix} \tag{3}$$

Parameter G_1 is the elastic modulus of the polymer in the region close to the particles. Generally speaking, due to change of the polymer conformation near the particles, G_1 can differ from the modulus G_0 of the pure matrix.

The total stress in the composite can be presented as:

$$\sigma = G_0 \varepsilon + \sigma_a \tag{4}$$

where σ_a is the stress induced by the aggregates. By using the results [16,17] for the stress in a system of chain-like polymer macromolecules, we get the following estimate:

$$\sigma_a = 2 \frac{N_{ch}}{V} \sum_{n=0}^{N-1} F_n (z_{n+1} - z_n) \tag{5}$$

where F_n is a force, the *n+1*-th particle acts on the *n*-th one; N_{ch} is number of the chain in the composite, *V* is the composite volume. Note that the polymer chains flexibility does not affect the relation (5).

By using eq.(1) we can present (5) as:

$$\sigma_a = 2\varphi \frac{1}{(2N+1)v} \sum_{n=0}^{N-1} \left(\frac{\kappa}{(d+u_{n+1}-u_n)^4} + f_{n+1,n} \right) (d + u_{n+1} - u_n) \quad (6)$$

Here φ is volume concentration of the particles in the composite, v is the particle volume.

This is convenient to introduce the dimensionless stress $\Sigma=\sigma/G_0$, displacement $U_n=u_n/d$, parameter of the interparticle magnetic interaction $K = \frac{6\kappa}{\pi d^6 G_0}$ and the elastic force $\Psi_{n+1,n} = 6f_{n+1,n}/(\pi d^2 G_0)$. In these notations we get from (4) and (6):

$$\Sigma = \varepsilon + 2\frac{\varphi}{(2N+1)} \sum_{n=0}^{N-1} \left(\frac{K}{(1+U_{n+1}-U_n)^4} + \Psi_{n+1,n} \right) (1 + U_{n+1} - U_n) \quad (7)$$

The dimensionless displacement U_n can be found from solution of the system (1).

Some results of calculations of the dimensionless stress Σ are shown in Fig.2. First, in magnetic field $(K \neq 0)$ the stress nonlinearly depends on the strain, in spite of the linear law of deformation assumed for the polymer matrix. The finite non zero stress takes place in the non-deformed sample (ε=0) placed in external magnetic field. The physical cause of these effects is the attraction of the magnetizable particles in the chain and appearance (increase) of the interparticle gaps by the action of the elastic forces in the elongated sample. Of course, the existence of the initial (at $\varepsilon = 0$) stress can be interpreted also as appearance of a finite stress jump at the infinitesimal elongation of the sample. It should be noted that the non-linear dependence of the stress on the tensile strain, similar to that described by the curve 1, has been detected in experiments [2,3]. The finite stress at ε=0 was observed in [2].

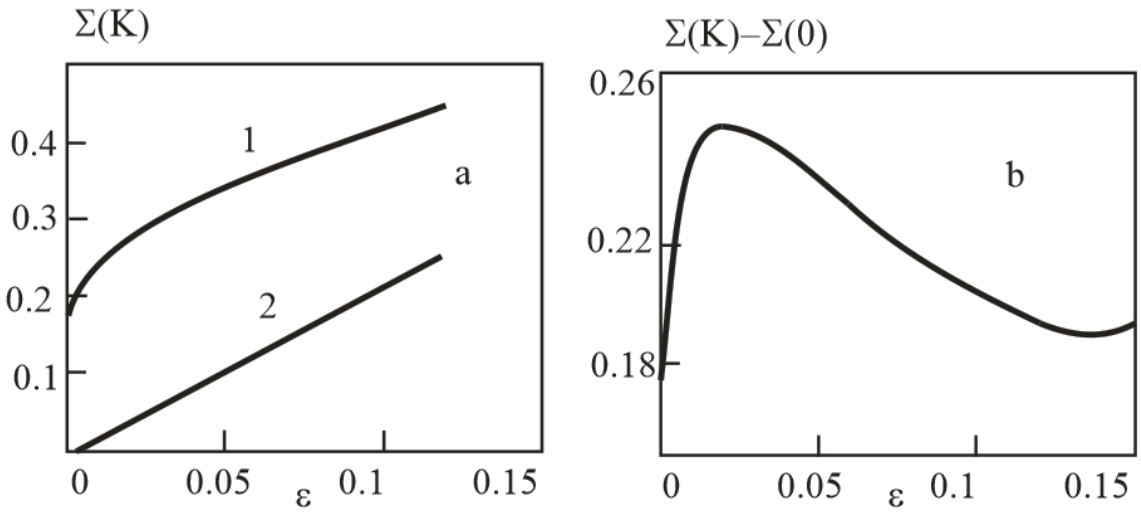

Fig.2. The dimensionless stress Σ(K) (a) and the stress difference $\Sigma(K) - \Sigma(0)$ (b) vs. the elongation strain ε when N=8, i.e. number of particles in the chain $2N$+1=17. Parameters of the system: G_1=G_0; β=2G_0; φ=0.15. a) lines 1 and 2: K=0.25 and 0 respectively.

In order to estimate effect of the magnetic field on the stress, we have calculates the difference $\delta\Sigma = \Sigma(K) - \Sigma(0)$ between the stress in the magnetic field ($K \neq 0$) and the stress without the field ($K = 0$). Our results demonstrate non-monotonic dependence of $\delta\Sigma$ on the elongation strain ε. The similar N-like shape of the dependence of $\delta\Sigma$ on ε has been observed experimentally and explained in [2] by the existence of the chains of various lengths in the composite and by the step-wise rupture of the different chains at the different magnitudes of the strain. The present analysis shows that the non-linear effects can be induced by the continuous deformation of the identical chains.

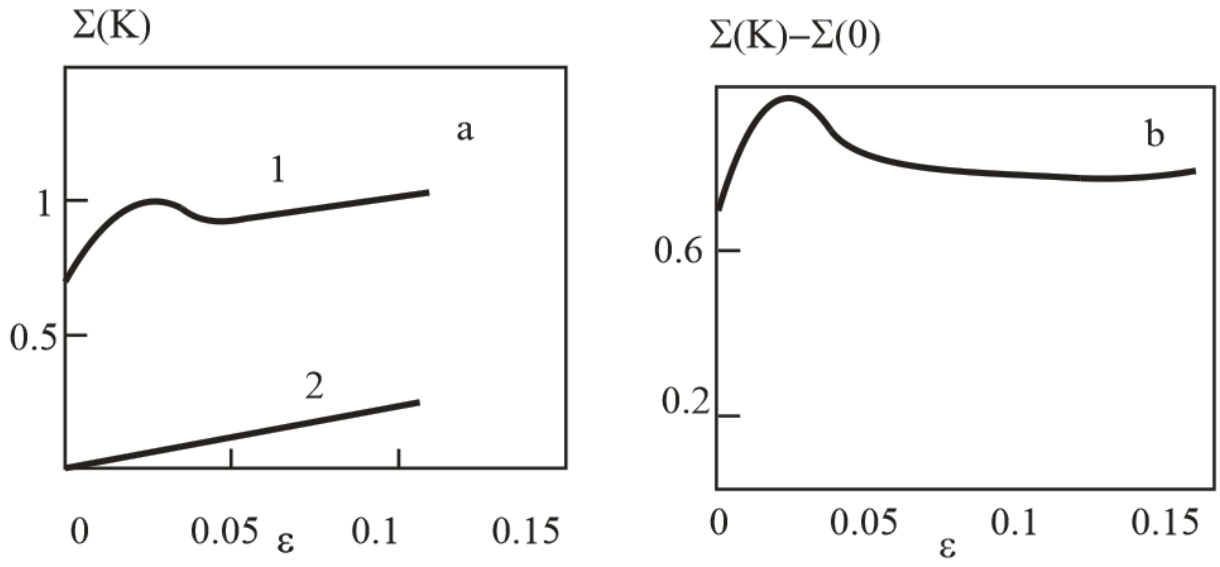

Fig.3. Same as in Fig.2 for K=1

Results of calculations for the same system, as in Fig.2, but for higher dimensionless magnetic field K are shown in Fig.3. They indicate non monotonic, with maximum, dependence of the stress on the strain. The physical cause of this non monotonic behavior is that the total stress presents a combination of the elastic forces in the deformed matrix and the forces of magnetic interaction between the particles. The last forces fast decrease while increasing of the strain ε. This leads to the appearance of the decreasing part of the rheogram at strong enough magnetic fields. It should be noted that the similar non monotonic dependence of the mechanic stress on the relative elongation has been detected in computer simulations [18].

Comparison of the calculations of the stress σ with the experiments [2], preformed with the carbonyl iron particles is presented in Fig.4. Parameter K is fitted as K=0.5; this corresponds to the particle magnetization $M = 400kA/m$. This means that the iron particles are non linearly magnetized, however not magnetically saturated. It was taken into account that the conformation of the macromolecules, as well the field of the deformations [19] in the thin gaps between the nearest particles in the chains, can differ significantly from that in the bulk of the matrix. That is why the thin interparticle layers can be more rigid than the pure matrix.

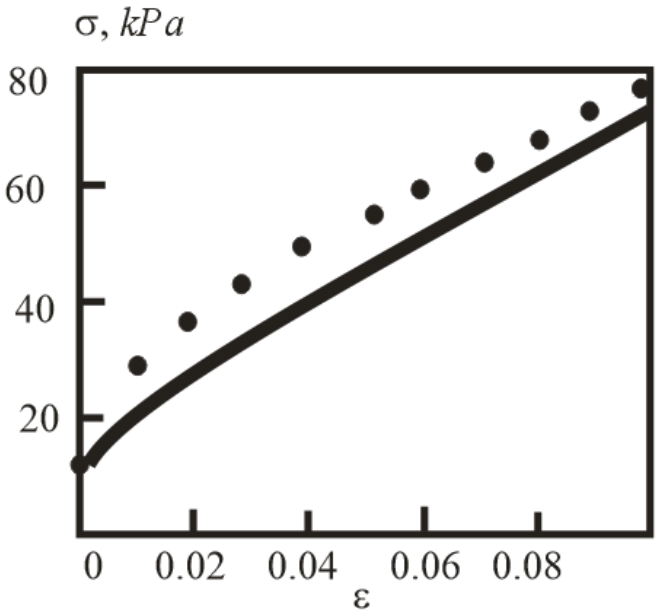

Fig.4. Dimensional stress σ calculated according to the present model (solid line) and results of measurements of [2] vs the sample elongation. Parameters of the system: the particles consist of the carbonyl iron; the particle diameter d=2μm; magnetic field inside the sample H=123kA/m; volume concentration of the particles φ=0.15; elastic modulus of the matrix G_0 =0.2MPa; $G_1 = 15G_0$ The number of particles in the chains is the same as in Figs.2,3.

The theoretical results are in reasonable agreement with the experimental ones. That indicates that the model is adequate, at least, in its main points. Some quantitative disagreement can be explained by the following factors. First, the presence of the hard particles in the relatively soft matrix leads to stiffness of the composite even without the magnetic interaction between the particles (see, for example, [19]). This stiffness takes place because of the local deformation of the matrix near the particles and appearance of an additional local elastic stress. Unfortunately, a theory of elastic properties of composites with the hard spheres, united in chain-like structures, has not been developed yet. Those are why here we restrict ourselves by the analysis of effects of magnetic interaction between the particles and omit the problem of the composite stiffness because of the mechanic effects in the matrix. Next, the used simple dipole-dipole approximation underestimates the force of magnetic interaction between the closely situated particles [20]. However even this simplest approach allows us to reproduce the main physical features of the mechanical properties of the polymer composites with the chain-like aggregates.

Conclusion.

We propose a simple mathematical model of the uniaxial elongation of a ferrogels with chain-like aggregates placed in magnetic field parallel to the chains. In spite of simplicity, this model describes experimentally [2,3] observed features of mechanical behavior of the system at their small elongation in the field direction: non linear dependence of the stress σ on the elongation strain ε; finite magnitude of the initial ($\varepsilon \to 0$) stress in the ferrogels placed in magnetic field; non monotonic dependence of the difference $\sigma(H) - \sigma(0)$ on the strain ε , as well as the *N*-shaped dependence of σ on ε , detected in computer simulations [18]. Generalization of the model can be performed in the following directions. First, one can use more realistic [20-22], than the dipole-dipole, approximations for the magnetic interaction between the particles. These approaches take into account multipolar interactions as well as non-linear mutual magnetization of the nearest particles in the chains. This generalization does not lead to principal problems, but makes the calculations much more cumbersome than those in the present simple model. Effects of the composite stiffness due to the rigid particles, united in the chains; fluctuations of the chain shape as well as their magnetic and elastic interaction require a special study. Since the present simple model reproduces the main features of the experimentally observed mechanical effects, it can be considered as a robust basement for the further detailed studies of these phenomena.

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