Magnetorheological response of highly filled magnetoactive elastomers from perspective of mechanical energy density: Fractal aggregates above the nanometer scale?

Vladislav V. Sorokin,[1,2] Inna A. Belyaeva,[3] Mikhail Shamonin,[3] and Elena Yu. Kramarenko[1,2,*]

[1]*Faculty of Physics, Lomonosov Moscow State University, Moscow, 119991, Russia*

[2]*A. N. Nesmeyanov Institute for Organoelement Compounds RAS, Moscow, 119991, Russia*

[3]*East Bavarian Centre for Intelligent Materials (EBACIM), Ostbayerische Technische Hochschule Regensburg, Seybothstrasse 2, D-93053 Regensburg, Germany*

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The dynamic shear modulus of magnetoactive elastomers containing 70 and 80 mass % of carbonyl iron microparticles is measured as a function of strain amplitude via dynamic torsion oscillations in various magnetic fields. The results are presented in terms of the mechanical energy density and considered in the framework of the conventional Kraus model. The form exponent of the Kraus model is further related to a physical model of Huber *et al.* [Huber *et al.*, J. Phys.: Condens. Matter **8**, 409 (1996)] that uses a realistic representation for the cluster network possessing fractal structure. Two mechanical loading regimes are identified. At small strain amplitudes the exponent β of the Kraus model changes in an externally applied magnetic field due to rearrangement of ferromagnetic-filler particles, while at large strain amplitudes, the exponent β seems to be independent of the magnetic field. The critical mechanical energy characterizing the transition between these two regimes grows with the increasing magnetic field. Similarities between agglomeration and deagglomeration of magnetic filler under simultaneously applied magnetic field and mechanical shear and the concept of jamming transition are discussed. It is proposed that the magnetic field should be considered as an additional parameter to the jamming phase diagram of rubbers filled with magnetic particles.

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I. INTRODUCTION

At the present time a particular class of smart materials [1–5], often designated as magnetoactive elastomers (MAEs), is receiving a lot of interest due to their enormous potential in industrial applications [2,3] and a plenitude of complex physical phenomena in search for explanations and appropriate models [4,5]. MAEs are somewhat similar to magnetorheological (MR) fluids, but the micrometer-sized magnetic particles are constrained in a soft elastomer matrix rather than in a carrier fluid [6]. The MR effect is the most prominent property of these materials. The MR effect is the large increase of the dynamic modulus in externally applied dc magnetic fields [7,8]. The same elastomers are often designated as magnetoactive [9–11] since other physical properties, such as dielectric permittivity [12] or electrical conductivity [11], etc., are influenced by external magnetic fields as well. Enhancement of the thermal conductivity in MAEs due to the alignment of ferromagnetic particles in chain aggregates, if the curing was performed in an external magnetic field, has been also demonstrated [13–15].

Obviously, MAEs also belong to a more general class of filled elastomers. Although the filler particles are much larger than conventional fillers carbon black and silica, MAEs display similar strain-induced nonlinear phenomena under dynamic mechanical loading conditions such as common rubber nanocomposites. An external magnetic field influences these nonlinear effects. In particular, the magnetic field enhanced Payne effect has been investigated in MAEs [16,17]. Moreover, this effect is not limited to elastomers but can also be observed in MR fluids [18] suggesting that the properties of the magnetic network are crucial. The influence of external magnetic fields makes the consideration of physical effects in MAEs even more complicated, since the corresponding physical quantities may vary over many orders of magnitude and it is not always possible to separate purely mechanical from purely magnetic effects. Moreover, the largest MR effects are observed at high filler concentrations, where the clusters of filler particles are likely to undergo a "jamming transition" [10].

Among filled elastomers, those filled with nanometer-sized particles have received a lot of attention due to their importance for industrial applications (e.g., tire industry) and the theory of soft matter. The physical theories explaining nanoparticle reinforcement in elastomers can rely on the fact that the size of nanoparticles is smaller than the typical size of polymer coils [19]. In recent years, substantial progress has been achieved in understanding the particle reinforcement in polymers beyond hydrodynamics [20]. Several types of theoretical models (cluster-cluster aggregation model, jamming theory, and rigidity percolation theory) have been proposed and were more or less successful in the explanation of experimental results. In MAEs the particles are about one thousand times larger and therefore comparable or larger than the polymer coils. Recall that in analogy to MR fluids, magnetic-field-induced reinforcement in MAEs is commonly attributed to rearrangement of filler particles into chainlike aggregates along the magnetic field lines due to magnetic forces acting between them [16,21–23]. This simplified physical picture for high concentrations of magnetizable particles has been recently doubted by Romeis *et al.* [24], whose numerical simulations showed that formation of elongated structures becomes impossible due to purely geometrical constraints. Can there be a "grain of truth" in physical models of polymers reinforced with nanometer-sized particles which can be transferred to MAEs? In search for the answer to this question, we resort to the investigation of magnetic-field-induced Payne effect in MAEs, because for the Payne effect there exists a generally accepted model for nanometer-particle reinforced polymers [25].

*kram@polly.phys.msu.ru

In spite of significant progress achieved in recent years, a unified and consistent theoretical description of dynamic behavior of MAEs in magnetic fields is still missing. Different approaches for describing the MR response of MAEs have been employed. The theoretical methods included the continuum-mechanics approach [26–32], microscopic theories [33–38], and first steps towards a scale-bridging description of magnetic elastomers [39]. As far as dynamic properties of MAEs are concerned, they have been phenomenologically modeled using either conventional viscoelastic schemes of macroscopic rheology comprising springs and dashpots [40–43] or more sophisticated approaches based on fractional calculus [44–46]. In the present paper, the MR experiments are critically examined from an unconventional perspective in view of creating experimental prerequisites for an alternative theoretical description of MAEs.

Hitherto, published works on MR properties of MAEs have conventionally presented the dependencies of the shear storage and loss moduli at fixed oscillation frequency f on the deformation amplitude γ. However, this is not the only possible way to represent the results. Wang and Robertson have found experimentally that using the product $\sigma\gamma$ of the shear stress and the deformation amplitude as the critical parameter can significantly simplify the phase diagram for filled rubbers [47,48]. They also hypothesized that mechanical energy density $\sigma\gamma$ may be related to the notion of effective temperature. It has been pointed out that, similarly to the product kT of the Boltzmann constant and temperature, this mechanical energy density is theoretically derivable from Hamiltonians, making it a natural choice as an axis for constructing phase diagrams [47,49]. Richter *et al.* did not find the isoenergetic character of normalized dynamic moduli with a constant value of critical mechanical energy density $\sigma_0\gamma_0$, at the mechanical transition (Payne effect) [50]. The critical strain amplitude γ_0 is defined as such strain amplitude where the maximum of the loss modulus G'' at a fixed frequency f is observed. The corresponding value of the critical stress amplitude is $\sigma_0 = [\sqrt{G'(\gamma_0)^2 + G''(\gamma_0)^2}]\gamma_0$. Note that for the experimental conditions of this paper, the condition $G' > G''$ is fulfilled well, so that the materials always show the solidlike behavior and the following approximate relationship is valid: $\sigma_0 \approx G'(\gamma_0)\gamma_0$. In this paper, the dependences of the shear storage modulus and loss modulus on the strain amplitude in different magnetic fields are systematically investigated. The analysis of obtained results is performed in dependence on the mechanical energy density $\sigma\gamma$, which in externally applied magnetic fields include magnetic, mechanical, and magnetomechanical contributions [27]. It provides alternative insight into the physics of the MR effect and allows one to emphasize the role of the magnetic network in strain-induced nonlinearity of filled magnetoactive rubbers. In particular, the previously reported phenomena of hysteresis and Payne effect in MAEs are revisited and investigated in more detail from the alternative perspective. In MAEs, critical mechanical energy density $\sigma_0\gamma_0$ depends on the external magnetic field. The further normalization of the mechanical energy density by its critical value $\sigma_0\gamma_0$ allows one to relate the results of MR measurements to the Kraus model described below and to raise the question about the fractal structure of the filler network and the influence of the magnetic field on it.

II. EXPERIMENT

A. Sample fabrication

1. Materials

The base polymer VS 100000 (vinyl-functional polydimethylsiloxane) for addition-curing silicones, the chain extender Modifier 715 (SiH-terminated polydimethylsiloxane), the reactive diluent polymer MV 2000 (monovinyl functional polydimethylsiloxane), the crosslinker 210 (dimethyl siloxane-methyl hydrogen siloxane copolymer), the Pt catalyst 510, and the inhibitor DVS were provided by Evonik Hanse GmbH, Geesthacht, Germany. The silicone oil WACKER® AK 10 (linear, nonreactive polydimethylsiloxane) was purchased from Wacker Chemie AG, Burghausen, Germany. The carbonyl iron powder (CIP) type SQ (mean particle size of 4.5 μm, provided by BASF SE Carbonyl Iron Powder & Metal Systems, Ludwigshafen, Germany) was used as the ferromagnetic filling.

2. MAE preparation

The fabrication of the polydimethylsiloxane (PDMS) samples was performed along the known recommendations [51]. The polymer VS 100000, the polymer MV 2000, the modifier 715, and the silicone oil AK 10 were put together and blended with an electric mixer (Roti®-Speed-stirrer, Carl Roth GmbH, Germany) to form an initial compound. In the next step, the initial compound was mixed together with the CIP particles (70% or 80% by mass) and the crosslinker 210. The crosslinking reaction was activated by the Pt catalyst 510. For the control of the Pt catalyst's activity, the inhibitor DVS was used; the recommended dosage is between 0.01% and 0.5% [52–54].

The Petri dishes (35 mm high, Greiner Bio-One GmbH, Germany) were filled with the finished, but uncured MAE composition (the thickness of the samples is about 1 mm). The air bubbles in the MAE samples were removed using a vacuum desiccator for about 10 min.

Finally, the MAE samples were precured in the universal oven Memmert UF30 (Memmert GmbH, Schwabach, Germany) at 80°C for 1 h and then postcured at 60 °C for 24 h with air circulation.

In the following, the synthesized samples containing 70 and 80 mass % of CIP are denoted as MAE-70 and MAE-80, respectively. The filler content corresponds to approximately 22 and 34 vol %.

B. Rheological measurements

The cut-out samples had a diameter of approximately 20 mm. The dynamic moduli of the samples, $G'(\gamma)$ and $G''(\gamma)$, were measured at the fixed oscillation frequency $f = 1.6$ Hz as functions of the strain amplitude. Previously we have found [9,17,55] that the dynamic moduli demonstrate pronounced hysteresis under consecutively increasing and decreasing strain amplitude. Existence of a field-induced magnetomechanical hysteresis in a pair of soft magnetic particles embedded in an elastomer matrix has been theoretically derived in Ref. [56]. It has been shown in Ref. [9] that a major modulus change takes place during the first increase of the strain amplitude when most of the magnetic-filler restructuring seems to occur. Subsequent ascending and descending strain amplitude

results only in minor shifts of the modulus values demonstrating some saturation for a large number of cycles. Thus, in this study the $G'(\gamma)$ and $G''(\gamma)$ dependences were measured with ten cycles of increasing and decreasing strain amplitude and the data recorded during the last cycle were further analyzed. The obtained dynamic moduli were presented as functions of energy density: $G'(\gamma) \to G'(\sigma\gamma)$, $G''(\gamma) \to G''(\sigma\gamma)$.

The shear storage modulus was normalized by its limiting value G'_0 at $\gamma \to 0$ in the linear viscoelastic region, while the shear loss modulus was normalized by its maximum value $G''_{\max}$:

$$G'_{\text{norm}} = G'(\sigma\gamma)/G'_0 \quad \text{and} \quad G''_{\text{norm}} = G''(\sigma\gamma)/G''_{\max}. \quad (1)$$

All rheological measurements have been made using a commercially available rheometer (Anton Paar, model Physica MCR 302) with the measuring "plate-plate" unit and the magnetic cell MRD 170/1 T. Measurements of the dynamic modulus were carried out at room temperature in the dynamic mode of forced torsion oscillation with controlled harmonically varying torque. In all measurements reported in this paper the frequency of oscillations was maintained constant at $f = 1.6$ Hz while oscillation amplitudes were varied. To avoid slippage of the sample, initial normal force $F_N = 1$ N was applied to the sample. The magnetic field was applied along the smallest dimension of the sample, i.e., perpendicular to its outer circular surfaces.

C. Kraus model, universality, and fractal structures

Although we are also convinced that there is no isoenergetic character of the behavior of the normalized dynamic moduli at the mechanical transition let us closely examine the behavior of the normalized dynamic moduli in the framework of the well-known semiphenomenological Kraus model [57,58]. This model is commonly applied in the elastomer industry for the evaluation of the strain sweep characteristics of filled rubbers [49]. It is considered to be a very good model for the practical applications. The corresponding equations were developed on the assumption of the deagglomeration and reagglomeration mechanism for aggregation of filler clusters [59]:

$$G' = G'_\infty + \frac{G'_0 - G'_\infty}{1 + \left(\frac{\gamma}{\gamma_0}\right)^\beta}, \quad (2)$$

$$G'' = G''_\infty + \frac{2(G''_{\max} - G''_\infty)}{1 + \left(\frac{\gamma}{\gamma_0}\right)^\beta}\left(\frac{\gamma}{\gamma_0}\right)^{\beta/2}, \quad (3)$$

where $G'_0 = G'(\gamma = 0)$, $G'_\infty = G'(\gamma \to \infty)$, $G''_\infty = G''(\gamma \to \infty)$ and $G''_{\max}$ is the value of the local maximum of the loss modulus. This local maximum $G''_{\max}$ of the dependence G' on the deformation amplitude γ is realized at the characteristic value $\gamma = \gamma_0$, while the ratio $[(G' - G'_\infty)/(G'_0 - G'_\infty)]$ is equal to 0.5. Notice that the ratio $[(G' - G'_\infty)/(G'_0 - G'_\infty)]$ monotonically declines with growing γ and it has its maximum value of 1 at $\gamma = 0$. It follows that the product $\sigma_0\gamma_0 = G'(\gamma_0)\gamma_0^2 = 0.5(G'_0 - G'_\infty)\gamma_0^2$.

In rubbers with carbon black or silica fillers, the exponent β in the dependences (2) and (3) is fairly well predicted in terms of the connectivity parameter for fractal aggregates [25] ($\beta \approx 1.2$) or by a simple Ising model approach ($\beta \approx 1.0$) [49]. In this context, the Kraus model indeed reflects the universal properties in the dynamical deformation of filled elastomers. However, there seem to be no obvious restrictions on the value of β imposed by the laws of physics. We are aware of the shortcomings of the Kraus equations [59]. In particular, the deagglomeration and reagglomeration concept does not distinguish between the response of an ensemble of disjoint clusters corresponding to small filler concentrations and that for a filler network occurring in elastomers with high concentrations of filler particles. The latter is the most interesting case for MAEs where large magneto-induced effects are observed at high filler concentrations. It is also well known that in general G' and G'' dependences cannot be fitted with exactly the same sets of fitting parameters. This is a tolerable inaccuracy for industrial applications and it becomes negligible if $G' \gg G''$.

The original model of Huber *et al.* [25] was based essentially on the assumption that the clusters forming the filler network have a self-similar, i.e., fractal, structure which can be described by correlations similar to those that appear in the percolation model. This approach resulted in the following relation for the parameter β:

$$\beta = \frac{2(2 - C)}{C - 1}, \quad (4)$$

where C is a connectivity exponent. The connectivity exponent, C, is related to the branching structure of fractal aggregates [60,61]. Recently, formula (4) was improved and the exponent β has been related to two exponents, d_f, the mass fractal dimension of the filler network and the connectivity exponent C [19,62]:

$$\beta = \frac{2}{C - d_f + 2}. \quad (5)$$

It is reasonable to assume that, in composites comprising magnetic particles, both d_f and C may be influenced by external magnetic fields. Very recently, an alternative (but similar) functional form for Eq. (2) has been proposed in Ref. [62]. This model also relies on the fractional structure of the filler network.

Let us normalize the mechanical energy density $e_m = (\sigma\gamma)/(\sigma_0\gamma_0)$. It can be easily seen that within the Kraus model e_m is a monotonously growing function of the normalized strain amplitude $s = \gamma/\gamma_0$ depending only on the parameter β. Therefore, an unambiguous change of variable $s \to e_m$ is possible in Eqs. (2) and (3). The resulting system of implicit equations for G'_{norm} and G''_{norm} as functions of e_m can be easily solved numerically.

The typical dependences of the normalized shear storage and loss moduli on the normalized mechanical energy density calculated according to the Kraus model for various values of the exponent β are presented in Figs. 1(a) and 1(b), respectively. In Fig. 1(c) we also show the dependence of the damping factor, $\tan\delta$, which is defined as the ratio of the shear loss modulus to the shear storage modulus, $\tan\delta = G''/G'$, on e_m; it plays an important role in determining the damping ability of materials. The parameters of the model were chosen as follows: $G'_0 = 1.0$, $G'_\infty = 0.5$, $G''_{\max} = 0.6$, $G''_\infty = 0.2$, and $\gamma_0 = 1\%$ so that the elastic contribution dominates at any strain which is typical for the MAE samples under study.

It is seen that the normalized storage modulus is a sigmoid function of e_m. At low strains, i.e., low e_m, the

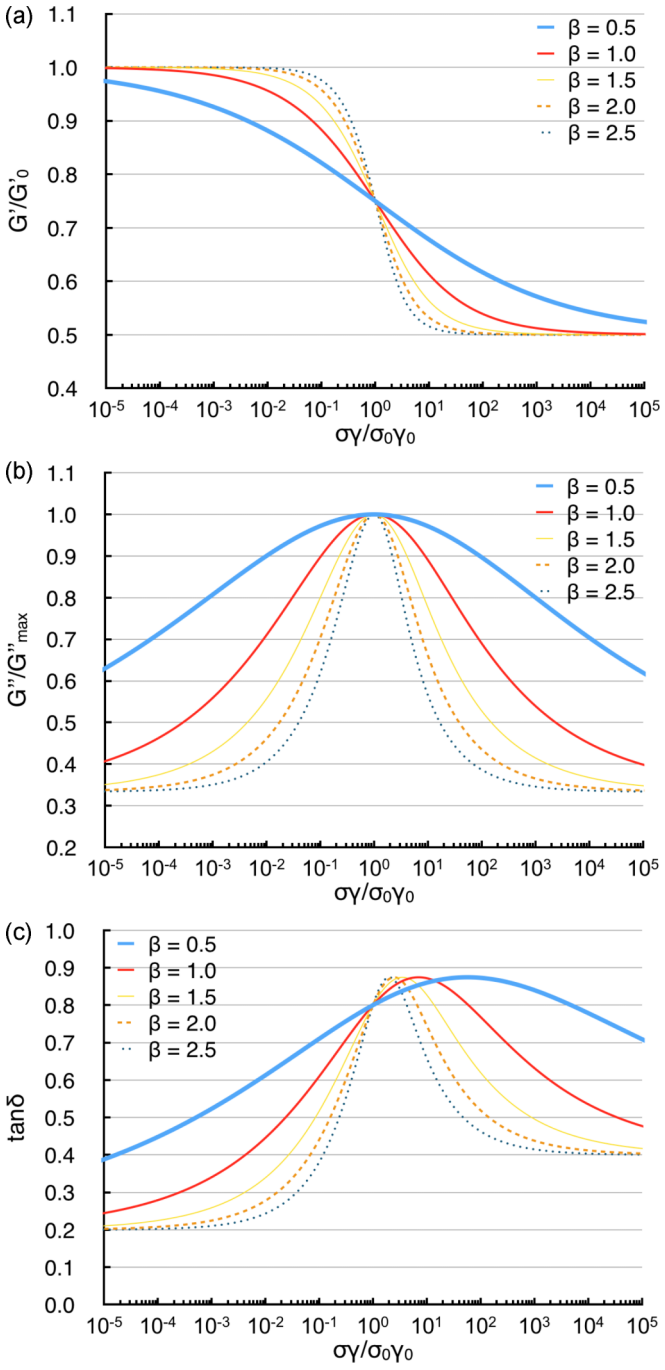

FIG. 1. Dependences of the normalized moduli (a,b) and damping factor (c) on the normalized mechanical energy density for the Kraus model.

linear viscoelastic regime is described by the model where a strain-independent state is usually realized. With e_m increased, the storage modulus diminishes while the loss modulus passes through a local maximum [Figs. 1(a) and 1(b)]. The value of the exponent β determines the sharpness of the storage modulus drop with e_m and, at the same time, the peak width of the loss modulus. An increase of β leads to the shift of the maximum of $\tan\delta$ towards the smaller values of the mechanical energy density and the local maximum becomes somewhat sharper. The limiting values of $\tan\delta$ are defined by the relationships between G'_0, G'_∞, $G''_{\max}$: $\tan\delta \cong G''_\infty/G'_0$ at $\gamma \to 0$ and $\tan\delta \cong G''_{\max}/G'_\infty$ at $\gamma \to \infty$.

As it has been mentioned above, parameter β is related to the parameters d_f and C characterizing the fractals of filler particle clusters. If the difference $(C-d_f)$ does not change, the dependencies of dynamic moduli on the normalized mechanical energy are expected to follow a single master curve. A universal behavior of the dynamic moduli for rubber samples filled with different fractions of carbon black was observed in [47].

III. RESULTS AND DISCUSSION

A. Influence of magnetic field on the strain-induced nonlinearity of MAEs

Figure 2 presents the experimental dependences of the normalized storage $G'(\sigma\gamma)/G'_0$ and the loss moduli $G''(\sigma\gamma)/G''_{\max}$ on the mechanical energy density for various magnetic fields. Continuous lines denote dependencies measured with the increasing strain amplitude while dotted lines refer to the decreasing strain amplitude. At each particular drive current, presented moduli dependences for the increasing strain amplitude do not coincide with those obtained for the decreasing strain amplitude; i.e., a pronounced hysteresis is demonstrated. Hysteresis behavior of the dynamic moduli in dependence on ascending and descending magnetic fields or increasing and decreasing strain amplitudes has been studied in Ref. [9] where it was concluded that such a hysteresis is an intrinsic property of MAEs. The physical reason is presumably the dependence of filler restructuring on the history of material deformation.

Table I shows the values of the storage modulus G'_0 corresponding to the smallest strain amplitude $\gamma \to 0$ in the linear viscoelastic regime and the values of the maximum loss modulus, $G''_{\max}$. Due to the strain hysteresis, the values of G'_0 and $G''_{\max}$ are somewhat different for ascending and descending strain amplitudes.

As was shown in numerous previous studies, application of an external magnetic field causes considerable increase in both MAE elasticity and energy dissipation [7,8,10,63–66]. The absolute storage modulus increment, $G'_0(5A) - G'_0(0A)$, is larger for the sample containing 80 mass % of the magnetic filler. At the same time, the relative modulus increase, $[G'_0(5A) - G'_0(0A)]/G'_0(0A)$, is maximal for the sample with the smaller iron content; its value reaches 287 for MAE-70 while it is equal to 91 for MAE-80. This tendency confirms the conclusion formulated in Ref. [17] that the relative modulus increment is highly dependent on the initial modulus of the material.

One can see in Fig. 2 that an increase of drive current I (i.e., increasing external magnetic field) causes some shift of the maximum in loss modulus dependences to higher strain amplitudes; simultaneously, the linear viscoelastic regime widens. The absence of any isoenergetic behavior, i.e., clear difference in critical mechanical energy $\sigma_0\gamma_0$ values for different magnetic fields, is quite natural. It is caused by strengthening of the magnetic-filler network due to enhancement of magnetic interactions in stronger fields [17]. The values of the mechanical energy $\sigma_0\gamma_0$ corresponding to the maximum of the

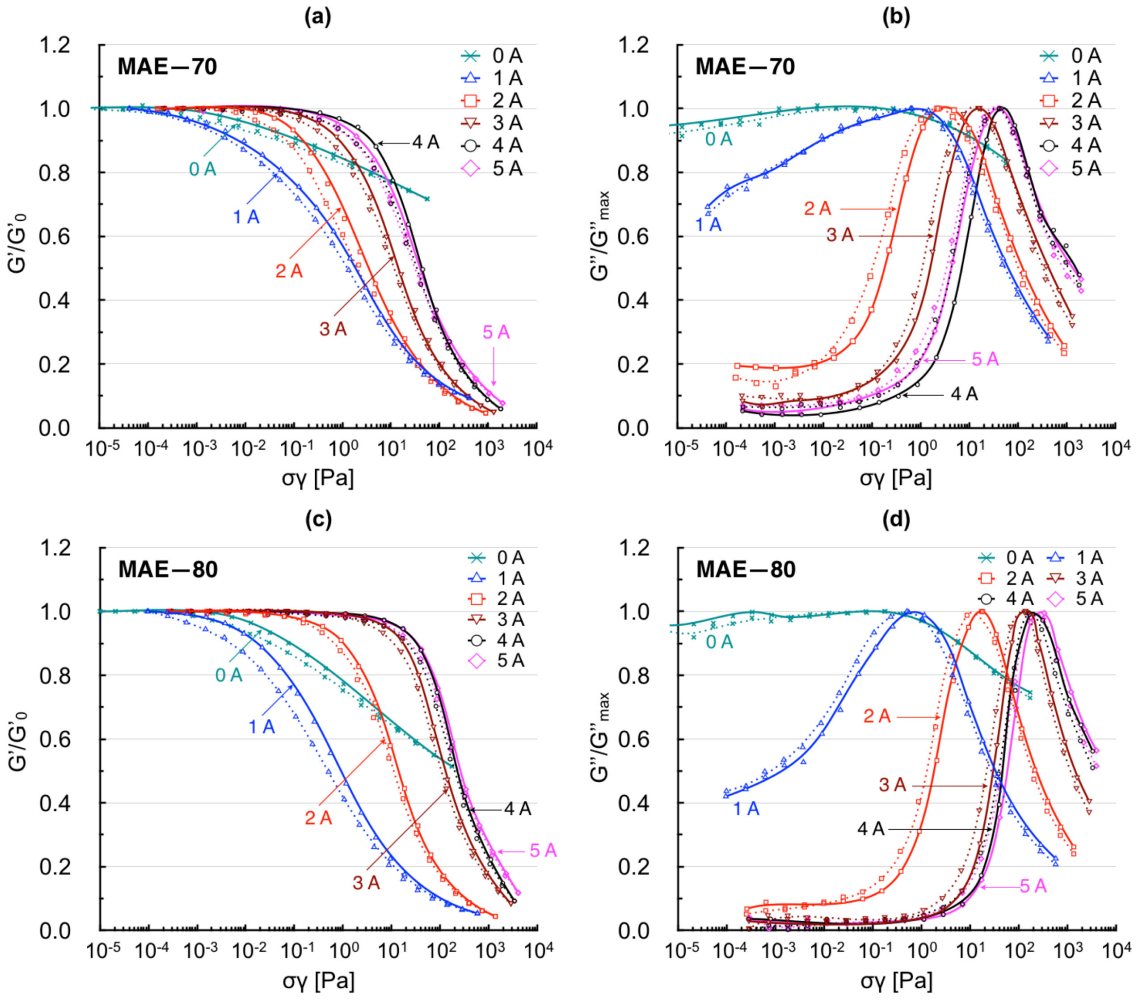

FIG. 2. Dependences of the normalized storage G'/G'_0 (a,c) and loss $G''/G''_{\max}$ (b,d) moduli on the mechanical energy density $\sigma\gamma$ for MAE-70 (a,b) and MAE-80 (c,d) samples and different drive currents I (0, 1, 2, 3, 4, and 5 A). Continuous lines denote dependencies measured with the increasing strain amplitude while dotted lines refer to the decreasing strain amplitude.

loss modulus at different currents are summarized in Table II while their dependences on current are plotted in Fig. 3.

One can see in Fig. 3 that the experimental dependences $\sigma_0\gamma_0(I)$ resemble sigmoid functions. More specifically, for the 70% sample the curves $\sigma_0\gamma_0(I)$ do look like a sigmoid function, while the curves for the 80% sample may be interpreted as the initial part of a sigmoid function where the current I is not large enough for the saturation to be reached. One may expect that in small fields magnetic dipolar interactions are weak and the conventional contribution to the mechanical energy typical for ordinary rubbers filled with nonmagnetic particles is prevailing. On the contrary, in strong fields magnetic contribution should be considerable and larger mechanical energy is needed to destroy magnetic

TABLE I. Values of G'_0 and $G''_{\max}$ for various electric currents at increasing (↑) and decreasing (↓) strain amplitude.

	MAE-70				MAE-80			
	G'_0 (kPa)		$G''_{\max}$ (kPa)		G'_0 (kPa)		$G''_{\max}$ (kPa)	
I (A)	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$
0	7.64	8.46	1.37	1.39	32.9	32.6	5.47	5.57
1	421	419	53.9	56.5	981	995	112	121
2	1650	1650	186	202	2540	2520	304	326
3	2110	2110	240	258	2890	2890	406	437
4	2260	2250	264	281	2950	2960	371	412
5	2190	2180	243	259	3030	3020	372	401

TABLE II. Values of $\sigma_0\gamma_0$ for both samples at increasing (↑) and decreasing (↓) strain amplitude cycles.

	$\sigma_0\gamma_0$ (Pa)			
	MAE-70		MAE-80	
I (A)	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$
0	0.209	0.181	0.0842	0.0776
1	0.845	0.650	0.736	0.458
2	3.32	2.52	17.0	12.9
3	16	13	141	114
4	50	37	225	185
5	40	35	281	230

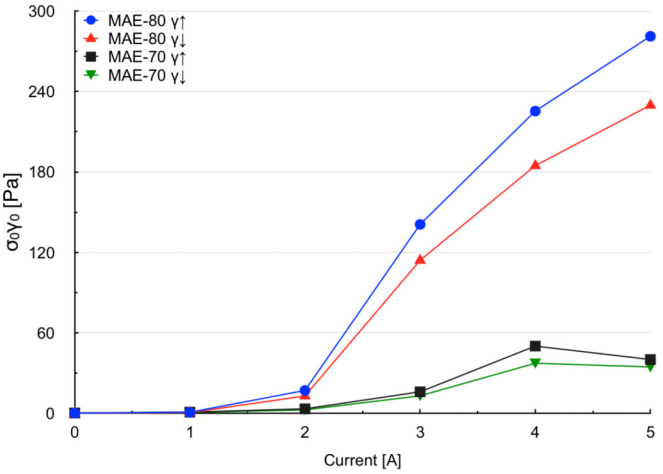

FIG. 3. Critical mechanical energy $\sigma_0\gamma_0$ as a function of current.

aggregates. The saturation of $\sigma_0\gamma_0(I)$ with the drive current I may be attributed to the saturation of the magnetization M of ferromagnetic particles in a sufficiently strong external magnetic field.

Indeed, in small magnetic fields ($I \leqslant 1$A) the values of the critical mechanical energy $\sigma_0\gamma_0$ are small and they are comparable for both samples. However, the difference in $\sigma_0\gamma_0$ for the samples containing 70 and 80 mass % of magnetic filler increases with field and in the strongest magnetic field at $I = 5$ A the value of $\sigma_0\gamma_0$ is 5 times larger for the MAE-80 than for the MAE-70. This fact also indicates the dominating role of magnetic interactions in stronger magnetic fields.

A kind of $\sigma_0\gamma_0$ saturation at $I > 4$ A is observed for the MAE-70 sample, while at the higher filler content (MAE-80 sample) the critical mechanical energy increases in the whole range of electric current change without any saturation. The difference in the behavior of two samples could be explained by different types of magnetic particle restructuring in magnetic field. While for MAE-70 the percolation threshold for the filler is probably not reached in the zero field, for MAE-80 one could expect the existence of the three-dimensional magnetic-filler network already in the absence of magnetic field. As a result, agglomeration and deagglomeration processes could proceed differently. At higher filling larger aggregates can be formed upon material curing and higher fields are needed to saturate the structure.

A similar S-shaped dependence has been obtained for the critical mechanical energy as a function of carbon black filler concentration in [48] (cf. Fig. 12 of [48]). It has been shown that $\sigma_0\gamma_0$ increases first with the filler concentration but after some critical concentration it saturates. This type of behavior was attributed to the jamming transition [48]. One could speculate that in MAE a kind of the jamming transition could be induced by an application of the external magnetic field. Indeed, it has been confirmed by various experimental techniques [22,23,67] that under external magnetic fields magnetic-filler particles can restructure within soft polymer matrices and form chainlike aggregates oriented along the field lines. The number of chains as well as the density of particles in chains depends on the magnetic field [23,68]. The higher is the field, the tighter are the aggregates. One could interpret the structuring of magnetic filler in magnetic fields as a change from an unjammed state to a jammed one. While the overall density of particles stays constant within the material the density of particles within chain aggregates formed in magnetic field increases (i.e., there is "crowding" of particles in a chain). One could expect some similarities between, for instance, a system of weakly attractive particles undergoing gelation with an increase of their concentration and a system of particles at a constant concentration but increasing attraction. Increase of attraction is caused by magnetic field in case of MAE; furthermore, this attraction is directional and thus does not lead to macroscopic phase separation but rather microscopic structuring. Simultaneously applied magnetic field and mechanical stress could serve as external stimuli affecting jamming processes in MAE. The idea that the behavior of MAEs in magnetic fields resembles that of a jammed material is also supported by the recent observation of the so-called crossover phenomenon in MAEs [10]. Obviously, the magnetic flux density B must be considered as an additional parameter to the jamming phase diagram in MAEs.

B. Fitting the Kraus model to experimental data

In Fig. 4 we present storage modulus versus strain curves normalized on both axes. One can see that qualitatively these dependences resemble quite well those of the Kraus model.

Experimental curves obtained with different currents correspond to theoretical dependencies with different values of the exponent β (Fig. 1). Normalized representation on both vertical and horizontal axes facilitates the comparison with the Kraus model. Variation of the current, i.e., magnetic field applied, corresponds to changing the exponent β in Eqs. (2) and (3).

The experimental strain dependences of the moduli were fitted according to the Kraus model. It appeared to be impossible to fit the experimental strain dependences of the storage modulus measured in magnetic fields with one set of the fitting parameters. Thus at each particular value of the current I we have performed two independent fits for the $G'(\gamma)$ dependences covering small ($\sigma\gamma < \sigma_0\gamma_0$) and large ($\sigma\gamma > \sigma_0\gamma_0$) strain amplitude ranges. As an example we present the fitting of MAE-80 storage modulus curves for two different driving currents in Fig. 5. The obtained fitting parameters for all experimental dependences are presented in Tables III and IV.

Let us analyze the first set of the parameters that fits the experimental curves at small strain amplitudes well. One can see that the value of the exponent β depends considerably on I; it is small at $I = 0$ A to 1 A and it increases strongly between $I = 1$ A and 2 A. On the contrary, $\gamma_0(I)$ shows minimum values in the same range of I where the major change of β takes place. This change of β values can be explained by the change in fractal properties of magnetic-filler structure under the influence of an external magnetic field. Crucial restructuring should take place in such a field where magnetic forces acting between magnetic particles start to overcome elastic forces of the polymer matrix trying to keep magnetic particles in their initial equilibrium positions.

At large strain amplitudes the exponent $\beta \approx 0.9$ stays practically constant, independently of the magnetic field strength.

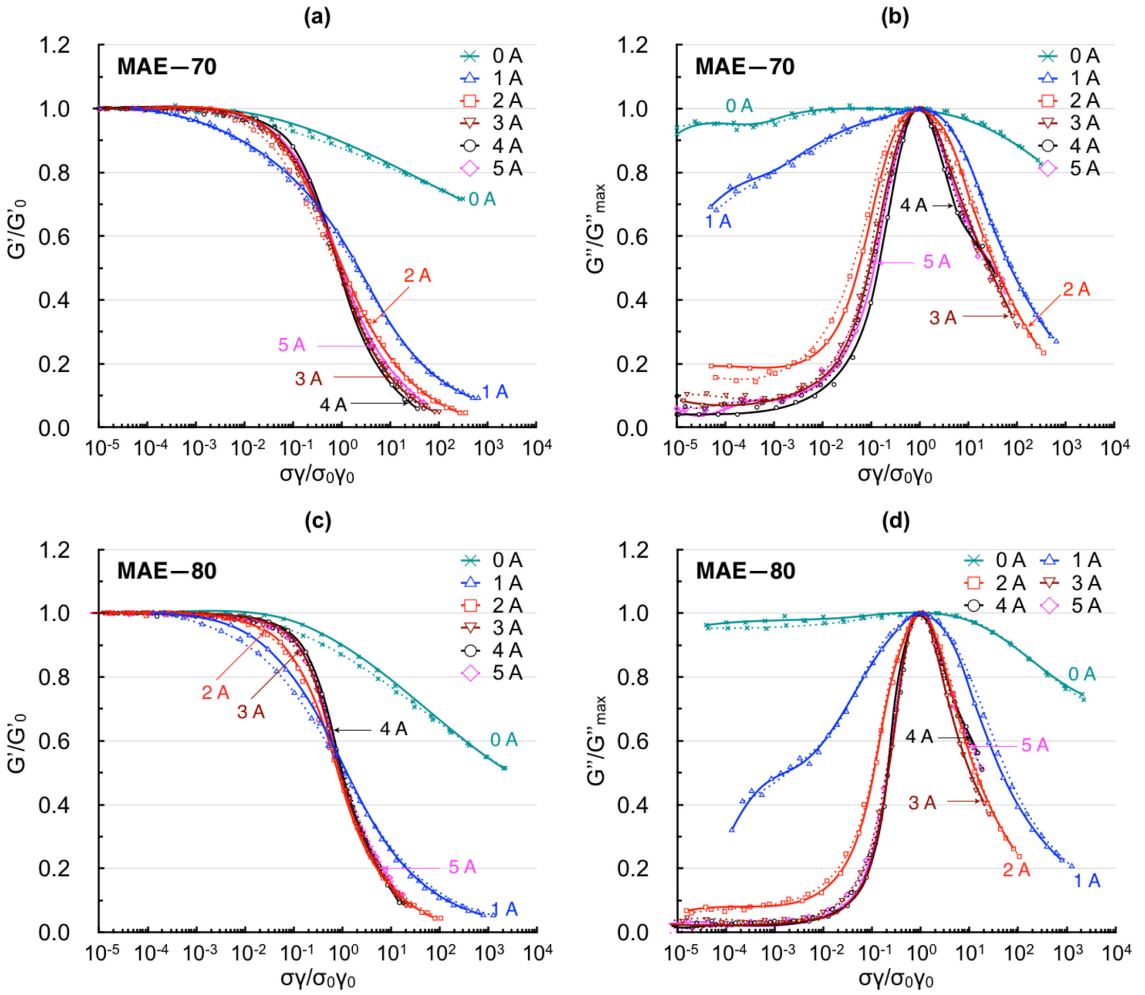

FIG. 4. Dependences of the normalized shear storage G'/G'_0 (a,c) and loss $G''/G''_{\max}$ (b,d) moduli on the normalized mechanical energy $(\sigma\gamma)/(\sigma_0\gamma_0)$ for the MAE-70 (a,b) and MAE-80 (c,d) samples at different drive currents I (0, 1, 2, 3, 4, and 5 A). Continuous lines denote dependencies measured with the increasing strain amplitude while dotted lines refer to the decreasing strain amplitude.

This can be considered as an internal property of the magnetic particle network, because large mechanical deformations destroy interactions of filler particles via the matrix. The necessity of another set of fitting parameters to describe material behavior at large strains is an indication of a change in the filler fractal dimensions under mechanical loading.

The importance of magnetic field in formation of a network of magnetizable filler particles can also be seen from the following observation. Notice that the variation of $\beta(|\Delta\beta| \approx 0.03-0.3$; relative variation $|\Delta\beta|/\beta$ is about 24% at its maximum) for increasing and decreasing strain amplitudes at a given value of drive current I is several times smaller

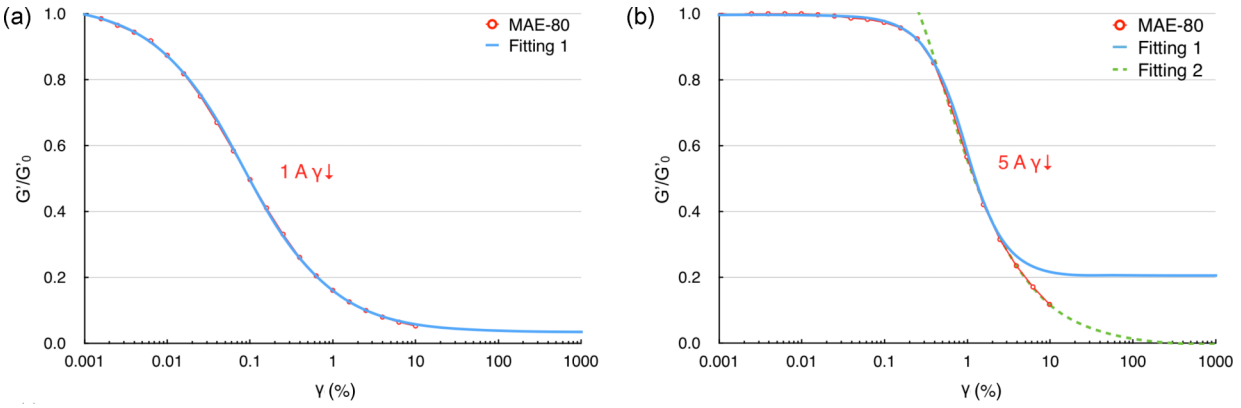

FIG. 5. Fitting of storage modulus curves at decreasing strain amplitude cycles with Kraus model for the sample MAE-80 for different driving currents: $I = 1$ A (a) and $I = 5$ A (b).

TABLE III. Fitting parameters β and γ_0 for both samples at increasing (↑) and decreasing (↓) strain amplitude cycles (small deformation).

	MAE-70				MAE-80			
	β		γ_0		β		γ_0	
I (A)	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$
0	0.67	0.541	2.246	2.448	0.891	0.844	0.744	0.500
1	0.677	0.65	0.268	0.209	0.831	0.784	0.115	0.085
2	1.495	1.203	0.087	0.081	1.538	1.479	0.215	0.179
3	1.529	1.429	0.219	0.188	1.871	1.731	0.681	0.639
4	1.628	1.406	0.411	0.332	2.028	1.776	0.876	0.820
5	1.503	1.396	0.356	0.336	1.928	1.746	0.908	0.922

than the maximum change of β ($|\Delta\beta| \approx 1$; maximum relative change $|\Delta\beta|/\beta$ is more than 100%), which can be induced by an external magnetic field.

Finally, some comments are due to be made about the corresponding dependences of the shear loss modulus G''. Qualitatively, all the conclusions made for G' apply to the G'' dependences. However, the experimental results for G' and G'' cannot be quantitatively fitted with the same sets of parameters β and γ_0, which is a known shortcoming of the Kraus model [59]. The agreement is then only semiquantitative.

Fortunately, from the practical point of view, G'' is less important for MAEs since $G'' < G'$. The latter condition simply means that the material behaves like a solid.

IV. CONCLUSIONS

In this paper, an alternative analysis of the behavior of the shear modulus in magnetoactive elastomers in terms of the mechanical energy density has been presented. The experimental results have been interpreted in the framework of the conventional Kraus model. The following conclusions can be made:

(1) Behavior of the dynamic modulus with the deformation amplitude is related to the mass fractal dimension d_f of the filler network and connectivity exponent C of the filler aggregates [19]. In MAEs, these parameters can depend on external magnetic fields.

(2) At small deformation amplitudes, the exponent β of the Kraus model changes in an externally applied magnetic field because of the rearrangement (structuring) of ferromagnetic particles. There is an optimum network microstructure in a particular magnetic field.

(3) At large deformation amplitudes, the exponent β of the Kraus model seems to be independent of the external magnetic field.

(4) The critical mechanical energy density grows with increasing external magnetic field. It has purely mechanical, purely magnetic, and magnetomechanical contributions, which cannot be easily separated in the framework of magnetorheological experiments.

(5) Magnetic field could serve as an additional control parameter for the jamming phenomena in rubbers filled with magnetic particles.

We believe that the alternative representation of conventional magnetorheological experiments with MAEs in terms of the mechanical energy density and the Kraus model could provide additional insight into the physics of these promising, intelligent materials.

TABLE IV. Fitting parameters β and γ_0 for both samples at increasing (↑) and decreasing (↓) strain amplitude cycles (large deformation).

	MAE-70				MAE-80			
	β		γ_0		β		γ_0	
I (A)	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$	$\gamma\uparrow$	$\gamma\downarrow$
0								
1								
2	0.791	0.75	0.153	0.121	0.927	0.897	0.164	0.137
3	0.917	0.881	0.295	0.25	0.9	0.91	0.445	0.386
4	0.97	0.93	0.507	0.421	0.91	0.908	0.576	0.536
5	0.91	0.885	0.449	0.398	0.879	0.873	0.627	0.587

V. OUTLOOK

The results and their analysis presented above do not give direct proof that the concept of fractal aggregates is applicable to MAEs with micrometer-sized filler particles, but they do not contradict it. Which experiment can be done in order to support or reject this concept? It has been pointed out previously by several authors that "revealing the filler structure in the matrix is the key for understanding the reinforcement mechanism" [20]. The same statement should be applicable to the magnetic-field-induced reinforcement as well. In particular, it is crucial to determine the fractal dimension d_f of clusters of micrometer-sized particles. In the case of nanometer filled elastomers many studies have been done using small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) to study the statistical three-dimensional (3D) structure of fillers such as silica and carbon black [20]. In the case of MAEs with larger filler particles, ultrasmall angle neutron scattering (USANS) may shed light on the filler structure. These experiments seem to be feasible, although an obvious problem is that in highly filled MAEs, the necessity of elimination of multiple scattering would require preparation of thin-film samples. USANS experiments can be performed in the absence and in the presence of magnetic field and the effect of magnetic field on the characteristic parameters of filler aggregates can be extracted.

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