SANS investigation of a ferrofluid based silicone elastomer microstructure

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Abstract. Structural peculiarities of ferroelastomers composed of polydimethylsiloxane with magnetite particles embedded during polymerization are studied by small-angle neutron scattering. The effects of ferroparticle concentration in the range up to 6 mass.\% and external magnetic fields of induction up to 1 kG, applied while curing, on the structure of the polymer and the particle spatial distribution in matrix are analyzed.

1. Introduction

The study of the properties of filled elastomers is a challenging and exciting topic for both fundamental science and industrial application. It is known that adding of hard particulates to a soft elastomer matrix results in the properties that do not follow a straightforward rule of mixtures. The progress of the structure vs. properties relationships research of such systems evolves into several directions: filler type and structure, magneto(electro)-mechanical reinforcement and interactions between the fillers and elastomers. Development of novel technologies of magnetic nanomaterials shows the trends of creation of the composites with anisotropic molecular and magnetic structures such as elastomers filled with fine ferroparticles. The combination of polymers with magnetic materials displays new and often enhanced properties. Due to the presence of the magnetic particles, the shape of the elastomer composite responds the external magnetic field. In general, the cross-influence of the magnetic and elastic properties of such compounds leads to a number of striking phenomena occurring in response to imposed magnetic and stress fields [1-42]. On the other hand, the ability to control and characterize the multiple forming structures inside the elastomer is an example of morphological engineering for reinforced and modified polymers valuable for a variety of applications.
The synthesis and study of structure and physical properties of these advanced materials, which combine the functional properties of elastic polymers and ferromagnetic substances should be considered as a perspective way to provide the understanding of construction principles of a wide class of materials for electronics, electrical engineering, medicine, aero- and cosmic industries. From the fundamental point of view, a comprehensive analysis of the relationship between macromolecular and disperse phase structures and their ordering under the action of magnetic field and by the variation of magnetic component content is needed. Neutron and X-ray scattering techniques are highly useful for determining the morphology of the emerging filler structures [43-52].

The aim of present work is the small-angle neutron scattering examination of subtle structural features of the polymeric matrix and the ensemble of embedded ferroparticles as resulting from the conditions of preparation of ferroelastomers by the variation of ferroparticle concentration and the strength of external magnetic field applied during polymerization.

2. Experimental

Ferroelastomers were prepared [34] using the radical polymerization of dimetylsiloxane with addition of ferrofluid based on magnetite. In the samples, the concentration of the magnetic component (ferrofluid) [53-59] was equal 1.27; 3.9; 5.88 mass.%, respectively. The magnetic field ($B = 0; 280; 560; 1120$ Gauss) was applied perpendicular to the plane of the polymer film of thickness ~ 0.5 mm, see Table 1. A reference sample, i.e., a polymer film without ferroparticles was also was prepared. The small-angle neutron scattering experiments (SANS) were carried out at ambient temperature (20°C) on the “Membrane” diffractometer (PNPI) in the range of momentum transfer $q = (4\pi / \lambda) \sin(\theta / 2) = 0.03-0.8$ nm$^{-1}$, where $\theta$ is the scattering angle and $\lambda = 0.3$ nm is the neutron wavelength ($\Delta \lambda / \lambda = 0.25$ [52]. The incident beam was orthogonal to the plane of the elastomer films. In all the experiments, the samples, which are isotropic in scattering plane, studied. Thus, the scattering intensities were dependent just on the modulus $q$ of the scattering vector. Since the neutron beam transmission for the samples was relatively high (Tr ~ 0.8), the multiple scattering processes were neglected.

| № of the sample | Content of Fe$_3$O$_4$, C mass.% | $B$, Gauss |
|-----------------|---------------------------------|-----------|
| $P_{1,}$ matrix | 0                               | 0         |
| $P_{12}$        | 5.88                            | 0         |
| $P_{13}$        | 5.88                            | 280       |
| $P_{14}$        | 5.88                            | 560       |
| $P_{15}$        | 5.88                            | 1120      |
| $P_{22}$        | 3.9                             | 0         |
| $P_{23}$        | 3.9                             | 280       |
| $P_{24}$        | 3.9                             | 560       |
| $P_{25}$        | 3.9                             | 1120      |
| $P_{32}$        | 1.27                            | 0         |
| $P_{33}$        | 1.27                            | 280       |
| $P_{35}$        | 1.27                            | 1120      |

3. Results and discussion

The scattering patterns for the elastomers containing 5.88; 3.9 and 1.27 mass.% of magnetite are presented in Figures 1-3, where the data for the matrix are shown also. It is evident (Figure 1) that the
scattering from original polymeric matrix is relatively strong at $q \leq 0.2$ nm$^{-1}$. The addition of ferroparticles into matrix does not cause any substantial contribution to the total scattering intensity at low momenta even at the highest concentration of magnetite (5.88 mass.%). The scattering from ferroparticles dominates only at larger momenta, $q \geq 0.4$ nm$^{-1}$, due to their small size as compared to the inhomogeneities in the polymer matrix. It should be noted that application of a magnetic field ($B = 1120$ G, sample P$_{15}$) during polymerization, did not initiate any dramatic structural changes. Indeed, the observed increase of scattering is moderate: the ratio of intensities for samples P$_{15}$ (strong field) and P$_{12}$ (no field) does not exceed factor 2 in the interval $q = 0.4 - 0.8$ nm$^{-1}$. This means that the polymer network prevents aggregation of ferroparticles and ensures their more homogeneous spatial distribution to be achieved for required material quality. Large-scale inhomogeneities in the polymer matrix are visible despite of low scattering ability of the polymer having the density of coherent length $K_s = 6.3 \times 10^8$ cm$^{-2}$. It is by two orders in magnitude lower than that for magnetite having $K_M = 6.97 \times 10^{10}$ cm$^{-2}$. Thus, the contrast factor for magnetite regarding to matrix is also high, $\Delta K_{M} = K_{M} - K_{s} = 6.91 \times 10^{10}$ cm$^{-2}$, but it is compensated by small characteristic volume of a particle as compared to the large inhomogeneities in matrix, as it is seen in Figures 2 and 3.

The decrease of the ferroparticle concentration makes the difference in the scattering intensities between the ferroelastomers and matrix progressively smaller. A detailed analysis of $q$-dependencies of scattering intensity for matrix enables us to propose a two-level model structure and the related scattering function

$$I(q) = I_{01} \exp \left[ -\left( qR_g \right)^2 / 3 \right] + I_{02} \left[ 1 + \left( qR_g \right)^2 \right]^{-2}.$$  (1)
Here the first Guinier-term describes the large scale inhomogeneities (domains of the gyration radius $R_G$), and the second Debye-term is related to the smaller globular objects (domains) with correlation radius $R_C$. The coefficients $I_{01}$ and $I_{02}$ are proportional to the squared contrast factors, volume contents and characteristic volumes of the corresponding objects. This model function approximates the data for matrix satisfactory (Figures 1–3) with parameters given in Table 2.
Therefore, the radius of a large polymer domain is about $R_G \sim 40$ nm that is approximately seven times greater than that for a small domain: $R_C \sim 6$ nm. As we assume, these large structures in the matrix are composed of small domains, whose centers are situated at the minimum distance $\sim 2R_C \sim 13$ nm corresponding to characteristic domain diameter. It can be expected that the ferroparticles penetrating between domains should be spaced at the same distance. For the ferroelastomers we have used a model that takes into account the scattering from large-scale polymer domains (gyration radius $R_G$) and ferroparticles (correlation radius $r_c$) separated in space by the distance $L$ comparable to the small polymer domain diameter $\sim 2R_C$:

$$I(q) = I_{01} \exp\left[-\frac{(qR_G)^2}{3}\right] + I_{02}\left[1 + (qR_C)^2\right]\left[1 + n \sin(qL) / (qL)\right].$$

Here the parameters $I_{01}$ and $I_{02}$ represent the contributions of large polymer domains and ferroparticles in the scattering intensity at $q \to 0$, while $n$ is the average number of the particles correlated with a given particle at the characteristic distance $L$. Function (2) describes in a satisfactory way the behaviors of the scattering intensities for ferroelastomers at all the concentrations and the magnitudes of induction $B$; the fitting parameters are listed in Table 2.

In Figure 4 the obtained dependencies of the correlation radius $r_c(B)$ of the magnetic inclusions (single particles, clusters) and the forward scattering intensities $I_{02}(B)$ vs. magnetic induction $B$ for sample series $P_{22}-P_{24}$ are represented.

### Table 2. Parameters of functions (1), (2) for matrix and ferroelastomers.

| Sample | $N$ | $B$ (Gauss) | $I_{01}$ (arb.un.) | $R_G$ (nm) | $I_{02} \times 10^5$ (arb.un.) | $R_C$ (nm) | $r_c$ (nm) | $n$ | $L$ (nm) |
|--------|-----|-------------|-------------------|------------|-------------------------------|------------|------------|----|--------|
| $P_1$  | 0   | 0.487±0.002 | 39.3±0.1          | 4590±60    | 6.37±0.04                     | -          | -          |    |        |
| $P_{12}$ | 0   | 0.249±0.001 | 38.1±0.1          | 617±3      | 2.33±0.01                     | 1.21±0.01  | 15.6±0.1  |    |        |
| $P_{13}$ | 280  | 0.273±0.001 | 38.8±0.1          | 563±5      | 2.35±0.01                     | 1.30±0.02  | 15.4±0.1  |    |        |
| $P_{14}$ | 560  | 0.436±0.001 | 39.2±0.1          | 895±5      | 2.43±0.01                     | 1.26±0.01  | 15.9±0.1  |    |        |
| $P_{15}$ | 1120 | 0.363±0.002 | 38.8±0.1          | 762±8      | 2.35±0.02                     | 1.27±0.02  | 15.5±0.1  |    |        |
| $P_{22}$ | 0   | 0.490±0.002 | 39.0±0.1          | 1160±19    | 3.42±0.03                     | 1.30±0.03  | 15.7±0.1  |    |        |
| $P_{23}$ | 280  | 0.448±0.001 | 38.9±0.1          | 1007±7     | 3.21±0.01                     | 1.32±0.02  | 15.6±0.1  |    |        |
| $P_{24}$ | 560  | 0.399±0.001 | 38.6±0.1          | 985±10     | 3.19±0.02                     | 1.33±0.02  | 15.6±0.1  |    |        |
| $P_{25}$ | 1120 | 0.603±0.001 | 39.9±0.1          | 1406±11    | 3.71±0.02                     | 1.22±0.01  | 16.2±0.1  |    |        |
| $P_{32}$ | 0   | 0.353±0.002 | 39.6±0.1          | 1993±32    | 4.95±0.04                     | 0.76±0.02  | 18.4±0.2  |    |        |
| $P_{33}$ | 280  | 0.422±0.001 | 39.4±0.1          | 2146±24    | 4.77±0.02                     | 0.78±0.01  | 17.6±0.1  |    |        |
| $P_{35}$ | 1120 | 0.440±0.001 | 40.0±0.1          | 2242±26    | 4.94±0.03                     | 0.74±0.01  | 17.8±0.1  |    |        |
Figure 4. Effective correlation radius of magnetic inclusions $r_c(B)$ and forward intensities $I_{02}(B)$ vs. the induction $B$ of magnetic field applied during the samples synthesis.

Similar behavior of $r_c$ and $I_{02}$ curves vs. the magnetic field induction $B$ (Figure 4) occurs because these functions are correlated through the relation:

$$I_{02} \sim \left(\Delta K_M\right)^2 \varphi V_1,$$

where $\Delta K_M$ is the contrast factor between magnetite and the polymer, $\varphi$ is the volume fraction of the magnetic phase, $V_1$ is the volume of a single object. In Eq. (3) we assume that the scattering object is a characteristic cluster with the reference size $r_c(B)$ and volume $V_1(B)$. The latter is defined by the relationship

$$V_1 \sim r_c^{-D},$$

where parameter $D$ refers to the geometry (fractal dimension) of the cluster [60-62]. For example, a linear chain has the fractal dimension $D=1$, for a flexible (polymer-like) chain $D=2$. Branched chain-like entities are characterized by a larger parameter, $2 < D < 3$; the exponent for globular objects is $D=3$.

In the case of ferroelastomers we have found the dimension $D \approx 2.3$ using the data approximation with function (4) in log-log coordinates, see Figure 5. Note that on the base of the presented data we can only estimate the exponent $D$. The variation of magnetic induction should vary this exponent, but to evaluate this fine effect, more detailed studies are needed.

In the presented series of SANS-experiments, the field-induced structural changes in the ensembles of ferroparticles during the polymerization process were observed, which increased the strength of the resulting magnetic elastomer samples; the field range for these observations is from zero to $B \sim 1$ kG.

Application of weak and moderate fields ($0 < B < 500$ G) leads to an unusual clusterization effect easing, therefore, the cluster characteristic size and volume decrease for 6% and 20%, respectively.
Application of stronger magnetic fields $B \sim 1$ kG enhances the cluster by 15% in size and 40% in volume in comparison with the minimal obtained level (Figure 4).

These nonmonotonic cluster size and volume changes with the increase of the applied magnetic field at relatively weak field values $B \leq 500$ G, indicate the field-induced breaking of the original (at zero field) distribution of the ferroparticles inside the elastomer. The more intense fields, make the particles to chain along the field direction.

Without external field, the particles strive to organize in the associates with minimal free energy that requires magnetic closure inside the cluster (e.g. ring-shaped structures). When imposed, the external field favors the alignment of the particle magnetic moments, thus “opening” the above-mentioned structures. This competition leads to the weakening of the original local magnetic order. However, when the magnitude of external field $B \sim 1$ kG is exceeded, the particles with aligned moments organize in chain-like structures. The aggregates of such a type are usually observed in ferrofluids under magnetic field.

4. Conclusions

The parameters in Table 2, if summarized, enable us to compare the structural features of the ferroelastomers prepared at different concentrations of magnetite and magnitudes $B$ of the magnetic field. The data evidences that embedding of ferroparticles into a polymer matrix does not disturb its large structures significantly. The gyration radius still remains at the level $R_c \sim 38 - 40$ nm, while the forward scattering intensity $I_{01}$ from these entities becomes lower. Thus, the ferroparticles loosen initial polymer structures. However, the application of an external field induces the opposite effect, i.e. at a stronger field the structures are more pronounced (parameter $I_{01}$ increases).

At a high content of magnetite (5.88 mass.%), under the change of the applied field we observe practically the same size of magnetic inclusions, $r_c \sim 2.3 - 2.4$ nm. At the same time, the forward
scattering intensity $I_{02}$ demonstrates a growth by 40% that should be attributed to the ordering in the particle ensemble (strengthening correlations along the field direction). A similar effect is found at moderate concentration of magnetite (samples $P_{22} - P_{25}$): at a practically constant size of scattering objects the forward intensity is enhanced by 40% (Table2). Note, the characteristic spacing of ferroparticles remains at the same level $\sim 15 - 16$ nm. So, it is practically independent on the concentration and the field strength. At a low content of the particles, their observation is complicated due to the scattering from small-size polymeric matrix inhomogeneities which mask the ferroparticles.

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