Experimental Report

28/05/2014

Proposal: **1-04-78** **Council:** 10/2012

Title: Reversible and irreversible effects of magnetic field upon hard-segment-domains in magnetorheological elastomers

This proposal is a new proposal

Research Area: Materials

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Samples: Polyurethane-based magnetorheological elastomer

Instrument	Req. Days	All. Days	From	To
D11	2	2	28/05/2013	30/05/2013

Abstract:

Elastomers with embedded carbonyl iron particles, anisotropically arranged during the material curing in magnetic field form “smart” magnetorheological elastomers (MREs). They are capable of significant (here: up to nine-fold) changes of their mechanical properties under external magnetic field. These novel materials are becoming of utmost importance for industry. We have already studied relaxation properties of MRE based on polyurethane (PU) by SAXS (speckle analysis, XPCS). The latter yielded plausible, yet qualitative and ambiguous description. In view of a number of open questions still remaining unanswered, the proposed experiment is aimed at complementing XPCS with the study of elastomer matrix through SANS analysis. Morphology and arrangement of PU hard domains (3–10 nm in size), considered embedded nanoobjects, will be studied in relaxed MRE and under internal strain. The latter is caused by the action of organised structures of iron particles, responding to external magnetic field. By including samples long pretreated with alternating magnetic field the effect of material wear will be seen. The results will facilitate further improvement of the performance of these MREs.

Reversible and irreversible effects of magnetic field upon hard-segment domains in magnetorheological elastomers

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The development of hi-tech coupled mechanical systems with enhanced energetic effectiveness calls for leading-edge technology of implementing active elements made of "smart" materials. Such are magnetorheological elastomers (MREs) due to their rheological properties, that can be changed continuously, rapidly and reversibly, by varying an external magnetic field. They can be thought of as analogues of magnetorheological fluids (MRFs), in which the fluid component is replaced by a cross-linked material like rubber or elastomer. They consist of μm-sized magnetically permeable particles (usually ferromagnetic) in a non-magnetic matrix. Exactly as in MRFs, the particles tend to align along the direction of the magnetic field. For simplicity, this direction will be hereafter referred to as the sample anisotropy axis. After curing of the matrix, such a microstructure becomes fixed, as shown in Fig. 1. The material so prepared becomes anisotropic, and capable of responding to an external magnetic field with a fast and reversible change of macroscopic mechanical properties (so called "magnetorheological effect"). Magnetorheological elastomers developed at Warsaw University of Technology exhibit extremely large relative magnetorheological effect (above 900%). It was found that the volume fraction of ferromagnetic particles, their size and arrangement, have crucial influence on the MRE properties, not to speak of the matrix choice.

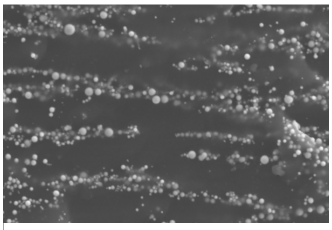

Fig. 1. Typical microstructure of MREs obtained from PU matrix with 11 vol. % of carbonyl iron particles, cured in magnetic field of 300 mT.

The SANS experiment was performed on thin flat samples aligned with their anisotropy axes oriented vertically, perpendicular to the incident beam. The incident neutron wavelength $\lambda = 5.999$ Å was chosen, and two sample-detector distances of 8 m and 40 m, were used, resulting in $0.008\ \text{Å}^{-1} < Q < 0.013\ \text{Å}^{-}1$. The sample environment involved magnetic field perpendicular both to the direction of incident beam ad to the sample anisotropy axis. Two matrix types were tested, the "soft one" (the ratio of soft/hard segments eq. 70/30) and the "hard one", with the soft/hard segments ratio reversed (30/70). The influence of mechanical history upon the domain structure was checked by measuring scattering from the samples that had undergone 0, 50, and 1000 field-on/field-off cycles prior to the experiment. Samples with two concentrations of carbonyl iron, namely 11.5 vol% and 33 vol% were selected in order to assess the role of Fe concentration upon the measured characteristics. The scattering from the elastomer relies on the in-sample contrast variation caused by density fluctuations within material of domain structure. In summary, the following measurements were performed, given the amount of beam time allocated :

	Matrix type (soft/hard segments)	**on/off cycles**	**Fe 11.5 vol%**				**Fe 33 vol%**	
			No field	**100 mT**	**300 mT**	**500 mT**	**No field**	**300 mT**
Cured in field	70/30	none	●		●		●	●
		50 cyc.	●	●	●	●		
		1000 cyc.	●		●		●	●
	30/70	none	●		●		●	●
		50 cyc.	●	●	●	●		
		1000 cyc.	●		●			
Isotropic	70/30	none	●		●			

Fig. 2 illustrates the kind of SANS spectrum anisotropy brought about by the magnetic field of 300 mT applied to the cured-in-field samples.

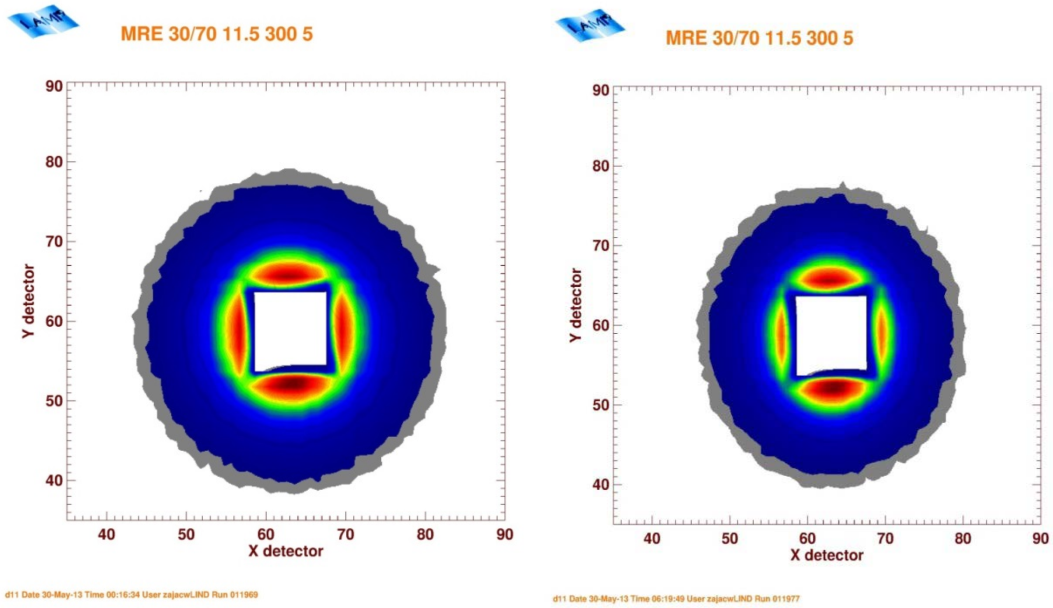

Fig. 2. The influence of the applied magnetic field of 300 mT upon small angle scattering. Samples as in the figure titles.

As in this case the small angle scattering comes from elastomer domains being irregular objects of undefined shape and often lacking regular boundaries, we had to rely on shape-independent model scattering functions. The one, originally developed for gels, proved very useful [1-2]:

$$I(Q)=I(0)_L\frac{1}{\left(1+\frac{D+1}{3}Q^2a_1^2\right)^{\frac{D}{2}}}+I(0)_G\exp\left(-Q^2a_2^2\right)+B,\quad \text{where } a_2^2\approx\frac{R_g^2}{3}.$$

The “G” and “L” indices refer to the Guinier and Lorentzian scales, respectively; *a’s* are the correlation lengths, *D* is the fractal dimension and R_g is the radius of gyration (or Guinier radius).

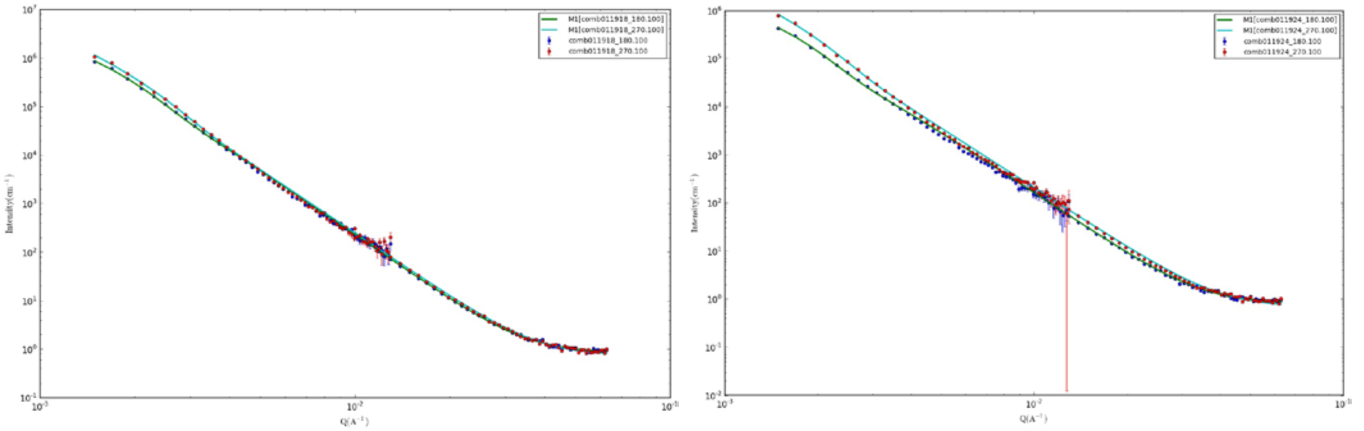

Fig. 3. The influence of the applied magnetic field of 300 mT upon small angle scattering. Model fit to the data for the same sample as in Fig. 2.

Fig. 3 presents sample yet representative fits of the above model to data collected. Model fitting was performed on combined data (information from both detector bank positions concatenated), hence noisy points in the middle of the graphs.

Tentative conclusions:

1. Not only does the model applied give reasonably good fits to the data, but also the dependence of the resulting parameter values upon sample parameters is consistent and allows to draw sensible conclusions.
2. In both anisotropic matrix types, magnetic field has the effect of increasing apparent R_g,
3. Magnetic field has the same effect on both matrix types, i.e. “soft” and “hard”,
4. In “soft” matrix (70/30), greater SANS anisotropy seen for samples with 11.5 vol% Fe, as compared to 33 vol% Fe,
5. Samples with 33 vol% Fe show more average SANS contrast than those with 11.5 vol% Fe. This requires explanation.
6. Similarly, “harder” matrix has higher average SANS contrast than “softer”. This effect was expected.
7. The influence of sample “training” (field on/off cycling) is evident. Even 50 field on/off cycles gives markedly greater apparent R_g, and there is no much difference between 50 and 1000 field on/off cycles. This means that such sample “training” has the effect of relaxing residual stresses resulting during material curing, rather than material fatigue. The latter, if at all present, might be sought after orders of magnitude more such cycles.

<u>References</u>:

[1]. M. Shibayama, T. Tanaka, C.C. Han, J. Chem. Phys. **97** (9) 6829-6841 (1992),
[2]. S. Mallam, F. Horkay, A-M. Hecht, A.R. Rennie, E. Geissler, Macromolecules **24** 543-548 (1991