XPCS study of dynamic correlation in polyurethane gel–carbonyl iron composite under magnetic field

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Abstract. An X-ray photon correlation spectroscopy (XPCS) study of composite-type material consisting of polyurethane gel and carbonyl iron micrometric spheres was performed under magnetic fields of 0, 300 and 600 mT. The onion-like spheres structure was destroyed during the composite processing. The following conclusions were obtained from the study: -The polyurethane matrix is preferred as a source for the observed dynamic effects. –Below 300 mT the material dynamics in direction of the outer magnetic field are very clear. –For 600 mT the dependence of the dynamics on magnetic field direction disappears, but the correlation rate is much higher. These findings may be caused by a disturbance of the polymer mesostructure by larger strain leading to its cross-linking.

1. Introduction

The polyurethane gel-carbonyl iron composite (PU) belongs to magnetorheological elastomers which reveal a change of their mechanical properties under an external magnetic field. These elastomers consist of magnetically permeable particles (such as iron or other ferromagnetic particles) of sizes ranging from a few to several hundreds of micrometers, added to a viscoelastic polymeric material prior to cross-linking. The origin of the magnetorheological property of such materials is still a major challenge for condensed matter physics although the interest in these materials has increased rapidly during last years due to their potential application in many fields of industry.

According to our knowledge, no XPCS study of magnetorheological composite dynamics was published so far. The nearest materials studied by XPCS under a magnetic field are ferrofluids, consisting of small, nanometric ferromagnetic particles in a pure viscous liquid as a carrier. It occurred that due to the magnetic dipole-dipole interaction between particles under a magnetic field, the particles joined in dimers, trimers or chains oriented along the field direction. XPCS indicated in these cases that the correlation effects and diffusion should be slowed down perpendicular to the field direction and enhanced parallel to it, caused by an unfolding of individual particles and / or the formation of particles assemblies [1-3].

![Fig.1 SANS curve of loose carbonyl iron particles (blue) and PU composite (red)]
The gels and polymers dynamic relaxation influenced by various parameters, as temperature, aging etc. were also studied using the method [4-7], and some features of their dynamic relaxation are close to those observed in the present work.

A possible model of the dynamic response of the studied composite PU to an outer magnetic field should take into account the suppression of the field-induced particle motion along the field lines by the viscoelastic polymer matrix. Then the strain is generated in both components of the composite. Slow dynamic relaxation of the strain in supercooled liquids was studied also with the attempt XPCS [8-10] to describe the mechanism of their dynamic response.

The great size of carbonyl iron (CI) particle in relation to the X-ray scattering scale should be a reason that X-rays will register mainly single particles, not particle groups. On our initial SANS image of the loose CI spheres an intense broad diffraction ring, centered at about 420 Å was detected which is typical for the CI sphere onion-like structure with such inter-shell distance. However, SANS images of PU show no such diffraction ring, which seems to be an evidence of the complete destruction of the shells structure during the processing (Fig.1) [11]. The destroyed shell structure rather should not be able to react on the stress induced by magnetic field in a specific way, as it is e.g. for compact hard sphere metallic structure, but it rather will be a sum of not coordinated very weak events generated in the shell remains.

2. Experimental

Materials. The investigated material was produced at the Faculty of Materials Science, Warsaw University of Technology. It consists of a polyurethane gel matrix and embedded carbonyl iron (CI) spheres of 7 µm size. The polyurethane gel is formed of isocyanate and polyl compounds with a proportion of hard and soft segments equal to 30/70. To obtain magnetorheological composite (PU), the polyurethane gel was processed together with 11.5 vol% of CI for 24 hours under a magnetic field of 300 mT at a temperature of 25°C. As it was shown using SEM, short CI chains were formed inside the material during the processing [12].

The XPCS experiment was carried out at the ID10C branch of the Troika Beamline at the European Synchrotron Radiation Facility (ESRF). The sample in form of a slice of PU of about 40 µm thickness was held in the sample cell located between electromagnet poles filled with helium to avoid air scattering effects on the long way of the X-ray. The magnetic field lines were oriented perpendicular to the X-beam and parallel to the sample surface and the embedded inside CI chains, respectively (Fig.2).

The angle (q) and time (t) resolved measurements of the speckle pattern, I(q, t), were recorded using a partially coherent X-beam of 1.75 Å wavelength (to suppress any X-ray fluorescence signal from Fe of 1.74 Å), by a direct illumination CCD area detector (Princeton Instruments) of pixel size 22.5 microns located 2.3 m downstream of the sample. It occurred that the relaxation times (t₀) ranged from 10×10² sec to 100×10² sec. The speckle patterns were recorded with about 1 sec acquisition time and 6 sec lag-time. The long-time series of the sample measurements, I(q,t), obtained from the speckle patterns, were performed under magnetic fields of: 0, 300 and 600 mT. An on-line correlation software was applied to calculate the one-time averaged intensity autocorrelation functions, g²(q,t) according to the formula:}

![Fig.2 Sketch of the experimental arrangement](image-url)
\[ g^{(2)}(q,t) = \frac{I(q,t')I(q,t' + t)}{I(q,t')}^2, \]

where: \( q = 4\pi \sin \theta / \lambda \), \( t \) – lag time, \( t' \) – time, and the brackets denote a time average. Software masks were used to determine the dependence of the correlation functions \( g^{(2)}(q,t) \) on the direction of the magnetic field, i.e. for the scattering parallel (par) and perpendicular (per) to the field lines.

3. Results and Discussion

The \( g^{(2)}(q,t) \) curves gained at 0 mT, i.e. reference curves, show an extremely slow dynamics with correlation times reaching about \( 10^4 \) sec. Under a field of 300 mT the dynamics is faster (correlation time \( \sim 2 \times 10^3 \) sec) and differences dependent on the directions are visible. Under a field of 600 mT the correlation time becomes even faster, on the average 1000 sec, while the anisotropy disappeared.

All correlation functions \( g^{(2)}(q,t) \) exhibit a simple exponential character, as observed for some polymers for temperature below \( T_c \), when besides of viscous also an solid factor of relaxation exists, but without an “stretched” form arising from an additional relaxation barrier [8]. In this work, the simply exponential character of the curves could be expected, because this polyurethane structure is of the gel type, i.e. it is not as strong ordered as it can be for this kind of polymers.

The correlation rates, \( \Gamma \) (1/sec), were found by fitting exponential functions, according to the formula: \( y = a \cdot e^{-\Gamma t} \), to the subsequent \( g^{(2)}(t,q) \) curves in their regions of correlation. Fig. 3 shows \( \Gamma \) (1/sec) curves for subsequent magnetic field values (0, 300 and 600 mT) in sets of 2 curves at each direction (par and per). Within each set the higher relaxation rate is observed in the direction parallel to the magnetic field (par), the lower one in the direction perpendicular to the magnetic lines (per).

### Table I. Diffusion coefficients [Å/sec]

| Magnetic field | 0 mT | 300 mT | 600 mT |
|----------------|------|--------|--------|
| Parallel       | 0.003| 0.018  | 0.011  |
| perpendicular  | 0.001| 0.003  | 0.009  |
The next parameter determined from the measurements is the diffusion coefficient, $D$ [Å/sec]. In the case of linear $\Gamma$, as obtained for all $\Gamma(q)$ curves, the relation between relaxation rate and diffusion coefficient is given by the formula: $\Gamma = D \times q$. The values of the diffusion coefficient, $D$ [Å/sec], were found from the slopes of straight lines fitted to $\Gamma$ (1/sec) (Table I).

The discussion of the obtained results dependent on magnetic field value (Fig.3 and Table I): is as follows:

# For the reference sample at 0 mT very moderate values of $\Gamma$ and $D$, exhibiting only a very weak anisotropy, are observed. The formation of short chains of CI particles as documented by SEM, aligned in the parallel (par) direction, do not result in a distinct anisotropic dynamics, manifested in the rate of correlation or diffusion. It is an argument for insignificant role of the CI particles in dynamic behavior of the composite.

# For the intermediate value of the magnetic field (300 mT), the same parameters are strongly dependent on the magnetic field direction and of larger values. The obtained sample response to the outer magnetic field is similar to the response of other polymers and gels to an absorbed additional internal energy, for example to an increase in temperature, where at higher temperature the $\Gamma$ slope becomes more steep [9].

# Contrary, at 600mT the dependence of $\Gamma$ and $D$ on the magnetic field direction completely disappears. This could be caused by reaching a kind of saturation, but the unexpectedly large correlation rates $\Gamma$, suggest a much more fundamental change in the system. To get a clear picture of these changes, without direction-dependent parameters, we considered the $\Gamma(q)$ curves obtained from XPCS measurements in isotropic mode (without mask). Figure 4 shows the corresponding data for all used magnetic fields together with a linear fit extrapolating to $q = 0$.

A dramatic increase of the isotropic $\Gamma(0)$ values of about ten times for 600 mT as compared with to 300 mT is observed, whereas the slopes of the both $\Gamma(q)$ curves are similar. As it is known, for $q \to 0$, $\Gamma \to E / \eta$, where $E$ is the elasticity yielding a frequency-independent storage modulus, and $\eta$ is the shear viscosity of the material [9]. A change in the ratio of elasticity and shear viscosity can presumably be associated with a modification of the gel mesostructure.

Gels are materials with a tendency to change their mesostructure to a more dense and more cross-linked phase even without any outer influence, which is known as an aging process [13]. As it was observed in many cases that the mesostructure disturbance is followed by its quick rebuilding through cross-linking and domains growth inside a mesostructure [13].

The polymer strain, caused by the urge of the CI particle to shift along the field line, during an increase of the magnetic field to 600 mT, would reach a high enough value to cause a disturbance of the gel mesostructure. The next step upon these changes is a rebuilding and reinforcement of the mesostructure according to one of the gelation mechanisms [13]. This reinforcement might cause here the decrease of susceptibility of the dynamic features in one direction, and domain growth results in an increase of elasticity $E$, observed as larger correlation rates, $\Gamma(0)$.

On the other hand, the magnetorheological effect in PU was measured at the Warsaw University of Technology as the material’s response to an outer magnetic field in form of the displacement of a bend sample deflection.

Figure 5[12] shows the displacement effect for a PU sample under the outer magnetic field in the range 0 – 900 mT, for various contents of CI. For 11.5vol% CI (the sample used for the XPCS study) an exponential-type displacement is observable in the range of 0 – 600 mT, but for higher magnetic fields no further displacement was obtained [12]. These findings also agree with the hypotheses of reinforcement of the PU mesostructure by a magnetic field of more than 600 mT.
4. Concluding remarks

The results of the study seem to prefer polyurethane gel matrix as the source of the main dynamical effects observed by XPCS, arising from a stress transferred from the embedded magnetic particles to the matrix under an external magnetic field.

The magnetic field strongly affects the material dynamics. For its moderate value of 300 mT the dependence of the material dynamics on the direction of the external magnetic field is very clear with the parallel direction showing larger relaxation rates, $\Gamma(q)$.

For higher magnetic field (600 mT) the material’s dynamic response to the magnetic field changes dramatically. The dependence of the obtained parameters on the magnetic field direction disappears, but the correlation rate increases by about ten times. This dynamical behavior as a function of the magnetic field strength can be caused by a disturbance of the polymer mesostructure at higher fields, leading to its cross-linking and reinforcement. Further studies are needed to confirm the hypothesis about a rebuilding of the mesostructure.

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5. References

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