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THE INFLUENCE OF MICROSTRUCTURAL ANISOTROPY ON THE MAGNETORHEOLOGICAL EFFECT IN ELASTOMER-BASED COMPOSITES WITH IRON PARTICLES

The results presented in this paper are a part of the studies on development of magnetorheological elastomers based on ferromagnetic particles in a polyurethane matrix. The influence of the amount of the ferromagnetic particles and their arrangement in relation to the external magnetic field was investigated. Scanning electron microscopy was used to observe MRE microstructure. The particles orientation and their arrangement were also investigated with vibrating sample magnetometer (VSM). Rheological properties of obtained MREs were studied with and without application of an external magnetic field. It was found that the microstructure of the MRE depends on the amount of ferrous particles. The orientation of the iron particles into aligned chains is possible for a lower volume content of ferromagnetic filler. Magnetic measurements confirmed the existence of microstructure anisotropy for MREs with 1.5; 11.5; 18 and 25 vol. % of iron particles. This structural and magnetic anisotropy has not been found in the the MRE with 33 vol. % of carbonyl-iron. Both the particles content and their chains direction have significant effect on the rheological properties of magnetorheological urethane elastomers. Application of an external magnetic field leads to a significant increase in elastic modulus. Relative changes of storage modulus, calculated from obtained curves, show that the samples microstructure has a significant effect on their magnetorheological effect.

Keywords: **carbonyl iron, elastomer, magnetorheological properties, polyurethane**

WPŁYW ANIZOTROPII MIKROSTRUKTURY NA EFEKT MAGNETOREOLOGICZNY W KOMPOZYTACH ELASTOMEROWYCH Z CZĄSTKAMI ŻELAZA

Wyniki zamieszczone w tej pracy są częścią badań prowadzonych nad magnetoreologicznymi elastomerami zawierającymi cząsteczki ferromagnetyczne w poliuretanowej osnowie. Zbadano wpływ zawartości i sposobu rozmieszczenia cząstek w aspekcie zewnętrznego pola magnetycznego. Do obserwacji mikrostruktur MRE wykorzystano skaningowy mikroskop elektronowy. Ukierunkowanie i rozmieszczenie cząstek zbadano za pomocą magnetometru z wibrującą próbką (VSM). Właściwości reologiczne wytworzonych materiałów badano zarówno bez pola, jak i w zewnętrznym polu magnetycznym. Stwierdzono, że mikrostruktura MRE zależy od zawartości cząstek ferromagnetycznych. Ukierunkowanie cząstek w jednokierunkowe łańcuchy jest możliwe dla niższych zawartości ferromagnetycznego komponentu. Pomiary magnetyczne potwierdziły występowanie anizotropii strukturalnej dla MRE o zawartości 1,5; 11,5; 18 i 25% obj. cząstek żelaza. W przypadku kompozytów o zawartości 33% obj. żelaza karbonylkowego nie zaobserwowano strukturalnej i magnetycznej anizotropii. Na właściwości reologiczne elastomerów uretanowych ma wpływ zarówno zawartość cząstek, jak i kierunek łańcuchów przez nie tworzonych. Przyłożenie zewnętrznego pola magnetycznego prowadzi do znacznego wzrostu modułu sztywności. Względne zmiany modułu zachowawczego G', wyliczone z otrzymanych krzywych, świadczą o znaczącym wpływie mikrostruktury na uzyskiwany efekt magnetoreologiczny.

Słowa kluczowe: **żelazo karbonylkowe, elastomer, właściwości magnetoreologiczne, poliuretan**

INTRODUCTION

Magnetorheological (MR) materials change their rheological properties under the influence of an applied magnetic field. Magnetorheological elastomers (MREs) are solid analogues of magnetorheological fluids (MRFs). These both consist of micrometer-sized magnetically permeable particles in a non-magnetic matrix material. As in the case of MR fluids, the particles try to arrange themselves in the direction of the magnetic field [1-3]. The advantage of MREs over MRFs is that ferrous particles do not undergo sedimentation. In comparison with MRFs, the MREs have a field-responsive modulus and the amount of the particle filler can also be lower. Due to the characteristic MRE microstructure, the response time and strain magnitude versus magnetic field intensity can be shortened. Interest in such intelligent materials has increased recently as they hold promise in enabling variable-stiffness devices and adaptive structures in aerospace, automotive, civil and electrical engineering applications [4].

Different elastomers and fillers can be used for MRE fabrication [5, 6]. A strong external magnetic field is applied before the polymer curing process. Particle chains with collinear dipole moments are formed and curing of the polymeric host material locks the chains in place [7, 8]. In terms of orientation, the particles can form separate chains, three-dimensional simple lattice structures (consisting of separate chains), or even more complex structures, in which particles have multiple interaction points [9].

MATERIALS AND METHODS

Magnetorheological elastomers were manufactured by using polyurethane gel, synthesized from polyether polyol VORALUX® HF 505 used in a blend with 14922 polyol and isocyanate compound HB 6013, supplied by Dow Chemical Company. The substrates were mixed and cured at room temperature.

Polyurethane gel is characterized by relatively low density, hardness and stiffness [10]. The low hardness and stiffness of the matrix can lead to higher relative property changes of the MRE in an external magnetic field. Low viscosity of the matrix before curing during MRE processing allows particles to arrange easily into aligned chains [10].

The ferromagnetic component used in the MREs, was carbonyliron powder with particle size ranging from 6 to 9 μm, produced by Fluka. The amount of the carbonyl iron particles was equal to 1.5; 11.5; 18.0; 25.0 and 33.0 vol. %, respectively.

The samples were produced with randomly dispersed and aligned carbonyl iron particles. They were subjected to a magnetic field during curing to produce aligned carbonyl chains within the elastomer. Magnetic field strength of 0.3 T was used.

The microstructure of MRE brittle fracture surfaces was observed by scanning electron microscopy (SEM) LEO 1530 Zeiss. Magnetic properties were studied by Lake Shore vibrating sample magnetometer (VSM). Rheological properties were evaluated with the application of ARES rheometer from TA Instruments (plate--plate system, plate diameter - 20 mm, gap - 2 mm, magnetic field range - 0÷0.6 T). Experiments were conducted at 25°C on samples with various particle content. The particle chains within the samples were oriented at 0, 90 or 45° to the magnetic field lines.

RESULTS AND DISCUSSION

Microstructure observations

Filler particles have to be aligned in the magnetic field during the curing of the matrix because the orientation of the particles is unfeasible when the elastomer is cured. Microstructure observations of the MREs brittle fractures by SEM showed the existence of aligned particles chains in the elastomer matrix (Fig. 1a). It seems that the alignment of the particles chains depends on the amount of the particles within the matrix. As shown in Figure 1b sample with 33 vol. % of carbonyliron has homogenous-like dispersion while for the sample with lower particles content chains of particles are clearly visible. It leads to the conclusion that the particles can arrange themselves easily into chains only for lower volume contents. High carbonyl-iron volume content (33 vol. %) in the PU matrix leads to the formation of more complex microstructures similar to the three-dimensional matrices. Investigations of magnetic properties were performed to confirm the existence of the structural anisotropy [11].

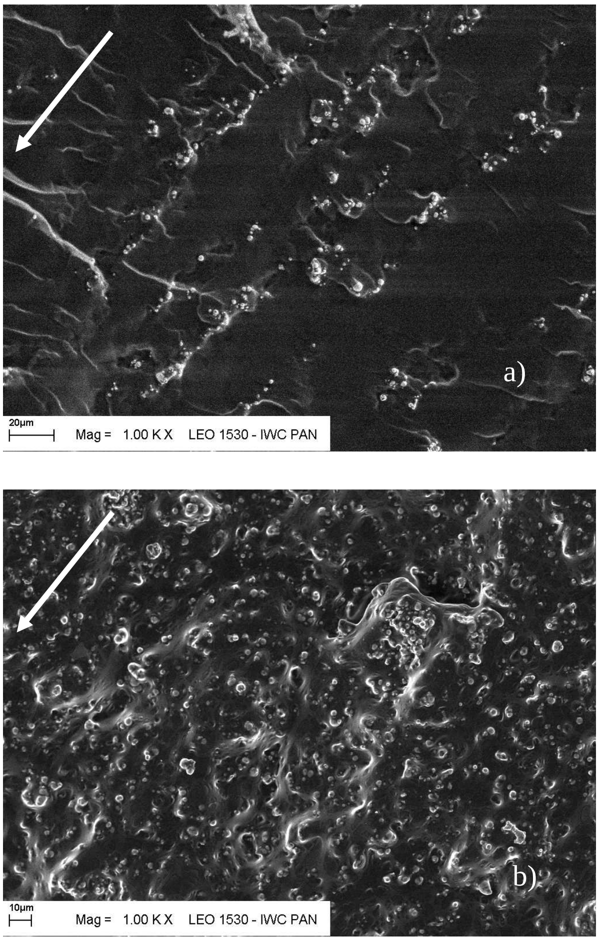

Fig. 1. SEM images of MREs with 11.5 (a) and 33 vol. % Fe (b) cured under magnetic field. White arrows show magnetic field direction

Rys. 1. Obrazy SEM próbek MRE z 11,5 (a) i 33% obj. Fe (b) utwardzanych w polu magnetycznym. Białe strzałki pokazują kierunek pola

Magnetic properties

Magnetic properties of the obtained MREs were investigated by vibrating sample magnetometer (VSM). The particles orientation and their arrangement were examined. Tests were carried out parallel and perpendicular to the sample long axis, corresponding to the magnetic field direction during curing. Hysteresis loops for the MREs with particles content varying from 1.5 to 25 vol. % proved structural and magnetic anisotropy [11]. SEM observations and hysteresis loops indicate that for the highest ferrous particles content (33 vol. %) an isotropic network of particles is formed.

The anisotropy coefficient (A_b) was calculated from the hysteresis loops and was expressed by the ratio of magnetic moments measured at a magnetic field strength of 0.2 T, respectively parallel and perpendicular to the alignment direction. The relationship between anisotropy coefficient and carbonyl-iron particle volume content is shown in Figure 2.

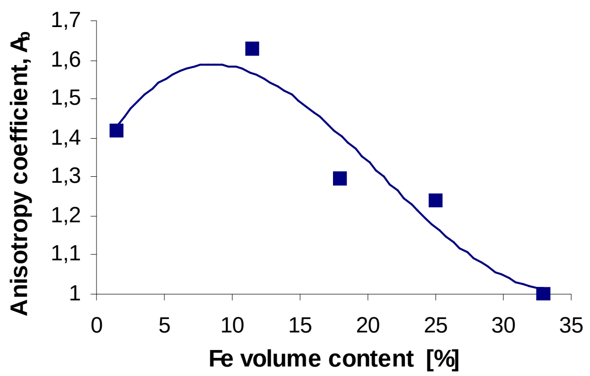

Fig. 2. Anisotropy coefficient (A_b) for MRE with different amount of carbonyl-iron, cured under magnetic field strength of 0.3 T

Rys. 2. Współczynnik anizotropii (A_b) dla MRE o różnej zawartości żelaza karbonylkowego utwardzanych w polu magnetycznym 0,3 T

Material anisotropy coefficient (A_b) changes with the amount of magnetic particles in the composite. It was found that the (A_b) increases from 1.42 for 1.5 vol. % Fe to 1.63 for the 11.5 vol. % Fe specimen. There is the maximum value of the anisotropy coefficient corresponding to 11.5 vol.% of carbonyl-iron. Next the anisotropy coefficient decreases with further increase in the volume fraction of particles. Structural and magnetic anisotropy has not been found in the specimens having 33 vol. % of carbonyl-iron, therefore, the anisotropy coefficient is equal to 1 for these specimens. The result can be attributed to the formation of the particles network, in contrast to the particle chains that characterize anisotropic composites. This was also visualized by SEM observations. The higher the amount of the particles over 11.5 vol. %, the lower the magnetic anisotropy observed until 33 vol. %, where the structure of the MRE becomes magnetically isotropic.

Rheological properties

MR elastomers are normally operated with small deformations in the pre-yield regime of the linear viscoelastic region. The MREs are intended to be used as structural materials in applications where the load is often of a dynamic type. In cyclic dynamic loading, the material deforms and returns back to its original form during one cycle. The oscillating force is varied periodically, usually with a sinusoidal amplitude at the angular frequency ω.

In viscoelastic materials, some of the deformation energy input is stored and recovered during each cycle and some is dissipated as heat. The storage modulus, G' represents the ability of the viscoelastic material to store the energy of deformation, which contributes to the material stiffness. The loss modulus, G'' represents the ability of the material to dissipate the energy of deformation.

In this study, the elastic (storage) modulus G' was measured as a function of angular frequency ω or strain γ. Also tan(δ) expressed as G''/G' is presented, as well as relative changes of storage modulus.

As it is known from SEM and magnetic studies, the highest anisotropy coefficient was recorded for the sample with 11.5 vol. % of ferromagnetic particles. Therefore, the rheological properties of such MREs were compared to MREs with 33 vol. % Fe, which is characterized by a three-dimensional particles network (Fig. 3). Investigations were carried out with and without application of an external magnetic field of 0.1 and 0.2 T.

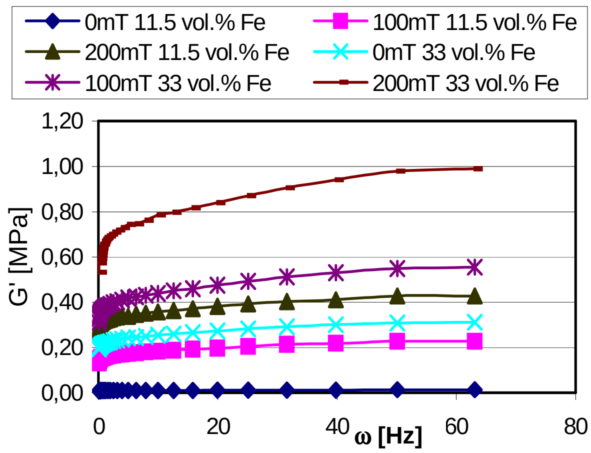

Fig. 3. Storage modulus G' versus frequency ω curves obtained under different magnetic field strengths for MRE with 11.5 and 33 vol. % Fe cured under 0.3 T. Particle chains parallel to the applied magnetic field

Rys. 3. Krzywe modułu zachowawczego G' w zależności od częstotliwości ω uzyskane przy różnym polu magnetycznym dla MRE z 11,5 i 33% obj. Fe, utwardzanych w 0,3 T. Łańcuchy cząstek ułożone równolegle do przyłożonego pola

As shown in Figure 3, the values of G' increase with the increasing of the magnetic field for MREs with 11.5 and 33 vol. % Fe. Due to the higher amount of ferromagnetic particles in the PU matrix, higher values of G' for MRE with 33 vol. % Fe are observed. To compare changes in elastic modulus under external magnetic field the relative change of storage modulus has been calculated (Table 2).

Additionally, the influence of an applied magnetic field on storage modulus for different strains and angular frequencies has been investigated (Figures 4 and 5). The influence of magnetic field on tan(δ) for different particles arrangements has also been presented (Fig. 6).

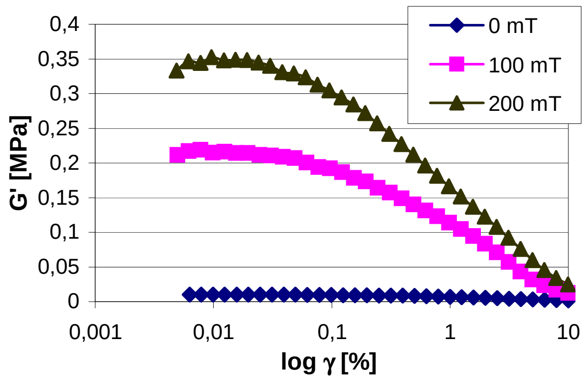

Fig. 4. Storage modulus G' versus strain γ obtained under different magnetic field strengths for MRE with 11.5 vol. % Fe, cured under 0.3 T. Particle chains parallel to the applied magnetic field

Rys. 4. Krzywe modułu zachowawczego G' w zależności od odkształcenia γ uzyskane przy różnym polu magnetycznym dla MRE z 11,5 i 33% obj. Fe, utwardzanych w 0,3 T. Łańcuchy cząstek ułożone równolegle do przyłożonego pola

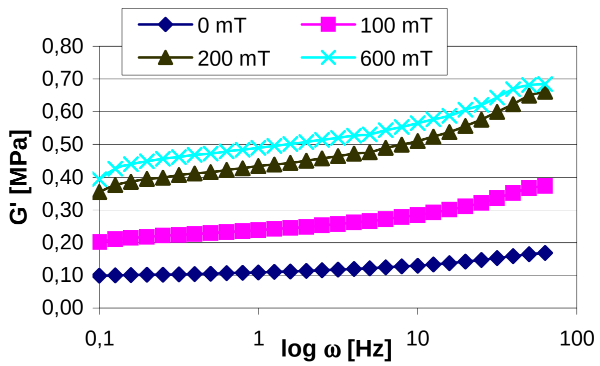

Fig. 5. Storage modulus G' versus frequency ω obtained under different magnetic field strengths for MRE with 11.5 vol. % Fe, cured under 0.3 T. Particle chains tilted 45° to the applied magnetic field

Rys. 5. Krzywe modułu zachowawczego G' w zależności od częstotliwości ω uzyskane przy różnym polu magnetycznym dla MRE z 11,5 i 33% obj. Fe, utwardzanych w 0,3 T. Łańcuchy cząstek ułożone pod kątem 45° do przyłożonego pola

It was found that the elastic modulus G' increases slightly with angular frequency and decreases with raising strain. The application of an external magnetic field leads to a significant change in elastic modulus. For the MRE with 11.5 vol. % Fe elastic modulus increases with an external magnetic field from 0 to 600 mT for all tested frequencies.

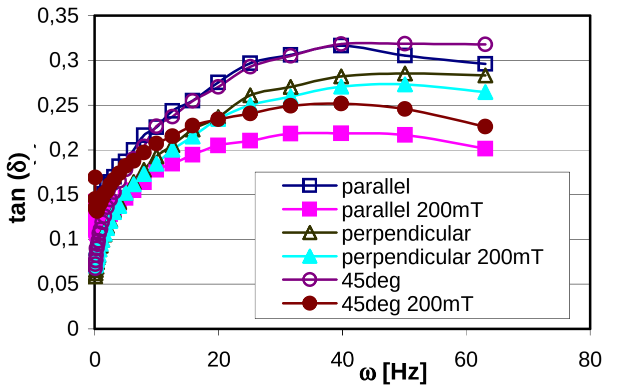

Fig. 6. tan(δ) versus frequency ω obtained for MRE with 11.5 vol. % Fe aligned at different angles under magnetic field of 0.3 T, with and without an applied magnetic field of 0.2 T

Rys. 6. tan(δ) w zależności od częstotliwości ω uzyskane bez i przy polu magnetycznym 200 mT dla MRE z 11,5% obj. Fe, utwardzanych w 0,3 T. Łańcuchy cząstek ułożone pod różnymi kątami do przyłożonego pola

tan(δ) curves show that there is a strong relation between changes of elastic modulus and microstructure of the sample. The highest drop of tan(δ) under applied magnetic field is observed for the sample with particle chains parallel to the magnetic field lines. Slightly lower change is observed in case of chains tilted at 45 degrees. Sample with particles aligned perpendicular to an applied magnetic field exhibits only slight change in tan(δ). These results show high anisotropy of MREs properties, which depend not only on microstructure but also on direction of an external magnetic field.

Relative change of storage modulus G' has been calculated for selected samples (Table 1).

TABLE 1. **Relative change of storage modulus for 10 Hz frequency, $\Delta G'_{200mT} = G'_{200mT} - G'_0$**

TABELA 1. **Względne zmiany modułu zachowawczego G' dla częstotliwości 10 Hz, $\Delta G'_{200mT} = G'_{200mT} - G'_0$**

Fe, vol. %	MF during curing mT	Particle chains orientation	$\frac{\Delta G'_{200mT}}{G'_0}$
11,5	300	45°	2,95
18	300	45°	2,42
33	300	45°	1,83

The highest relative change in G' modulus under magnetic field of 0.2 T has been obtained for the sample with 11.5 vol. % Fe. This can be correlated with the highest magnetic anisotropy coefficient obtained for this sample.

CONCLUSIONS

MREs are the novel materials, analogous to MR fluids, with many potential applications. To develop a functional composite material with good damping properties, it is important to monitor rheological properties and the magnetorheological effect. Rheological properties depend on the MRE microstructure, which in turn depends on the amount of ferromagnetic particles and their arrangement.

It was found that the microstructure of the MRE depends on the amount of ferrous particles. The orientation of the iron particles into aligned chains is possible for a lower volume content of ferromagnetic filler. High carbonyl-iron volume content in the matrix leads to the formation of more complex microstructures. Microscopic observations proved that the iron particles form chains aligned with the magnetic field direction when the particle content is less than 33 vol. %. At a particle content equal to 33 vol. % Fe, three-dimensional lattices of iron particles are formed.

Magnetic measurements confirmed the existence of microstructure anisotropy for MREs with 1.5; 11.5; 18 and 25 vol. % of iron particles. This structural and magnetic anisotropy has not been found in the the MRE with 33 vol. % of carbonyl-iron. Moreover, the results of the studies proved that the anisotropy coefficient expressed as the ratio of magnetic moments measured, respectively parallel and perpendicular to the alignment direction, depends on the particle content.

Both the particles content and their chains direction have significant effect on the rheological properties of magnetorheological urethane elastomers. The elastic modulus of MREs increases with increasing angular frequency and applied magnetic field strength. Application of an external magnetic field leads to a significant increase in elastic modulus. Relative changes of storage modulus, calculated from obtained curves, show that the samples microstructure has a significant effect on their magnetorheological effect.

The particle network structure of aligned MREs has a significant influence on the elastic and damping properties of the composite material. Inside the chains the effective filler content is higher than the average filler content. By optimizing the particle density and alignment, either the stiffness or the damping of MREs can be increased by applying a magnetic field.

Acknowledgements

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