Atomic force and electron microscopy of silicone composites with nanostructured iron

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Abstract. Novel magnetoactive thin film composites based on silicone elastomer with nano-structured iron fillers have been synthesized. Atomic force microscopy studies have established these composites surface topography unique sensitivity to restructuring induced by the atomic force microscope probe. Application low external magnetic field also resulted in changing the initial composites surface wrinkled structure. Scanning electron microscopy research allowed determine the filler agglomerates average size from about 100 nm to 5 μm and their distributions in the polymer matrix. These composite systems with variable surface properties, possess tunable microstructure morphology as a result of controlling small external influences. Such magnetoactive thin film smart surfaces with dynamic wrinkles can find wide practical applications in tunable optical and electronic devices with responsive microstructures.

1 Introduction

Magnetoactive elastomers (MAE) belong to the “smart” materials. This materials type has a wide range of properties such as:

- magnetorheological,
- magnetoelectrorheological,
- magnetodeformation,
- magnetostriction,
- magnetoresistive,
- piezoresistive,
- magnetopiezoresistive,

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- piezoelectric,
- magnetodielectric,
- magnetoacoustic,
- shape memory,
- magneto-optical effects and find numerous practical applications [1-6].

MAE are perspective for creation the magnetostrictive motors, actuators, sensors, various complex structures protection from vibration, aerospace vehicles and solar panels control and stabilisation, resonant characteristics control in robotics and tectonics using magnetic fields at minimal energy consumption, medical, biomechanical applications and so on. They are composites made with magnetic particles, dispersed in an elastic polymer matrix with a small elastic modulus about several tens kiloPascal. The characteristic response depends on the matrix nature, the ferromagnetic particles size, distribution, composition, and quantity. Microstructural carbonyl iron is widespread filler in MAE in the both isotropic and anisotropic composites creation. Magnetic nanoparticles are also popular research objects nowadays. In this work nano-structured iron was used as a filler to create MAE with silicone matrix. Atomic force and electron microscopy were used to reveal the synthesized composites surface microstructure features.

2 Materials and equipment

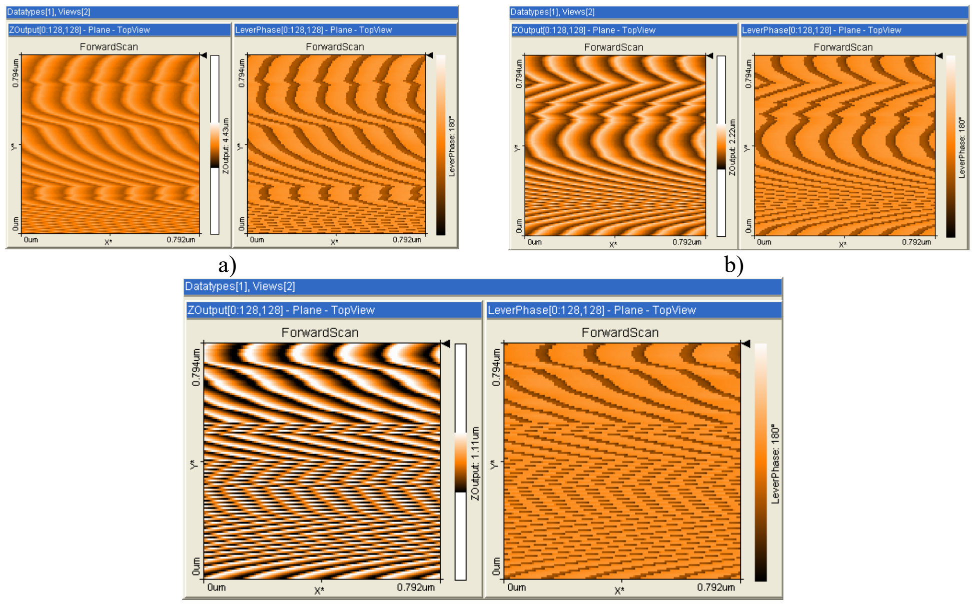
MAE samples with a silicone compounds polymer matrix SIEL (GNIICHTEOS, Moscow, Russia) with a nano-structured iron powder filler an average size about 120 nm (Advanced Powder Technologies LLC, Tomsk, Russia) were synthesized. These iron nano-powders were produced by the metallic iron electric explosion in gaseous media. Such nano-structured iron has unique characteristics: high chemical activity, weak agglomeration, possibility to regulate disperses composition etc. We additionally modified the obtained filler powder by coating it with a polymethylsiloxane oil film.

When preparing the polymer matrix, the silicone compound components of SIEL brand were mixed in the required proportions and thoroughly mixed. In the resulting mixture was added modified iron filler powder with a concentration 40 % wt %, all intensively mixed, vacuumed and poured a thin layer about 0.5 mm on a paper or polymer base. This system was left to polymerize for 40 minutes at 160 °C. This MAE composites surface structure was studied by an EasyScan atomic force microscope (AFM) (Nanosurf, Switzerland).

The microscope was operated in semi-contact mode in air at room temperature. The additional phase contrast mode was used. The AFM was protected from external disturbances using an anti-vibration stage TS-150 (Fabrik am Weiher, Switzerland). The synthesized composite structure features were also investigated using a KYKY EM6900 scanning electron microscope (SEM) (KYKY Technology Co., PRC) with a vacuum system equipped by the turbomolecular pump and a tungsten thermoemission cathode (6 nm resolution at an accelerating voltage 30 kV on a semiconductor four-section BSE detector).

3 Experimental results and discussion

The MAE composites surface AFM images are presented in Figure 1 a, b, c at an initial scanning height: a) 17.88 µm, with subsequent transitions to heights: b) 8.74 µm and c) 4.47 µm. In conventional composites the samples surface topography pattern does not change with these transitions. Only the images contrast and resolution are improved. In these composites a significant change in surface topography is observed at such transitions. These results demonstrate the synthesized composites surface structure significant restructuring induced by the AFM probe.



c)

Fig. 1. a, b, c. The MAE composites surface structure AFM images at initial scan height: a) 17.88 µm; b) 8.74 µm; c) 4.47 µm (left – Top view topography, right- phase contrast). Scans are 0.792 x0.792 µm.

The topography and phase contrasts images obtained by AFM (Figure 2, 3) also reveals a significant change in the composites surface patterning under influence the imposed external magnetic field about 500 Oe in addition to ordinary magnetostriction effects. The MAE composites examination using SEM KYKY EM6900 at low accelerating voltages 10 kV similarly reveals the wrinkled surface structure in these samples (Figure 4). Increasing the accelerating voltage to 20 kV allowed to determine the filler agglomerates average size from about 100 nm to 5 µm and their distributions in the polymer matrix (Figure 5).

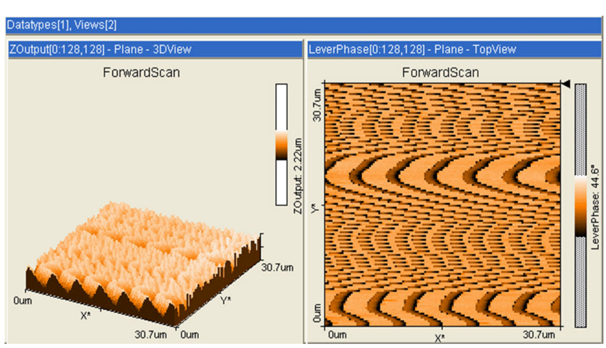


Fig. 2. The MAE composites surface structure AFM images without an external magnetic field (left – 3D view topography, right – Top view phase contrast). Scans are 30.7x 30.7 µm.

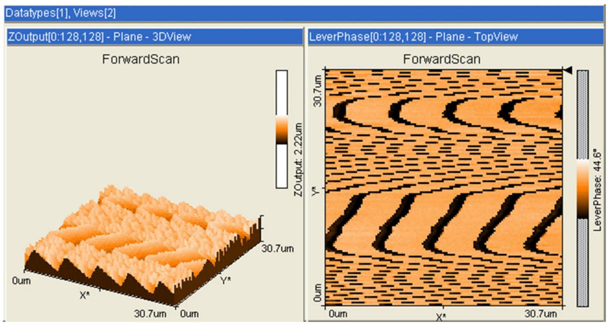


Fig. 3. The MAE composites surface structure AFM images with samples under the external magnetic field action (left -3D view topography, right -Top view phase contrast). Scans 30.7x 30.7 µm.

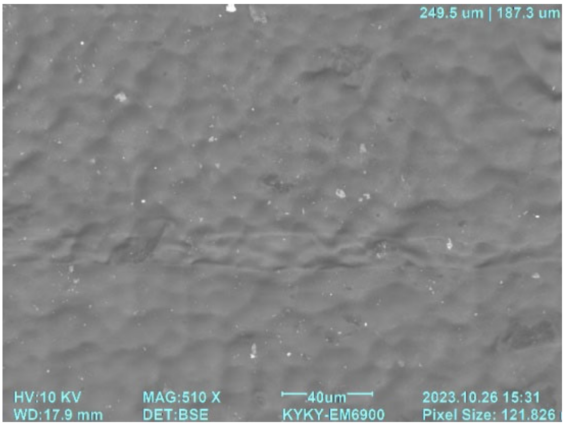


Fig. 4. The MAE composites SEM images at an accelerating voltage 10 kV.

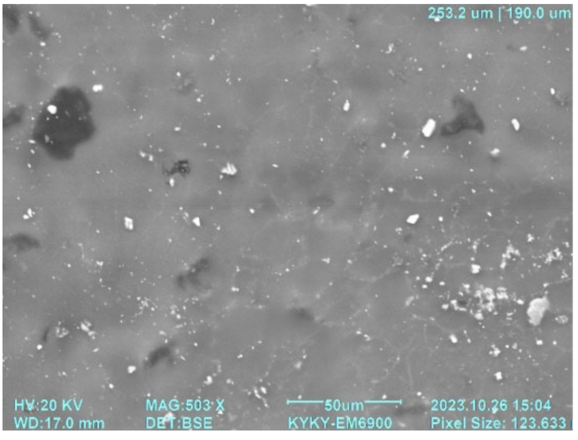


Fig. 5. The MAE composites SEM images at an accelerating voltage 20 kV.

This surface extremely sensitivity of the designed MAE composites to small mechanical and magnetic forces certainly is due to nano- micro-sised iron fillers mutual interactions with low Young's modulus elastic polymer matrix. Such composite systems with variable surface properties, possessing a tunable morphology as a result of controlling small external influences are currently in high demand [7-9].

4 Conclusion

In summary we demonstrate that the synthesized thin film MAE composites based on silicone elastomer with nano-structured iron fillers are very sensitive to external stimuli. The microstructure wrinkled surface topography can easily be changed under the atomic force microscope probe action. The low external magnetic field application also resulted in changing the initial composites surface wrinkled structure in addition to ordinary magnetostriction effects. The nano-structured iron filler agglomerates average size determined by scanning electron microscopy are in the micro and sub-micro range and distributed isotopically in the polymer matrix. So, these composite systems possess tunable surface microstructure morphology as a result of controlling small external influences. Such MAE surfaces with dynamic wrinkles can find wide applications. These may include tunable smart optical or flexible electronic devices, responsive microstructures, switchable wettability, new non-permanent adhesive and responsive microfluidic channels.

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References

1. V.A. Bautinac, E.V. Kostitsyna, N.S. Perov, N.A. Usova, Compos. Commun. **22**, 1-4 (2020).
2. M.M. Said, J. Yunas, R.E. Pawinanto, B.Y. Majlis, B. Bais, Sensor. Actuator. **245**, 85-96 (2016).
3. J. Yuan, Z.Q. Liu, Compos. Sci. Technol. **164**, 8-16 (2018).
4. D. Borin, Phil. Trans. R. Soc. A **378**, 20190256 (2020).
5. M. Watanabe, Y. Takeda, T. Maruyama, J. Ikeda, M. Kawai, T. Mitsumata, Int. J. Mol. Sci. **20**, 2879 (2019).
6. E.Yu. Kramarenko, G.V. Stepanov, A.R. Khokhlov, INEOS OPEN **2**, 178 (2019).
7. H. Hou, J. Yin, X. Jiang, Accounts. Chem. Res. **52**, 1025 (2019).
8. Z. Li, Y. Liu, M. Marin, Y. Yin, Nano Res. **13**, 1882-1888 (2020).
9. Qiu Xiaxin, Liang Shumin, Zhang Lidong, ACS Materials Lett. **5**, 2906-2912 (2023).