Aging of carbon nanotube-filled fluoroelastomer in oil-based drilling fluid

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Abstract: Carbon nanotube (CNT)-, carbon black (CB)-filled fluoroelastomer (FE) and unfilled FE compounds were prepared (CNT/FE, CB/FE and FE). The oil-based drilling mud (OBD) aging resistance of these elastomers were assessed by tests of atomic force microscopy (AFM), optical microscopy and X-ray diffractometry (XRD). Weight gain, swelling and hardness were also determined. The whole conclusion is that CNT/FE can be used as O-rings in OBD drilling while FE and CB/FE can not.

Keywords: carbon nanotube, fluoroelastomer, carbon black, oil-based drilling mud, aging test, atomic force microscopy, optical microscopy.

Starzenie fluoroelastomeru napełnionego nanorurkami węglowymi w płuczce wiertniczej na bazie oleju

Streszczenie: Metodami mikroskopii optycznej, mikroskopii sił atomowych (AFM) i dyfraktometrii rentgenowskiej (XRD) badano odporność starzeniową kompozytów na bazie fluoroelastomeru (FE) napełnianego nanorurkami węglowymi (CNT) lub sadzą węglową (CB), poddanych działaniu płuczki wiertniczej na bazie oleju (OBD). Oznaczano też przyrost masy, stopień spęcznienia i twardość próbek poddanych starzeniu w środowisku płynu wiertniczego. Stwierdzono, że fluoroelastomer napełniony nanorurkami węglowymi jest odporny na działanie płynu wiertniczego i można go stosować w materiale uszczelek w urządzeniach wiertniczych wykorzystujących płuczki na bazie oleju.

Słowa kluczowe: nanorurki węglowe, fluoroelastomer, sadza węglowa, płuczka wiertnicza, test starzeniowy, mikroskopia sił atomowych, mikroskopia optyczna.

Carbon nanotubes (CNTs) can improve many properties of fluoroelastomer (FE) for different applications especially in oil and gas drilling industries [1–3]. It is very important to verify scientifically that whether CNT/FE can be applied as sealing rubbers (for example O-rings) in OBD (oil-based drilling mud) drilling for oil and gas or not. Using CNT in FE can resolve the various problems of seals that are present in drilling by [4, 5]: firstly, reducing rupture and detachment of the seals and also by improving mechanical properties of the seals particularly improving the high temperature mechanical properties, secondly, providing resistance to commonly used drilling fluids through excellent chemical resistance, and thirdly, reducing areas of local heating through more excellent thermal conductivity. When CNT/FE is used as seal for drilling for oil, the drilling can be done for a long period of time, for example, under water at high temperature and pressure the drilling depth was able to be further deepened.

Some of the techniques that can be used to study whether CNT/FE can be applied as O-rings in OBD drilling are as follows: percentage weight gain and swelling study of nanocomposite in OBD can be used to study the resistance of CNT/FE to OBD. Furthermore, atomic force microscopy (AFM) and optical microscopy investigation of nanocomposite surface before and after subjecting nanocomposite to OBD test are useful and powerful techniques to study the resistance of CNT/FE to OBD. Many researchers have investigated the surface of CNT-filled and nanofiller-filled rubber using AFM. The parameters they studied included topography [6, 7], the degree of dispersion [8–10] and interaction of nanofiller and rubber, as well as interphase region between nanofiller and rubber matrix [11–14]. Some of them are mentioned below.

For example AFM could be used to study roughness of CNT-filled and unfilled rubber. In a study by Molavi *et al.* [6], AFM topography was used to show that micro roughness of the CNT-filled rubber is marginally higher than that of unfilled rubber.

As another example, AFM and optical microscopy were used to study the dispersion of CNT in rubber [10]. The AFM results for carboxylated-MWCNT (multi-walled carbon nanotube)-filled natural rubber exhibited

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that macroscopic dispersion of nanofiller was good, in agreement with optical microscopy observations.

Researches for finding out that whether CNT/FE can be used as sealing rubbers (for example O-rings) in OBD drilling for oil and gas were rather rare. Also researches on the verification of the weight gain and swelling of FE, CB/FE and CNT/FE in OBD and their comparisons and also investigation of their OBD tested surfaces by AFM as well as optical microscopy and XRD were rather rare. Furthermore, the comparison of the AFM and optical microscopy image of FE, CB/FE and CNT/FE before and after subjecting to OBD test, detailing the roughness and height parameters of the surface was seldom published. Also, the comparison of XRD spectra of these elastomers after subjecting to OBD test detailing the degradation products by OBD was seldom published. Therefore, this investigation was unique in the following senses. First, the knowledge of the changes in roughness and height parameters of the surface, second, the knowledge of the amount of weight gain and swelling, and third, the knowledge of the degradation products give an insight into the ability of CNT to improve the OBD resistance of CB/FE and FE composites. If CNT/FE is resistant to OBD, it can be used as sealing rubbers (for example O-rings) in OBD drilling for oil and gas. Original FE compound is not resistant to OBD therefore FE without CNT cannot be used as the above mentioned sealing rubbers.

In the present work, CNT was used as filler for FE with the aim of improving the OBD resistance of FE so that CNT/FE can be used as O-rings in OBD drilling for oil and gas. The OBD resistance of the composites *vis-à-vis* CB-filled and unfilled FE were assessed by AFM, weight gain, swelling test, optical microscopy and XRD. This was to ascertain whether incorporation of CNT could reduce the roughness and height parameters changes of the FE surface, and could reduce weight gain, swelling of the FE and furthermore could prevent producing degradation products in OBD test, compared to CB/FE or unfilled FE. Finally, it will be concluded that CNT/FE can be applied as sealing rubbers (for example O-rings) in OBD drilling for oil and gas.

EXPERIMENTAL PART

Materials

The following materials were used:

– Viton GF-600S fluoroelastomer (FE), a terpolymer of hexafluoropropylene (HFP), vinylidene fluoride (VDF), and tetrafluoroethylene (TFE) with a cure site monomer;

– organic peroxide, Luperox 101 XL-45;

– carbon nanotube, CNT (TNM8, outside diameter > 50 nm, purity > 95 %, and length of 10–20 μm);

– carbon black, CB (Ensaco 250);

– triallyl isocyanurate, TAIC.

They were supplied by: ERIKS Sdn. Bhd. (Malaysia), Arkema Sdn. Bhd. (Malaysia), Chengdu Organic Chemicals Co. Ltd. (Chinese Academy of Sciences, China), Age D'Or Industrial Sdn. Bhd. (Malaysia) and Liu Yang San Ji Chemical Trade Co. Ltd. (China), respectively.

Oil-based DF (drilling fluids) used contained ESCAID™ 110 Fluid and Enviromul Mud System, supplied by Exxon Mobil Corporation and Halliburton Manufacturing Services, Ltd., respectively.

Compounding

Three formulations were compounded: CNT-filled FE (CNT/FE), CB-filled FE (CB/FE) and unfilled FE (FE). In all compounds, the amount of FE, organic peroxide and TAIC were 70.0, 2.1 and 2.1 g, respectively. For CNT/FE and CB/FE, 7.0 g of CNT and CB, respectively, were added.

Mixing FE with additives was done using a laboratory scale two roll mill with a roll temperature of 48 °C. FE in the above mentioned composition was supplied to open roll. A uniform band was formed while three rolling cuts from each side of the mill were made, so that the polymer became homogenous and sufficiently warmed up. Then TAIC was added uniformly into the gum and three rolling cuts from each side of the mill were done. After setting the roll distance to 1.1 mm, CNT was then fed in. The compound was tight milled ten times. The roll distance was then adjusted to 1.1 mm, and peroxide was added. After the final five to six rolled up end passes, the mixture was supplied to the open roll and sheeted. After 24 hours, re-milling was done with a roll temperature of 26 °C. The same procedure was used for CB/FE and FE.

Curing and post-curing

Curing of FE compound was done with the mold (18 cm × 18 cm × 2 mm) in a heated press, at 177 °C under pressure of 10 MPa for 7 min. The post-curing was done in air oven at 232 °C for 2 hours. Conditions for curing and post-curing were recommended by the supplier.

Samples preparation

Samples preparation for DF aging test: a rectangle shaped samples with dimensions of 20 cm × 5 cm × 2 mm were prepared from post-cured filled and unfilled FE samples. Besides, the dumbbell shaped samples were cut from aforementioned filled and unfilled FE (five dumbbell shaped samples for each nanocomposite). These rectangles and dumbbells were subjected to DF test.

DF aging cell test

The weight, weight in water and dimensions of rectangular samples were measured before DF test. For each nanocomposite (for example CNT/FE) the rectangular sample and dumbbells were hung with a glass hanger inside a DF aging cell 316 Stainless Steel cylinder (500 cm^3). The aging cell was filled with oil-based

drilling fluid (OBD) until the samples were covered. The aging cell was closed and the air trapped inside aging cell purged by pressurizing the aging cell with nitrogen gas (N_2) up to 0.3 MPa (≈ 44 psi). Then the aging cell was pressurized more with N_2 to adjust the pressure so that the aging cell pressure will be *ca*. 2.05 MPa (300 psi) at 150 °C. Then the aging cell was moved to an air oven with the temperature of 150 °C and incubated for periods up to 168 hours. Then, the aging cell was removed from the oven and allowed to cool down to room temperature. The pressurized gas was released and the samples were removed from the aging cell. The samples were cleaned by tissue paper and the weight, weight in water and dimensions of rectangular samples were measured immediately after test. The rectangular sample was further analyzed as will be mentioned later. The same procedure was carried out for CB/FE and FE. The specimens were designated as, for example, CNT/FE-OBD where the OBD after the specimen designation meant the sample has been tested in OBD.

Methods of testing

Atomic force microscopy (AFM)

Filled and unfilled FE before and after subjecting to drilling fluids (DF) test were surface analyzed by atomic force microscopy (AFM). A rectangular area of 10 × 10 μm and 50 × 50 μm were scanned by Q-Scope Ambios AFM machine supplied by Ambios Technology, Inc. in Santa Cruz, California, USA. Three dimensional (3D) and two dimensional (2D) images of the surface of the nanocomposite and composites were obtained. Other analyses were including: AFM roughness parameters and AFM height parameters analyses. The sample dimensions were 5 cm × 20 cm × 2 mm.

Optical microscopy

Optical microscopy images of filled and unfilled FE and also filled and unfilled FE-OBD at different magnification were obtained with Nikon ECLIPES LV100 (Japan) optical microscope with 3 lenses with the following specifications: (1) 5×/0.15 A ∞/0 EPI, (2) 10×/0.30 A OFN25 WD 17.5 and (3) 50×/0.8 A ∞/0 EPI.

Swelling and dimension changes

The swelling and percentage weight gain of filled and unfilled FE in OBD test were calculated as follows [Eqs. (1) and (2)]:

$$\Delta V = \frac{(m_3 - m_4) - (m_1 - m_2)}{m_1 - m_2} \cdot 100 \quad (1)$$

here: ΔV – change in volume (%), m_1 – initial weight of specimen in air (g), m_2 – initial weight of specimen in water (g), m_3 – weight of specimen in air after immersion in OBD (g), m_4 – weight of specimen in water after immersion in OBD (g),

$$\Delta m = \frac{m_3 - m_1}{m_1} \cdot 100 \quad (2)$$

where: Δm – change in weight (%).

The dimension changes percentages were calculated as follows [Eq. (3)]:

$$\Delta L = \frac{L - L_0}{L_0} \cdot 100 \quad (3)$$

where: ΔL – change in length (%), L_0 – initial length of specimen (mm), L – length of specimen after immersion (mm).

The percent change in width, ΔW, and thickness, ΔT, can be calculated accordingly.

Hardness

Unaged and OBD-aged samples of FE, CB/FE and CNT/FE rubber sheets were used for hardness analyses. Hardness measurement was done according to ASTM D 2240 with analogue Zwick 3114/5 shore A hardness tester.

X-Ray diffraction (XRD)

OBD-aged samples of FE, CB/FE and CNT/FE rubber sheets were used for XRD analyses. XRD spectrometer, PANalytical Empyrean Model DY1032, was used for the characterization at 2θ of 5° to 80°.

RESULTS AND DISCUSSION

Surface investigation

Figures 1–3 show the AFM 3D and 2D images, cross-section height profile, and surface height distribution of filled and unfilled FE before and after subjecting to OBD test with scan scales of 10 × 10 μm, 50 × 50 μm and 5 × 5 μm.

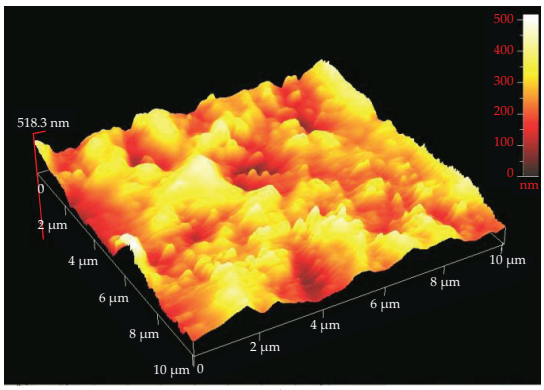
Figure 4 shows the AFM roughness parameters: R_a, R_q, R_t, R_{kr} and R_{sk} of FE and filler/FE before and after subjecting to OBD test. Figure 5 shows the AFM height parameters: average height, S_q and S_a, S_{sk} and S_{kr}, S_p, S_v and S_t of FE and filler/FE before and after subjecting to OBD test.

The parameters shown in these figures are defined as follows:

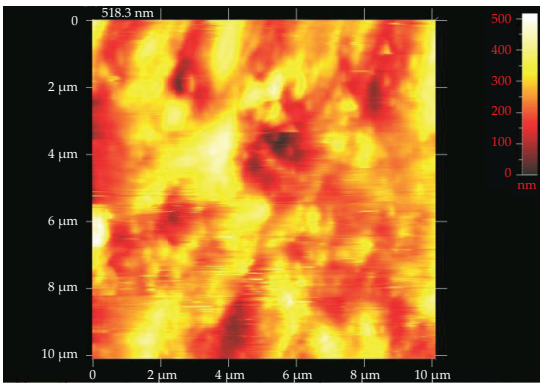
1) R_a – average roughness; R_q – root mean square (RMS) roughness; R_p – maximum profile peak height; R_v – maximum profile valley depth; R_t – total roughness: $R_t = R_p + R_v$;

R_{sk} – skewness: for the symmetrical height distribution R_{sk} is zero, whereas for the asymmetrical height distribution and the surface with more peaks than valleys the skewness moment is positive, while for the surface more planar and with predominant valleys the skewness is negative;

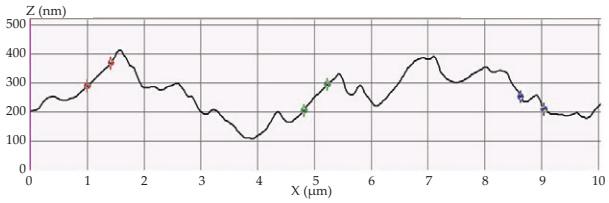
a)



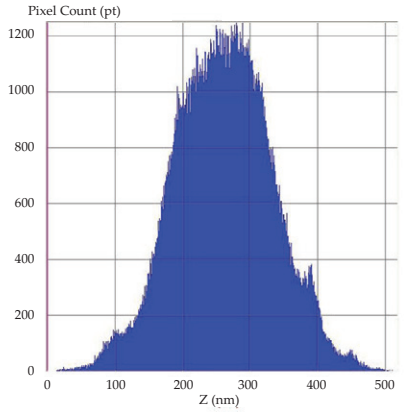
A-A



A-B

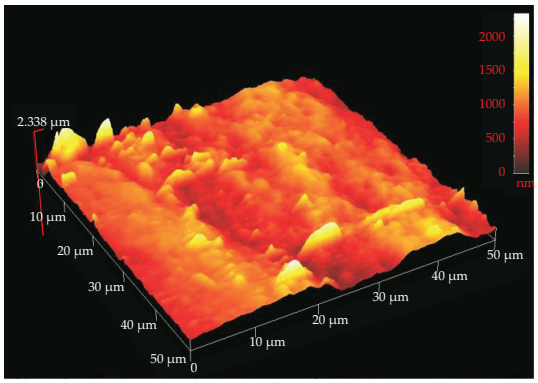


A-C

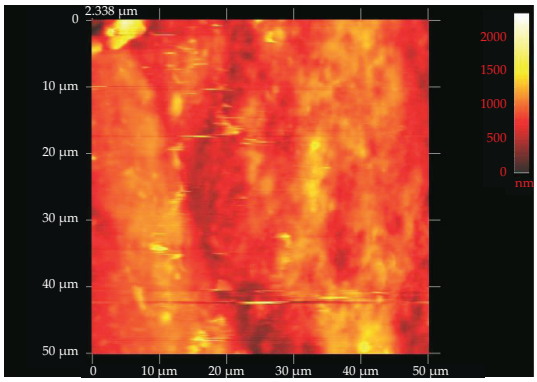


A-D

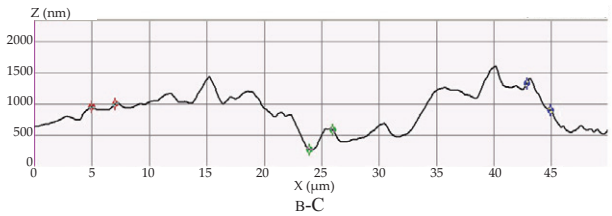
b)



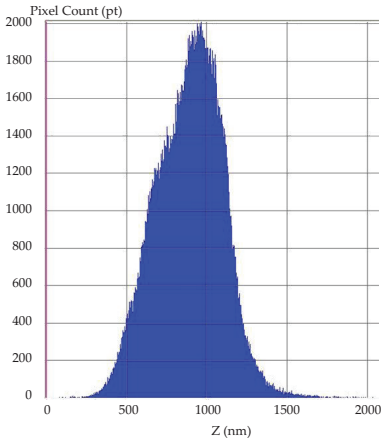
B-A



B-B



B-C



B-D

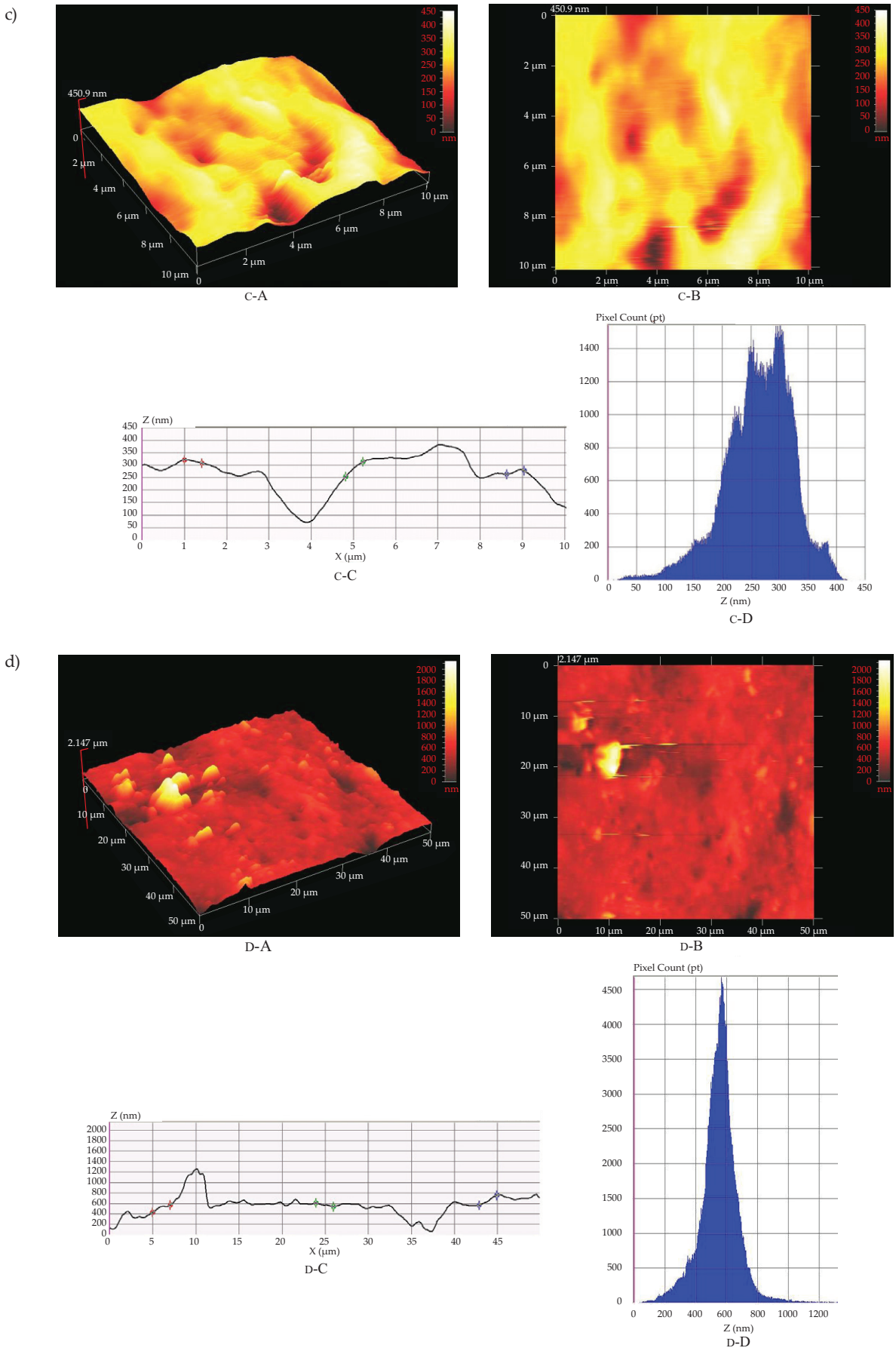


Fig. 1. AFM images and profiles of: a) 10 × 10 µm of FE, b) 50 × 50 µm of FE, c) 10 × 10 µm of FE-OBD, d) 50 × 50 µm of FE-OBD; in subfigures: A – 3D AFM image; B – 2D AFM image; C – cross-section height profile parallel to the X-axis across the middle of image B; D – surface height distribution of image A