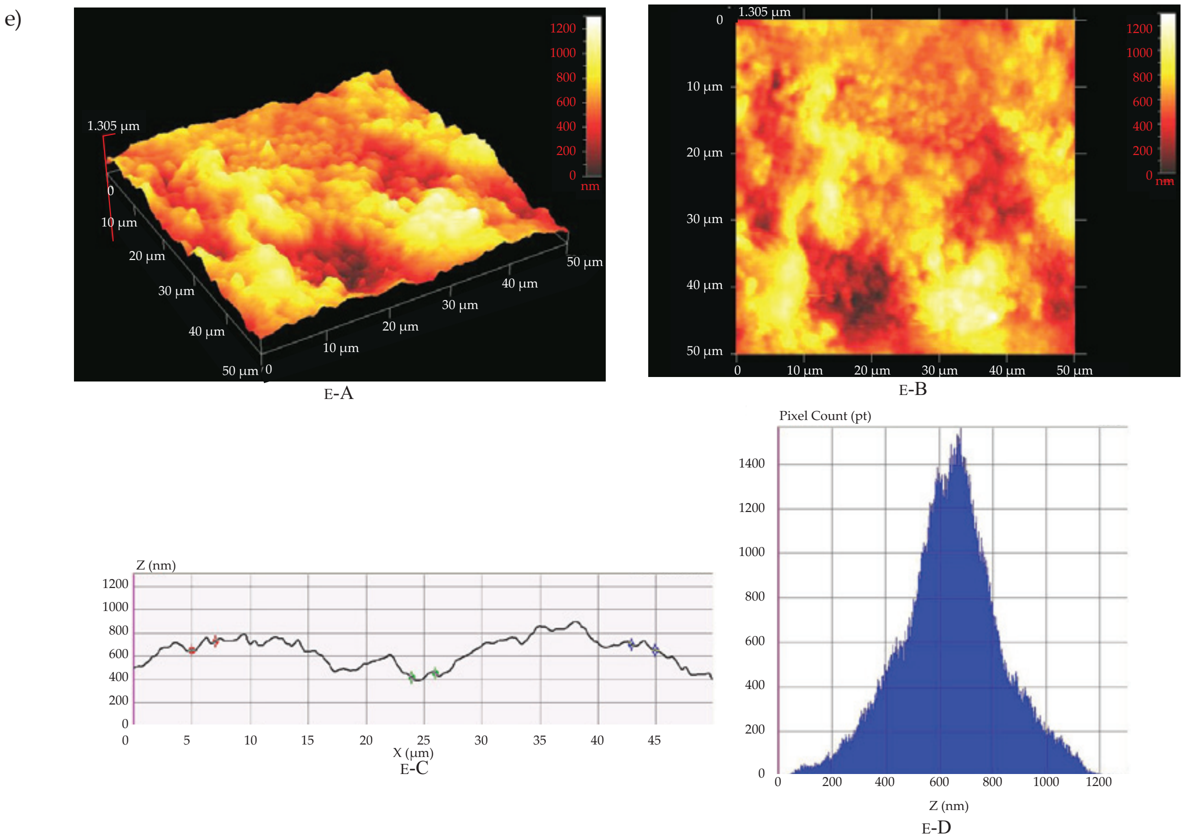

Fig. 3. AFM images and profiles of: a) 10 × 10 µm of CNT/FE, b) 50 × 50 µm of CNT/FE, c) 5 × 5 µm of CNT/FE-OBD, d) 10 × 10 µm of CNT/FE-OBD, e) 50 × 50 µm of CNT/FE-OBD; in subfigures: A – 3D AFM image; B – 2D AFM image; C – cross-section height profile parallel to the X-axis across the middle of image B; D – surface height distribution of image A

R_{kr} – kurtosis: for Gaussian amplitude distribution R_{kr} is 3 and surface is called mesokurtic, whereas for flat surface kurtosis is smaller than 3 and the surface is called platykurtic, while for surface with more peaks than valleys kurtosis is higher than 3.

2) Arithmetic average height; S_a – arithmetical mean height; S_q – root mean square height;

S_{sk} – skewness of the height distribution: a negative S_{sk} indicates that the surface is composed of mainly one plateau and deep and fine valleys. In this case, the distribution is sloping to the top. A positive S_{sk} indicates a surface with a lot of peaks on a plane, therefore, the distribution is sloping to the bottom. Due to the large exponent used, this parameter is very sensitive to the sampling and noise of the measurement;

S_{kr} – kurtosis of the height distribution: it qualifies the flatness of the height distribution;

S_p – maximum peak height; S_v – maximum pit height; S_t – maximum height.

FE and FE-OBD

A comparison between Fig. 1b-A and Fig. 1d-A as well as Fig. 1b-B and Fig. 1d-B show a rough surface of FE with tall peaks and deep valleys and a smooth surface of FE-OBD with small peaks. This result clearly could be confirmed by comparison of Fig. 1b-C and Fig. 1d-C as well as by comparing Fig. 1b-D and Fig. 1d-D. The latter comparison shows that for FE, the height distribution is very wide but for FE-OBD it is very narrow. Figures 4 and 5 further support these results quantitatively.

Figure 4a shows that AFM roughness parameters (R_a, R_q and R_t) of FE-OBD decreased considerably compared to that of FE. This shows that after subjecting FE to OBD the roughness is decreased. Figure 4b shows that for scan scale of 50 × 50 µm, R_{sk} of FE is negative and lower than R_{sk} of FE-OBD which is positive. The same figure shows that R_{kr} of FE is lower than 3 and also is lower than R_{kr} of FE-OBD and that R_{kr} of FE-OBD is more than 3. The negative skewness of FE indicates that the surface was more planar and valleys were predominant. Besides the skewness moment is positive for FE-OBD, therefore, the surface had more peaks than valleys. In addition, kurtosis is smaller than 3 for FE showing that the surface was flat (according ISO 23926-2). But in the case of kurtosis higher than 3 for FE-OBD the surface had more peaks than valleys. Furthermore, for FE, R_{sk} near zero and R_{kr} close to 3 show that the height distribution was symmetrical and amplitude distribution was Gaussian for FE. Considering all of above mentioned results it could be concluded that FE had tall peaks and deep valleys and rougher surface compared to FE-OBD which had mostly shorter peaks.

The same behavior also could be seen for height parameters (average height, S_q and S_a) and also other height

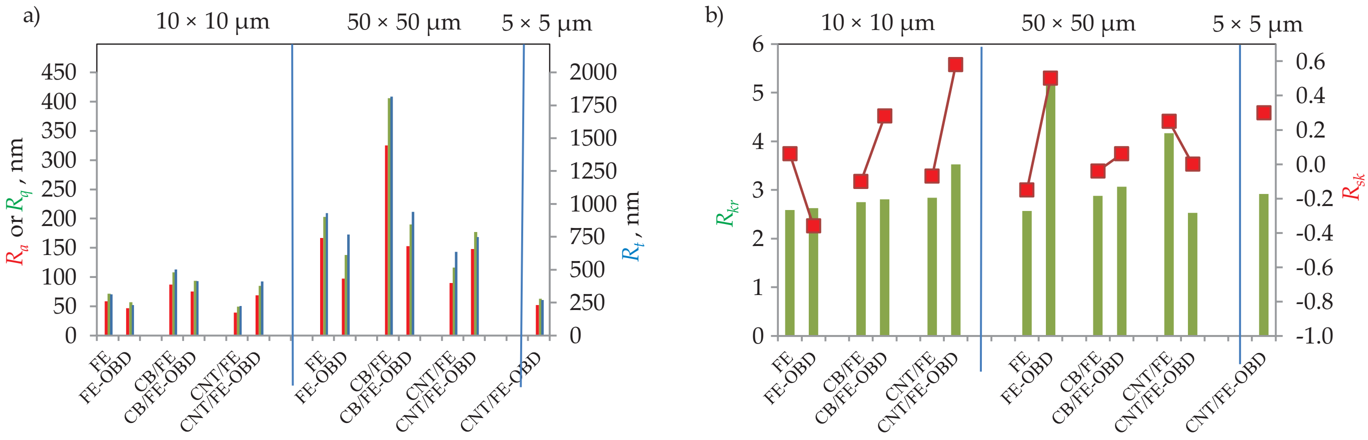

Fig. 4. AFM roughness parameters of FE and filler/FE before and after subjecting to OBD test: a) R_a, R_q and R_t, b) R_{kr} and R_{sk}

parameters (S_{sk} and S_{kr}) of FE and FE-OBD in Fig. 5a and Fig. 5b (for scan scale of 50 × 50 μm). Generally from the height parameters it could be concluded that FE had more height variations (taller peaks, deeper valleys and rougher surface) compared to FE-OBD that had lesser height variations (mostly shorter peaks and smoother surface). Additionally, for FE the height distribution was more symmetrical and amplitude distribution was closer to Gaussian compared to that of FE-OBD. For scan scale of 10 × 10 μm also similar behavior could be seen.

As shown in Fig. 5c for scan scales of 50 × 50 μm and 10 × 10 μm, the S_p, S_v and S_t of FE are bigger than those of FE-OBD what indicates more height variations in the case of FE.

All of the above mentioned AFM results show that the original pure rubber (FE) is not resistant to OBD and by subjecting it to OBD test, its rough surface could be smoothed, degraded and tall peaks and deep valleys could disappear and the reasons of these phenomena will be mentioned at the end of the paper.

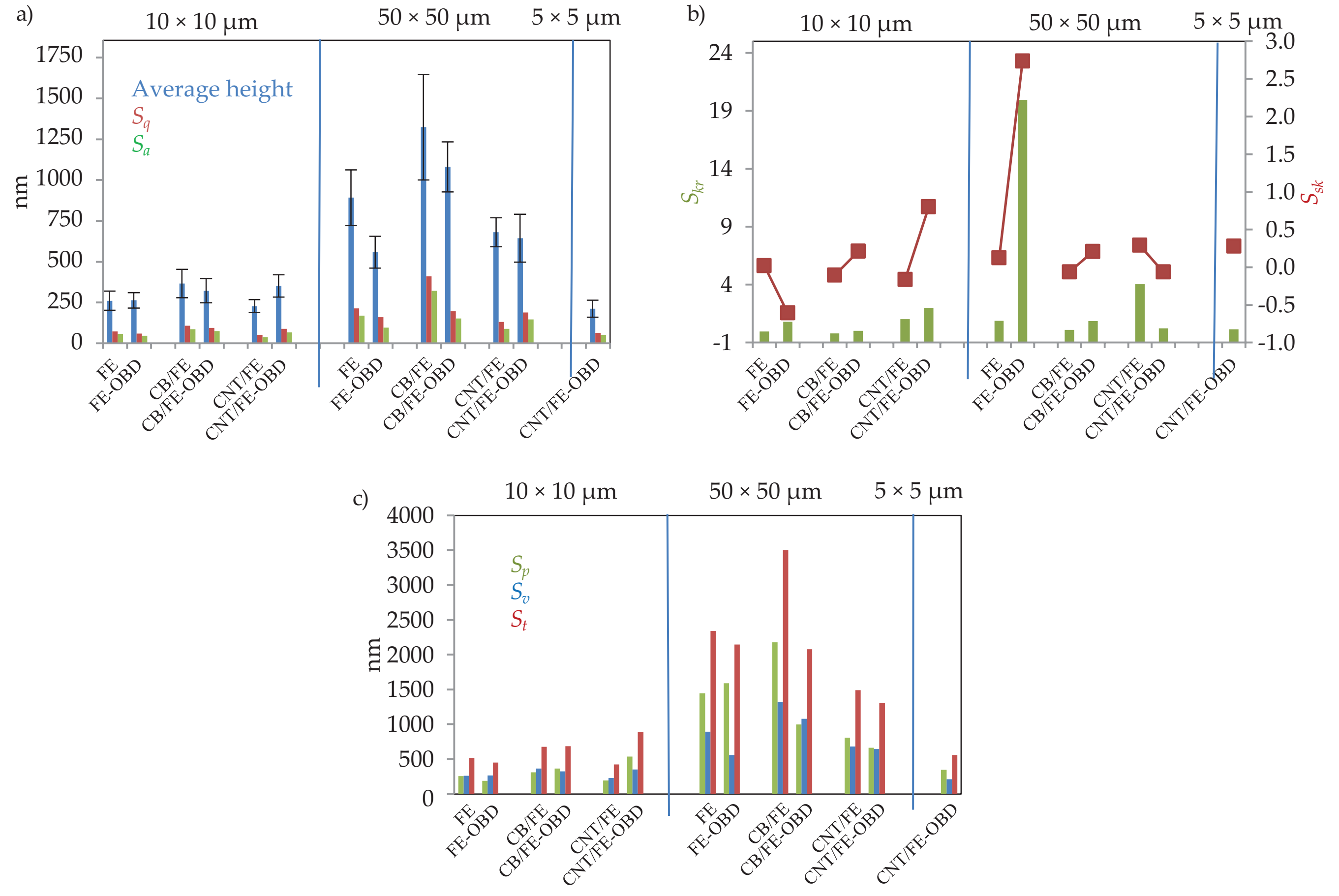

Fig. 5. AFM height parameters of FE and filler/FE before and after subjecting to OBD test: a) average height, S_q and S_a, b) S_{sk} and S_{kr}, c) S_p, S_v and S_t

CB/FE and CB/FE-OBD

From Fig. 2, and also Fig. 4 and Fig. 5, it could be seen that all of the comparisons mentioned for FE and FE-OBD are the same for that of CB/FE and CB/FE-OBD. As a general conclusion the roughness and average height of CB/FE-OBD were decreased considerably compared to that of CB/FE. Furthermore, CB/FE had a rougher surface with more height variations, taller peaks and deeper valleys compared to CB/FE-OBD that had smoother surface with shorter peaks. For CB/FE the height distribution was wider than that of CB/FE-OBD. For CB/FE, the surface was more planar and valleys were predominant, while for CB/FE-OBD the surface had more peaks than valleys. Additionally, for both CB/FE and CB/FE-OBD the height distributions were nearly symmetrical and amplitude distributions were close to Gaussian.

Again, the above mentioned AFM results show that the CB/FE is not resistant to OBD and by subjecting it to OBD test, its rough surface could be smoothed, degraded and tall peaks and deep valleys could disappear. Therefore, CB could not induce OBD resistance to FE and the reasons of these phenomena will be mentioned at the end of the paper.

CNT/FE and CNT/FE-OBD

Similar to comparisons mentioned above, Figs. 3–5 show that AFM 3D and 2D images, cross-section height profile, surface height distribution, roughness parameters (R_a, R_q, R_t, R_{kr} and R_{sk}) and height parameters (average height, S_q, S_a, S_{sk}, S_{kr}, S_p, S_v and S_t) of CNT/FE and CNT/FE-OBD are nearly the same. These results show that changes in surface properties of nanocomposite (CNT/FE) due to subjecting to OBD test (CNT/FE-OBD) were minor. These figures also show that for both CNT/FE and CNT/FE-OBD had surface with more peaks than valleys, the height distributions were nearly symmetrical and amplitude distributions were close to Gaussian. The height distributions for both CNT/FE and CNT/FE-OBD were much less wide compared to FE, FE-OBD, CB/FE and CB/FE-OBD. Furthermore, the roughness of all filled and unfilled FE under study had the following order: CB/FE > FE > CB/FE-OBD > FE-OBD > CNT/FE and CNT/FE-OBD.

The above mentioned AFM results show that the CNT/FE is resistant to the OBD and its surface could not be changed due to subjecting to OBD. Therefore, CNT induces OBD resistance to FE and the reasons of these phenomena will be mentioned at the end of the paper.

Aged and unaged elastomers surfaces perfection

Figure 6 shows surfaces perfection of filled and unfilled FE before and after subjecting to OBD (DF) test. As shown in these figures for CNT/FE there were no blisters, cracks, swelling and deformed or uneven surfaces. However, for FE and CB/FE the surfaces were deformed, cracked, swelled and also blisters could be seen. That's why FE or CB/FE could not stand high temperature and high pressure OBD but CNT/FE could do. The above results show that original compound rubber (FE) could not resist the OBD and also CB is not able to induce resistance of FE to OBD, instead introducing CNT into FE induce resistance of FE to OBD. These results further supported AFM results.

Swelling and dimension changes

The swelling and percentage weight gain results of filled and unfilled FE in OBD test are shown in Table 1.

These results show that CNT/FE had very low swelling, while for others (FE and CB/FE) the swelling were negative. Negative volume changes indicate the chemical degradation of rubber in that fluid [15]. Therefore, it could be concluded that FE and CB/FE were degraded in OBD under high temperature and pressure. According to the reference [16] the acceptable swelling percentage of rubbers in OBD is < 10 % for the application of O-ring. Furthermore, NORSOK M-710 [17] or ISO 23926-2 [18] defines the swelling or volume change of elastomer for most of oil field applications. According to these standards the volume change out of the range of -5 % to 25 % is not acceptable. Therefore, CNT/FE could be used as O-rings in oil-based drilling mud, while FE and CB/FE not. Percentage weight gain was low for all samples

Table 1. Percentage weight gain, swelling and change of dimensions of FE and filler/FE in OBD

Sample	m_1 g	m_2 g	m_3 g	m_4 g	Δm %	ΔV %
FE-OBD	5.23	2.93	5.34	3.40	2.1	-15.7
CB/FE-OBD	5.30	2.94	5.48	3.51	3.4	-16.2
CNT/FE-OBD	5.02	2.39	5.14	2.36	2.4	5.7

Sample	L_0 mm	L mm	ΔL %	T_0 mm	T mm	ΔT %	W_0 mm	W mm	ΔW %
FE-OBD	–	–	–	2.22	2.30	3.6	26.68	27.30	2.3
CB/FE-OBD	–	–	–	2.17	2.30	6.0	25.99	26.60	2.3
CNT/FE-OBD	49.78	49.78	0.0	2.17	2.24	3.2	24.33	24.42	0.4

Fig. 6. Photos of: a) FE, b) CB/FE, c) CNT/FE, d) FE-OBD, e) CB/FE-OBD, f) CNT/FE-OBD

under study. The degree to which a material expands or contracts during exposure to operating environments is an important factor to consider in any sealing application [16]. Operating fluids could be absorbed into a material causing its swelling. Operating fluids could also wash out ingredients within the material causing the decrease in volume. Sometimes both could happen with an initial swelling followed by shrinkage. High temperature and chemical environment could cause the cross-link structure to tighten causing a decrease in volume. Measurements of volume before and after exposure are expressed as a percent change. The low swelling of CNT/FE is due to the increased resistance to OBD and temperatures caused by using CNT in FE, and also barrier properties of CNT/FE-OBD toward permeation of drilling fluid components to nanocomposite. The reasons for increased resistance to OBD and also increasing barrier properties of FE by CNT will be explained at the end of the paper.

The influence of different types of drilling mud on size of rubber samples used as elastomer of mud motors are also reported [19]. It was proved that under long-term exposure, intensive change of rubber sample size takes place and was gradually stabilized for 200–250 hours. Total change of the sample size amounts 2–3 % relatively to the initial size. Oil drilling mud caused a decrease in the size of rubber. Besides, the influence of temperature on sample size of rubber put in hydrocarbon drilling mud has been analyzed. At room temperature decrease of a size in diesel fuel and oil was more intensive than under temperature equal to 50 °C. The reason for this was high evaporation degree of hydrocarbon volatile compounds and decrease in mud aggressiveness to the samples.

The swelling of polymer matrix by solvent depends on diffusivity as well as solubility of the solvent molecule, which are rate-dependent processes [20]. The penetration of solvent into a stiff polymer sample is usually described as a result of two different processes: firstly, the diffusion of solvent into the swollen matrix, secondly, the advancement of the swollen-unswollen boundary as a consequence of the stress induced in the polymer. Because in our CNT/FE-OBD sample the swelling was very low it could be concluded that diffusivity as well as solubility of the OBD into nanocomposite CNT/FE were low, while for those of FE-OBD and CB/FE-OBD they were not.

The effect of temperature on the diffusion process of selective solvents in rubber blends containing FE was studied by carrying out swelling in different temperatures [20]. It was found that the diffusion coefficient increased slightly with increase in temperature. The molecular motion associated with the chain flexibility allowed the solvent molecules to penetrate the polymer. As the temperature was increased the segmental motion was also increased with the result of more diffusion of the solvent molecules. However, the molecular network prevented the free diffusion of solvent. The swelling of the cross-linked polymer was the result of compromise between the osmotic swelling pressure and the elastic force of the macromolecular chain of the network opposing it. The net result was the migration of the solvent molecule, which was temperature dependent. In our filled and unfilled FE-OBD samples, also the high temperature of OBD test affected the swelling of these samples. However, in CNT/FE-OBD even at high temperature the swelling was low as well. Besides, the same verifications that mentioned above could be mentioned for low weight gain of all samples under study. Furthermore, the filler particles were able to interact with the chains and chain mobility restrictions could cause reduced sorption (weight gain) ability. Decreasing chain mobility could decrease free volume in the matrix and provide less space for the solvent absorption in the sample. The addition of nanofiller reduced the availability of these free spaces and also restricted segmental mobility of the rubber matrix [21, 22]. Therefore, in our CNT/FE-OBD due to high interactions of CNT and FE these free space and segmental mobility of the FE were low and the weight gain of this nanocomposite in OBD was also low. However, in CB/FE-OBD the weight gain in OBD was higher compared to that of CNT/FE-OBD. This was due to lower interactions of CB and FE compared to that of CNT and FE.

Table 1 also shows that the changes percentage in dimensions of all samples under study. The changes in dimensions of CNT/FE are very low compared to others and acceptable for applications of O-rings in drilling fluid. The reasons for low dimensional changes of CNT/FE were the same as those mentioned for low swelling of samples.

Optical microscopy

Figures 7–9 show optical microscopy images of filled and unfilled FE and also filled and unfilled FE-OBD at different magnification. As could be seen in these figures original compound of FE, CB/FE and CNT/FE had no cracks, while after subjecting them into OBD test at the surface of FE-OBD and CB/FE-OBD lots of cracks appeared, but CNT/FE-OBD surface was free of cracks. The surface of CNT/FE-OBD was the same as surface of original compound of CNT/FE.

Again, the aforementioned results show that original pure rubber (FE) is not resistant to the OBD, also, CB cannot induce resistance of FE to OBD but introducing CNT into FE induces resistance of FE to OBD and optical microscopy results support AFM results.

Mechanical properties of filled and unfilled FE

Hardness

Table 2 shows the hardness changes of filled and unfilled FE due to OBD test. It is also shown that the hardness of the original compound of elastomers and OBD-aged elastomers have the following order: CNT/FE > CNT/FE-OBD > CB/FE and CB/FE-OBD > FE > FE-OBD.

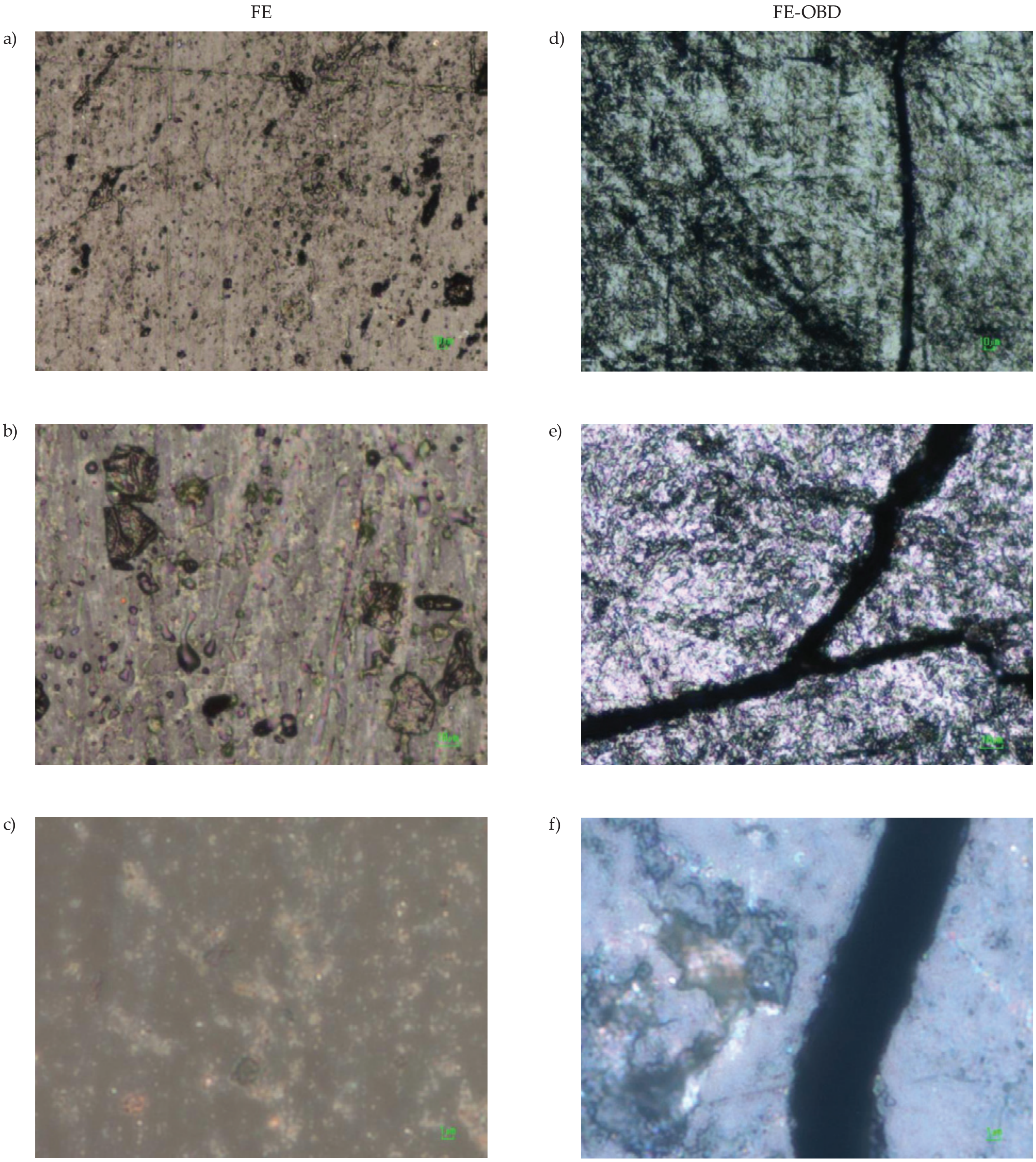

Fig. 7. Optical microscopy images of: a, b, c) FE, d, e, f) FE-OBD at different magnifications; a) and d), b) and e), c) and f) have the same magnifications