SCANNING ELECTRON MICROSCOPY FOR STRUCTURAL EVALUATION OF METALLIC NANOPARTICLES/POLYMER COMPOSITES DESIGNED FOR HIGH FREQUENCY APPLICATIONS

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Abstract

Metallic nanoparticles (NPs) hold a particular interest in view of their catalysis, environmental, electronics and high frequency applications. One of the factors limiting technological applications is the small size of the batch. The electric explosion of wire (EEW) is a technique for fabrication of large amounts of NPs suitable for industrial applications. In this work we have prepared spherical $Fe_{45}Ni_{55}$, Ni, Cu and Al NPs by the EEW and fabricated polymer-NPs and polymer-NPs-thin film composites. Electron microscopy and X-ray diffraction were used for structural characterization. Following polymers were selected for fabrication of composites: butylmethacrylate resin, poly(4,4'-oxydiphenylene-pyromellitimide and cycloolefine. We designed and developed the methodology for evaluation of the polymer-NPs composite structure based on scanning electron microscopy.

Key words: *metallic nanoparticles, electric explosion of wire, polymer-nanoparticles composite, scanning electron microscopy, electronic applications*

1. INTRODUCTION

Metallic nanoparticles (NPs) attract special interest due to their umpteen applications: catalysis (Roldan Cuenya B., 2010), environmental solutions (Schwertfeger DM 2016), electronics including different high frequency devices and flexible electronics (Lodewijk KJ 2016; Paul CR 2004) and biomedical applications (Ahmad MZ 2010). For many electronics and some biomedical applications MNPs form part of functional composites, i.e. polymer matrices with magnetic NPs. Complete characterization of such complex nanomaterials becomes a strict requirement of their applications (Kurlyandskaya GV 2015). Small size of the batch is an important factor limiting NPs applications. One of the efficient methods of fabrication of magnetic NPs with high production rates up to the order of 200 g per hour is the electrical explosion of wire technique (EEW) (Kotov Yu A. 2003; Bac LH 2011; Kurlyandskaya GV 2014)). EEW method allows producing relatively large amounts of NPs for low energy consumption and low environmental cost.

A systematic studies of a variety of EEW NPs, de-aggregated, essentially spherical, NPs of different compositions including pure (Ni, Fe, Al, Cu, Ag, etc.) and FeNi bimetallic systems were reported recently (Kotov Yu A, 1997, 2009; Safronov AP 2014). High degree of sphericity makes EEW NPs almost ideal model systems because the shape factor is responsible for the accuracy of characterization by many techniques: X-ray diffraction analysis (XRD), specific surface and magnetic measurements, etc. (Safronov AP 2012, 2014; Pizurova DB 2004). As-prepared EEW NPs are obtained as air-dry powders. They therefore require further processing for fabrication of composites. In the procedure for preparation of composites, one very important parameter is NPs high specific surface area which provides enhanced interaction at the polymer-NPs boundaries. Chemical properties of NPs surface strongly depend on the fabrication technology. EEW fabrication results in formation of intact surfaces of NPs, which lead to their oxidation and rapid combustion upon exposure to ambient atmospheric conditions. EEW NPs pyrophoricity can be reduced by the formation of a barrier surface layer, i.e. providing surface passivation (Kurlyandskaya GV 2014).

Two important parameters of polymer-NPs composites should be considered: the concentration of the metallic filler and the way in which NPs are distributed inside the composite. The first parameter is essential for obtaining high functional properties (for example, high magnetization values or electromagnetic field absorption capacity of the composite in the case of magnetic NPs). The second may contribute to the magnetization or conductivity values and also change such magnetic characteristics as coercivity and magnetization dynamics (Kurlyandskaya GV 2015). Different aggregation states affecting the distribution of NPs inside the composite can be therefore viewed as an additional parameter to tune magnetic, electric and microwave properties of the polymer-NPs composites. One should therefore conclude that the structure evaluation is very important step in the development of polymer-NPs functional composites.

In addition we should mention even more complex case. Polymeric films as flexible substrates for the deposition of magnetic layers offer a number of advantages in the area of sensor applications (low weight, excellent adaptability in multipurpose devices with complex shape, etc.) and emerge new research lines for solving the problems with the thermal energy dissipation, static charges or adhesion level at the interface among polymer magnetic deposit in film composite (Fernandez E 2012). That is it: there is a technological request for functional composites consisting of polymer-NPs film with a deposited metal layer. In the case of magnetic flexible electronics based on thin film elements there is a need in the development of the appropriate combinations of magnetic multilayered structures and compatible polymer-NPs composite stable for fabrication conditions of high quality magnetic material (Grimes CA 1995; Kurlyandskaya GV 2016).

In this work we have prepared spherical Ni, FeNi, Al and Cu nanoparticles by the electrophysical method of the electric explosion of wire and fabricated series of polymer-NPs composites aiming to develop a simple technology of structural characterization of functional polymer-based materials using scanning electron microscopy.

2. EXPERIMENTAL PROCEDURE AND RESULTS

Ni, FeNi, Cu or Al NPs were prepared by EEW method (Figure 1). Their specific surface area was determined by low temperature nitrogen adsorption using Micromeritics TriStar 3000 analyzer. Phase composition was characterized by X-ray diffraction, XRD (Bruker D8 DISCOVER) using Cu-Ka radiation (λ= 1.5418 Å) 40 kV operation voltage and 40 mA operation current values. Diffractometer was equipped with a graphite monochromator and a scintillation detector. Transmission electron microscopy (TEM) was performed using JEOL JEM2100 microscope. Scanning electron microscopy (SEM) was performed with JEOL JSM-640 (20 kV accelerating voltage) and TM3000 Hitachi (10 or 15 kV accelerating voltage) microscopes both equipped with energy dispersive x-ray (EDX) fluorescent detector for elemental analysis. Low-temperature physical adsorption of molecular nitrogen on MNPs was done with a Micromeritics TriStar 3000 analyser.

Thin metal films were deposited by magnetron sputtering onto Corning glass (rigid) or polymer film substrates at room temperature. Metallic FeNi, Cr or carbon layers were deposited using either $Fe_{19}Ni_{81}$ alloy, Cr or C targets. Conducting layers were deposited onto composite film surface in order to avoid overcharging due to poor conductivity. The deposition rates and the thicknesses of the deposited metal layers were determined in calibration procedure with sharp step 100 nm samples and atomic force microscopy. Deposition was performed onto commercial polymeric films poly(4,4'-oxydiphenylene-pyromellitimide) (capton), and cyclopolyolefine – Zeonor ZF14 100 μm, which were used as received and also onto casted composite polymeric films filled with NPs.

Polymer composites filled with NPs were prepared on the basis of commercially available polymers: acrylic copolymer (Isomer, Dzerzhinsk, RF) of 95% of butyl methacrylate and 5% of methacrylic acid (BMK-5), having molecular weight of 3.1×10^5 and cyclopolyolefine TOPAS 5013 (Topas Advanced Polymers GmbH, Germany), molecular weight 2.5×10^4. As the first step, the stock solutions of 25% BMK-5 in ethyl acetate and 10% TOPAS 5013 in toluene were prepared. Then, the certain volume of the stock solution was mixed with the appropriate amount of NPs. Two series of BMA-5-Ni composites were fabricated. In both series, the content of Ni by weight was in the range of 5 to 60%,

but series differ in the degree of aggregation of NPs. The series of aggregated composites were prepared by the direct mixing of Ni powder with the BMA-5 stock solution in a rotational dissolver DISPERMAT TU (VMA-Getzmann) at 3000 rpm for 30 min. The mixed suspensions of Ni NPs in BMA-5 solution were then cast onto the glass substrates and dried at ambient conditions for 48 hours. The resultant composite solid films were dried at 70 ^{o}C until a constant weight was reached.

The preparation of the second series included ultra-sound de-aggregation of Ni NPs prior to their mixing with BMA-5 stock solution. Therefore, the 50% (by weight) suspension of Ni NPs in ethylacetate was prepared separately and de-aggregated via ultra-sound treatment for 15 min by Cole-Palmer CPX-750 processor operated at 300W output. The resulting suspension was then added to the stock solution of BMA-5 in desired proportions. The mixing of NPs suspension and the BMA-5 stock solution was done using DISPERMAT TU (VMA-Getzmann) dissolver operated at 3000 rpm for 30 min. De-aggregated suspensions with certain polymer-NPs ratio were cast onto the glass substrates and dried the same way as in the first case. Composite films based on BMA-5 with Cu or Al and composite films based on TOPAS 5013 with Ni, Cu, or Al were prepared using the same protocol as de-aggregated composite BMK-5/Ni films.

Figure 1 shows selected examples of different materials used for the fabrication of composites. TEM images of representative NPs ensemble confirm that NPs are spherically shaped. The number average diameter (Beketov I.V., 2012) of FeNi NPs calculated from particle size distribution (PSD) was d_n = 46 nm (Figure 1 a), d_n = 54 nm for Ni NPs (Figure 1 b), d_n = 93 nm for Cu NPs (Figure 1 c), d_n = 100 nm for Al NPs (Figure 1 d).

The crystalline structure of FeNi NPs corresponded to the solid solution of Fe in the face-centred cubic (fcc) lattice of Ni with the unit cell parameter a = 3.584 °A. The average size of coherent diffraction domains estimated using the Scherrer approach was about 43 nm, i.e. close to the number average diameter calculated using PSD. The crystalline structure of Ni NPs according to XRD corresponded to the face-centred cubic lattice of Ni with the unit cell parameter a = 3.53 Å. The average size of coherent diffraction domains estimated by the Scherrer approach was 61 ± 5 nm, i.e. close to the number average diameter determined from the electron microscopy results (54 nm). The crystalline structure of Cu NPs according to XRD contained 96.6% of face-centered cubic lattice of Cu with cell parameter a = 3.618 Å and average size of coherent diffraction domains 61 ± 5 nm and 3.4% of cubic lattice of cuprite (Cu_2O) space group Pn3m with cell parameter a = 4.24 Å and average size of coherent diffraction domains 5 ± 2 nm. The crystalline structure of Al corresponded to fcc lattice with cell parameter a = 4.05 Å and average size of coherent diffraction domains 83 ± 2 nm.

Magnetic measurements of NPs, thin films and selected composites were made using vibrating sample magnetometry (VSM). The saturation magnetization value M_s = 48 emu/g at room temperature was obtained for Ni NPs, which is about 12% lower than the expected value for bulk fcc Ni (Cullity B. D., 1972; R. S. O'Handley, 2000). The apparent reduction in magnetization is consistent with the existence of 2 nm non-magnetic passivation surface layer on the surface of NPs.

The structure of the functional composite (NPs distribution features) and electromagnetic properties of designed nanomaterial crucially depend on the type of the polymer used as the matrix, which in the case of polymer-NPs composite film with deposited metal layer plays the role of the flexible substrate (Paul CR 2004). At the same time selected conductive materials (gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium, and graphite) are used in scanning electron microscopy as highly conductive covers. Coating by heavy metals might be advantageous from the point of view of the increase of signal-to-noise ratio for samples having low atomic number due to the enhancement of the secondary electron emission for high atomic number materials.

As the first step we evaluate possibility to avoid the polymer surface overcharging by deposition of additional conductive layers of different materials. As the first step Cu or Cr (non-magnetic) layers of 10 to 100 nm were deposited onto polymer-NPs composite film substrate. Both materials are also well known as good buffer layers widely used for thin films deposition onto rigid substrates (Svalov AV 2015).

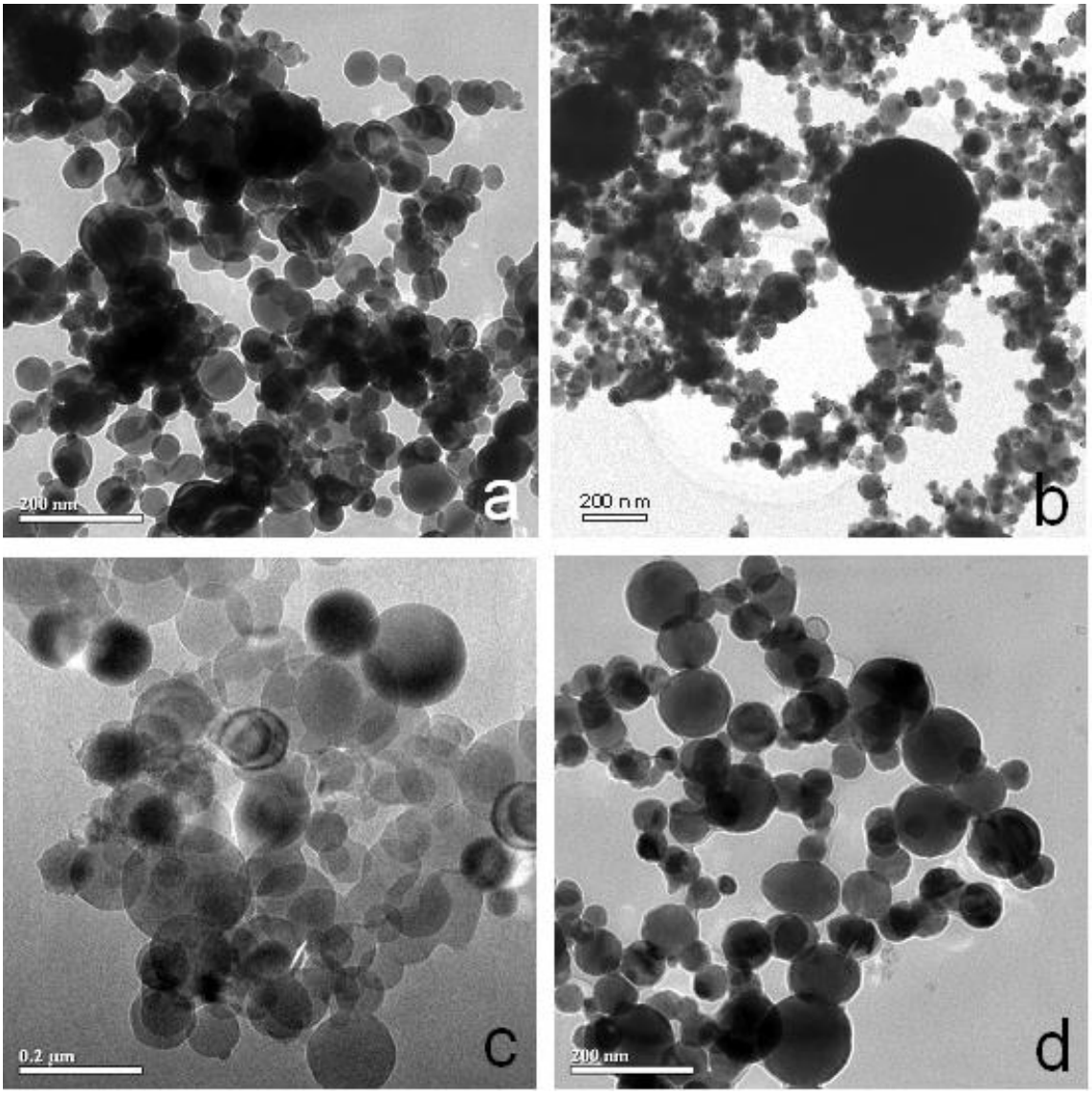


Figure 1. a - TEM images of NPs obtained by EEW technique: a – FeNi NPs, b –Ni NPs obtained, c - Cu NPs, d – Al NPs

Figure 2 shows selected examples of chromium 100 nm layer depositions onto different flexible substrates. Adhesion of Cr(100 nm) layer to the BMK-5 – 5 wt.% of FeNi NPs thin film substrate is very poor and deposited Cr film is very stressed (Figure 2 a-b): it is not simply cracked in rectangular pieces of the order of 100 microns but these pieces are tend to curl up. This means that Cr does not perform better from the point of view of the development of structure visualization technique. Even so we were able to observe a "star-sky" contrast of whiter areas of agglomerated groups of FeNi NPs for the observation mode through the Cr film or directly agglomerated groups of FeNi NPs near the Cr film crack at high magnification.

Among other flexible substrates poly(4,4'-oxydiphenylene-pyromellitimide (capton) was also investigated as the substrate for magnetic films deposition (Grimes C., 1999). The main advantage of this material is that it remains stable across a wide range of the sputtering deposition ranges and temperatures from −269 to +400 °C**.** Although qualitative estimation of curl up degree of Cr(100 nm) film deposited onto capton substrate indicated that stresses are lower comparing with Cr(100 nm) film deposited onto BMK-5 – 5 wt% FeNi NPs composite, they are high and Cr film is cracked into irregular pieces of the order of 30 microns average linear size.

As a continuation of the evaluation of the capacity of different polymer films to serve as substrates for thin film deposition $Fe_{19}Ni_{81}$ films (100 nm or 200 nm thick) were also selected for depositions onto pure BMK-5 substrates, i.e. onto polymer film without NPs filler. Figure 3 a-b shows the FeNi films surface features. Adhesion is again very poor but as-deposited film seems to be less stressed comparing with Cr film deposited in the same conditions. One interesting feature is observed in the case of FeNi films: they appear to have "wave-like" surface roughness caused by the whole FeNi film folding (for pure BMK-5 70 micron thick case). The average distances between two nearest peaks seem to be close to 20 microns. Comparison of the images of BMK-5-5 wt.% FeNi NPs/$Fe_{19}Ni_{81}$ BMK-5/$Fe_{19}Ni_{81}$ thin film composites at different magnifications indicates appreciable difference in the FeNi thin films surface structure. Although more studies are necessary for understanding of the origin of such difference we can suppose that it is mostly caused by the difference in the thermal conductivity of the polymer and polymer-NPs substrates.

In the case of electrically conducting NPs their thermal conductivity is higher and local overheating should be less pronounced. The discussion related to another possible reason, presence of magnetic NPs and their influence the local plasma behaviour due to the presence of local stray fields is absent in the literature. It seems to be less important being the effect of the secondary order but might be of the interest for further investigation. With this respect the composites with NPs of different kind are of the interest. Figure 3 c-d shows BMK-5-Ni NPs/$Fe_{19}Ni_{81}$(100 nm) composites at different magnifications. Comparison of the images of BMK-5-5 wt% FeNi NPs/$Fe_{19}Ni_{81}$(100 nm) thin film composite (not shown here) shows certain similarity: the adhesion of permalloy layers to the composite film is not sufficient and films themselves are very strained up to their disintegration and crack appearance. FeNi and Ni aggregates in the composite films are clearly noticeable in their planar view (Figure 3 c-d).

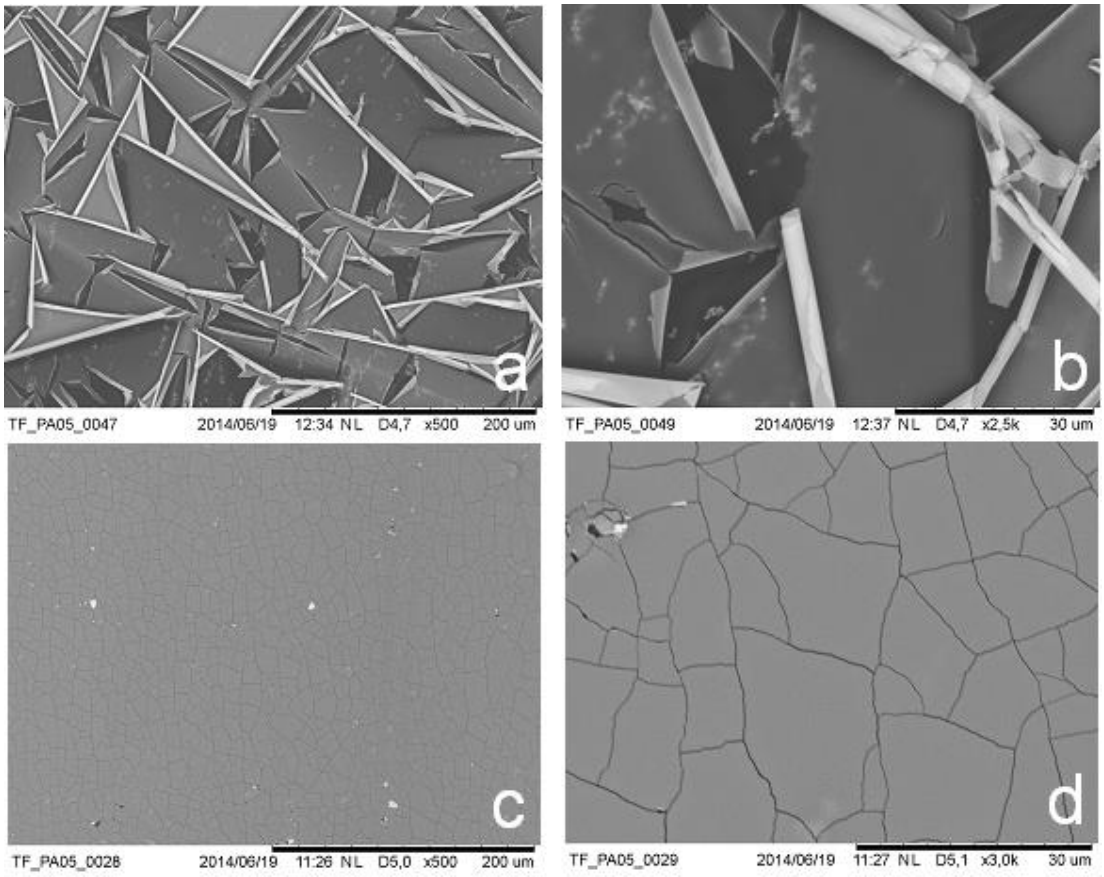


Figure 2. Scanning electron microscopy: a-b - BMK-5-5 wt% FeNi NPs/Cr(100 nm) thin film composite at different magnifications; c-d - poly(4,4'-oxydiphenylene-pyromellitimide (capton)/ Cr(100 nm) thin film composite at different magnifications

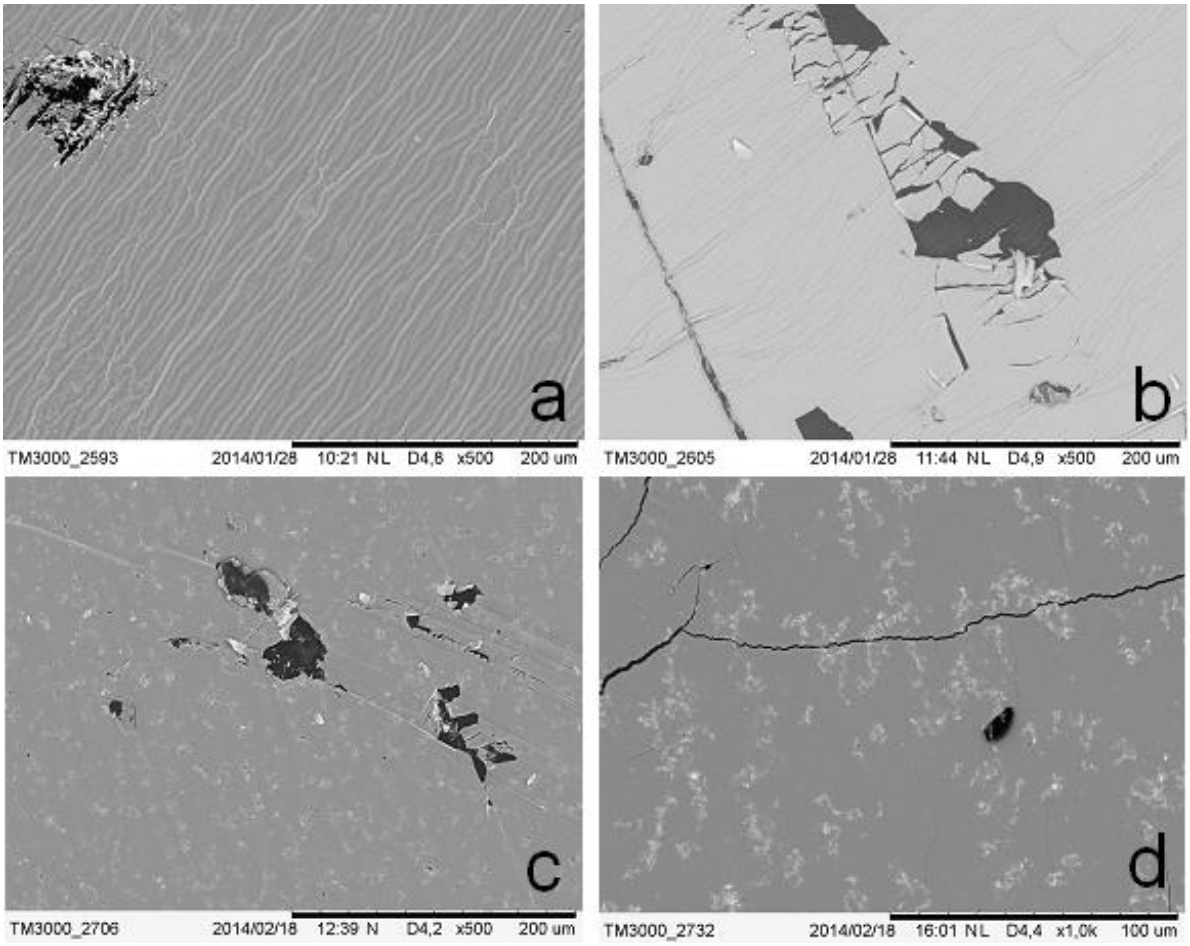
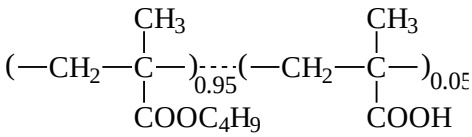


Figure 3. Scanning electron microscopy: a- BMK-5/$Fe_{19}Ni_{81}$(100 nm), b - BMK-5/$Fe_{19}Ni_{81}$(200 nm), c-d - BMK-5-Ni NPs/$Fe_{19}Ni_{81}$(100 nm) at different magnifications

However, the possibilities of higher resolution 46 nm (Figure 1 a), d_n = 54 nm for Ni NPs (Figure 1 b), d_n = 93 nm for Cu NPs (Figure 1 c), d_n = 100 were very limited at these images. We therefore proceed with different protocol to obtain better resolution.

As it was mentioned before the main problem of the polymer composite structural evaluation by electron microscopy is the charging of its surface. Polymers are composed of non-metallic elements with low atomic numbers. Carbon is the most common element in polymers. The chemical structure of the employed BMK-5 polymer base unit is shown below as an example



Carbon therefore can be considered as most compatible element for polymer covering. In the present study we were interested in the development of polymer compatible surface layer with enhanced conductivity. Graphite being a good electrical conductor satisfies both requests. As the first step we therefore deposited a series of carbon films using sputtering technique with the thickness ranging from 10 to 30 nm. Figure 4 shows the structure of BMK-5-5 wt % FeNi NPs with carbon deposited layer of 25 nm at different magnifications. The thickness of 25 nm was the best one for obtaining the highest quality of images. Indeed SEM microscopy is shown to be capable to reveal fine structure of polymer-NPs composites. One of the exciting features of fabricated material is quite uniform structure observed

for the composites of a millimetre size confirmed with nanoscale resolution. At the same time one can see that although for low magnifications very sharp and satisfactory images were easily available for high magnifications (× 10 000 and above) the accumulation of electrostatic charge become a problem in the case of very long observation times (above 5 minutes).

Figure 4 shows images taken in the following sequence: a, b, c, d. After a long observation time at high magnification (Figure 4c) the image starts to degrade due to an accumulation of electrostatic charge most probably caused by the evaporation of conductive carbon film. Figure 4 d shows larger area of the surface of the composite which includes the whole area visualized in the Figure 4 c: the shape of a group of FeNi NPs is easily recognizable in both images. Despite the decrease of magnification for Figure 4 d observation comparing with Figure 4 c case the charge problem is clearly enhanced. Such behaviour is consistent with the supposition about interaction between the conductive carbon film and an electron beam. Further exposition of the BMK-5-5 wt % FeNi NPs composite film with deposited carbon layer at the same or even lower magnification (Figure a-b) results in further accumulation of electrostatic charges up to the critical level and in complete loss of the resolution. Step by step process of charge accumulation can be seen in the image sequence: Figures 5 c-d and Figures 6 a-b. In addition it worth to mention that Figures 5 c-d show BMK-5-5 wt % FeNi NPs composite with carbon deposited layer structure for material contrast (COMPO) and Figures 6 a-b show the structure of the same composite for secondary electrons mode. The secondary electrons are emitted from locations close to the surface and produce very high-resolution surface images. Figure 6 shows very similar results obtained for BMK-5-10 wt % Ni NPs composite film, which confirm the validity of proposed protocol for Ni NPs case. Apparently there were no specific features of the imaging process for the case of composite polymeric film with Ni NPs as compared with the case of composites with FeNi NPs (Figures 4 and 6).

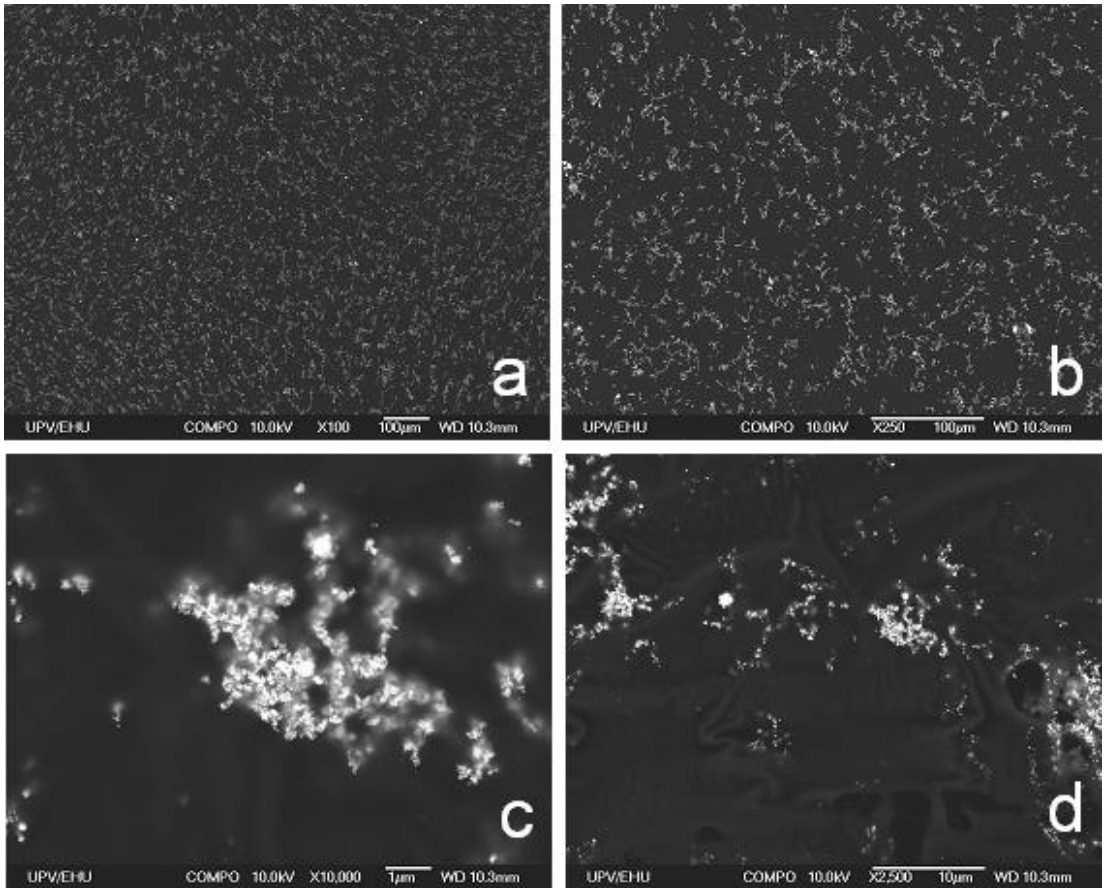


Figure 4. Scanning electron microscopy of BMK-5-5 wt.% FeNi NPs composite with carbon layer of 25 nm at different magnifications. Images were taken in the following sequence: a, b, c, d

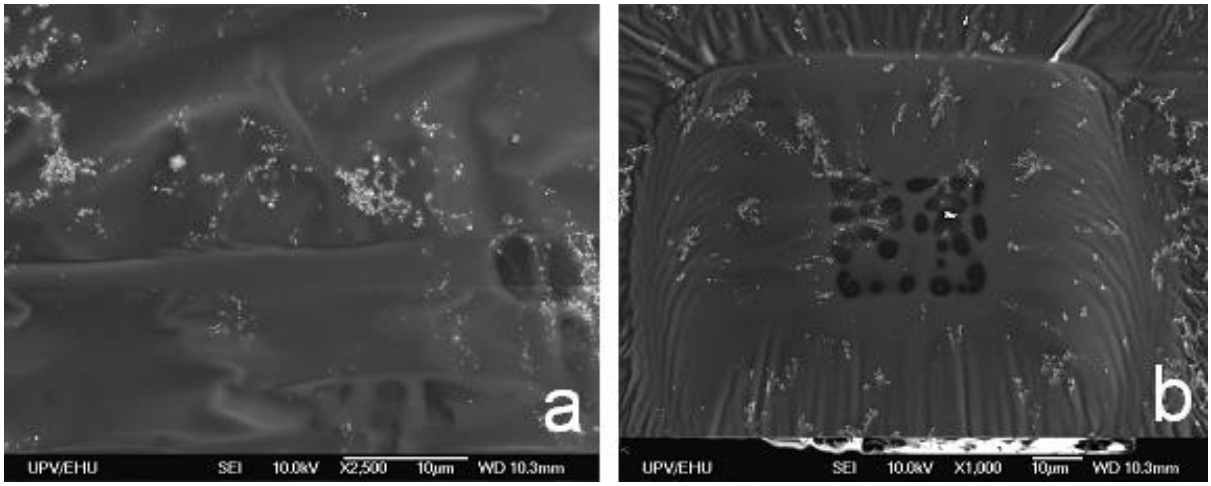


Figure 5. Scanning electron microscopy of BMK-5/ 5 wt % FeNi NPs composite with carbon deposited layer of 25 nm at different magnifications. Images were taken as continuation of the observations (Figures 4 c-d) in the following sequence: a, b

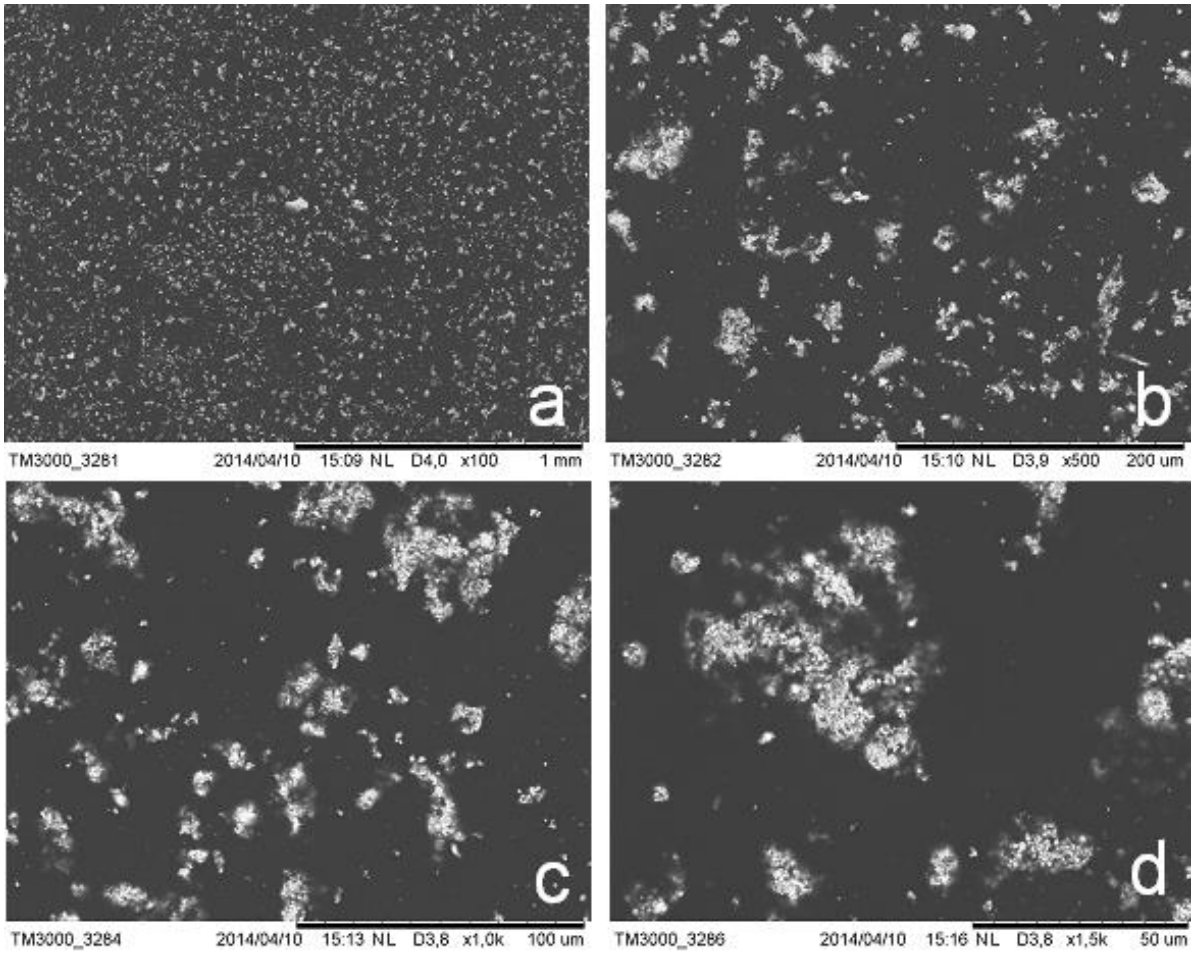


Figure 6. BMK-5 –Ni agr 10 % Scanning electron microscopy of BMK-5-10 wt % Ni NPs composite with carbon deposited layer of 25 nm at different magnifications

Backscattered electrons (BSE) are high-energy electrons that are reflected or back-scattered out of the volume of elastic scattering interaction with the atoms of the sample. High atomic numbers ("heavy") elements backscatter electrons stronger than elements with low atomic number. Therefore "heavy" elements appear brighter in the BSE image offering the possibility to use BSE for the detection of the contrast between areas with different chemical compositions (Goldstein GI 2012). Although the phase composition of the NPs was carefully checked in all cases under consideration by XRD analysis BSE was used as a part of analytical technique for the elemental analysis or chemical characterization of a sample. Energy dispersive X-ray analysis (EDX) is an analytical technique used for the elemental analysis of the sample based on the fundamental principle that each element has a unique atomic structure allowing a fingerprint set of peaks of electromagnetic emission spectrum (Goldstein GI 2012).

Figure 7 shows an example of EDX analysis for BMK-5-10 wt % Ni NPs composite film with deposited 25 nm carbon layer at different magnifications. One can clearly see that bright agglomerates of NPs correspond to elemental nickel in a composition map measured by energy dispersive X-ray analysis. Further we have also checked the capability of 25 nm carbon covering to reveal the structure of polymer-NPs composites with non-magnetic nanoparticles (Figures 8-10). Figures 8-9 show the structure of BMK-5-10 wt % Cu NPs composite film with deposited 25 nm carbon layer at different magnifications. One can confirm the capability of the structure evaluation by the proposed SEM-based protocol. Two important points should be mentioned: a) again, overall structural features correspond to reasonably uniform composite; b) despite the fact that Cu NPs are non-magnetic, clear tendency to the formation of aggregates is observed. At this point it is impossible to make thorough comparison of the structural peculiarities of BMK-5-10 wt % Cu, BMK-5-3.3 wt % Al, BMK-5-5 wt % FeNi or BMK-5-10 wt % Ni composite films as it is strongly conditioned by NPs size distribution details, shape of the NPs and surface features depending on composition and on the way of the NPs passivation.

The main focus here is to show the strength of the proposed very simple SEM-based technique to provide information about the structure of very different polymer-NPs composites. Figure 10 shows an example of EDX analysis for BMK-5-10 wt % Cu NPs composite film with deposited 25 nm carbon layer at different magnifications. One can clearly see that bright round agglomerates of NPs correspond to elemental copper in a composition map measured by EDX analysis. Here let us mention the absence of the surface overcharging. In part it is due to a correct thickness of the carbon covering and in part it is due to good conductivity of Cu NPs. Figure 10 shows very similar results for BMK-5 – 3.3 wt % Al NPs composite film.

Polymer-NPs material is a model example of critical link between the structure and the properties of the nanocomposite leading to desired improvements of their functional properties. The possibility to achieve the on-purpose developed morphology is inevitably linked to the fundamental understanding of polymer−particles interactions governed by thermodynamics that is - interactions that drive macroscopic behaviour. With this regard there is still long way to go prior to succeed in answering the question, how can we predict such interactions in the absence of experimental input.

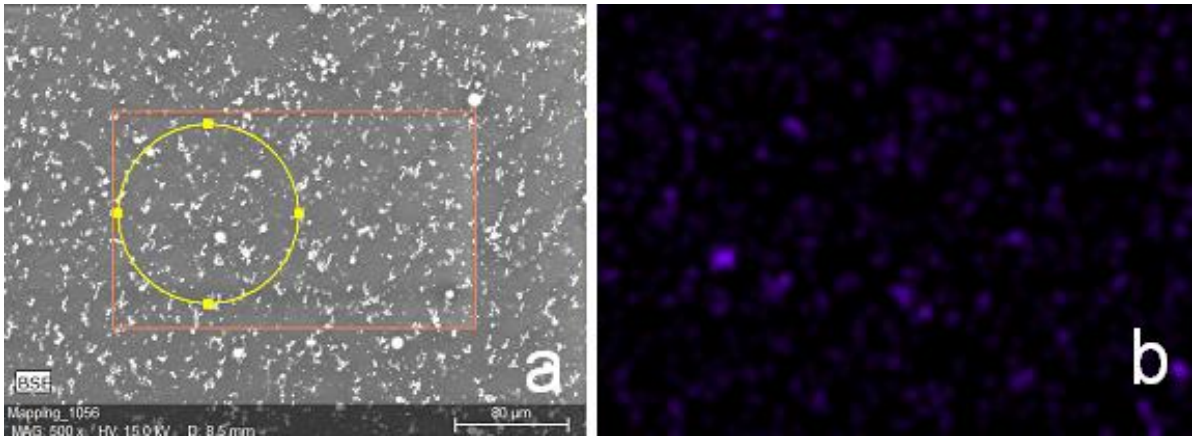


Figure 7. SEM, EDX analysis of BMK-5-10 wt % Ni NPs composite with C layer of 25 nm at different magnifications: a – BSE image with area selection, b – composition map for Ni identification

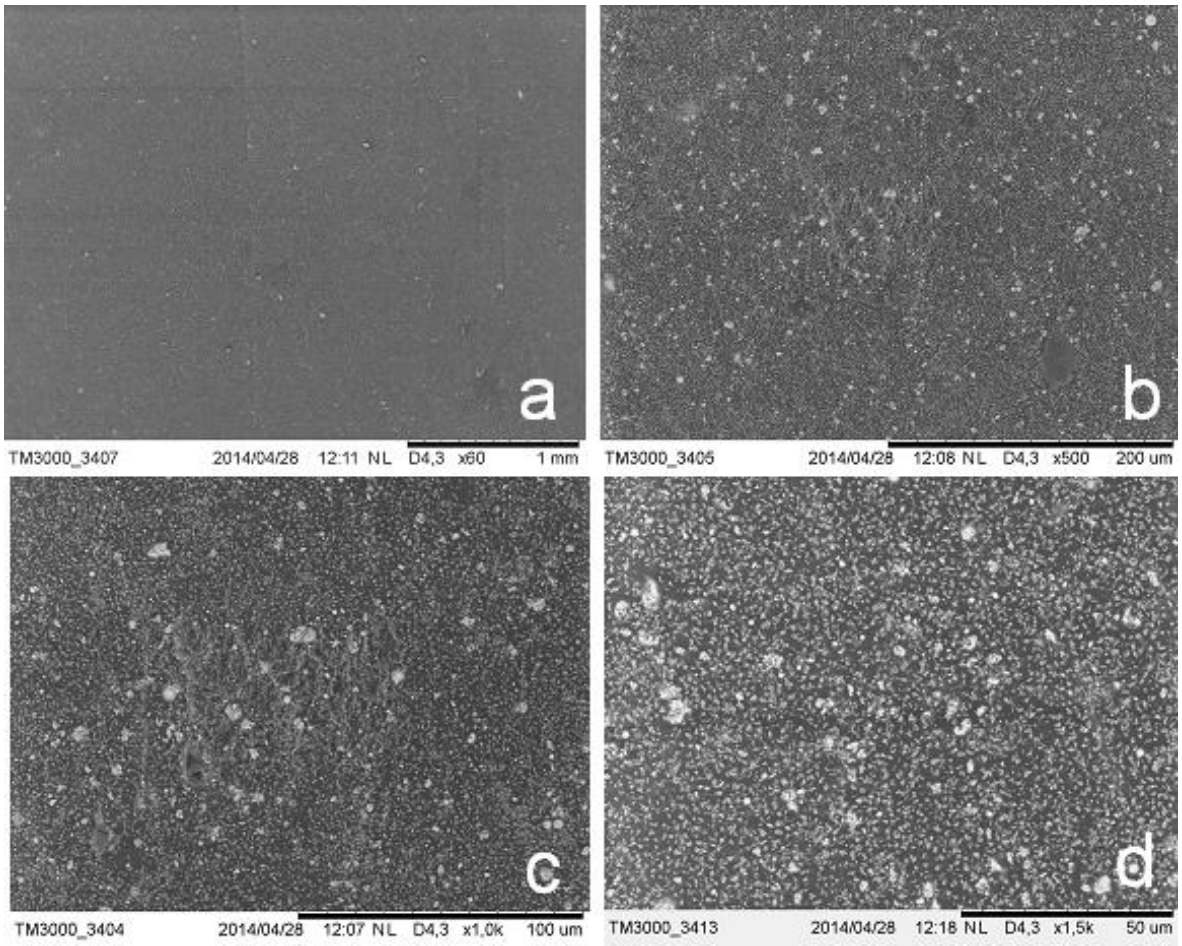


Figure 8. Scanning electron microscopy of BMK-5-10 wt % Cu NPs composite with deposited 25 nm carbon layer at different magnifications

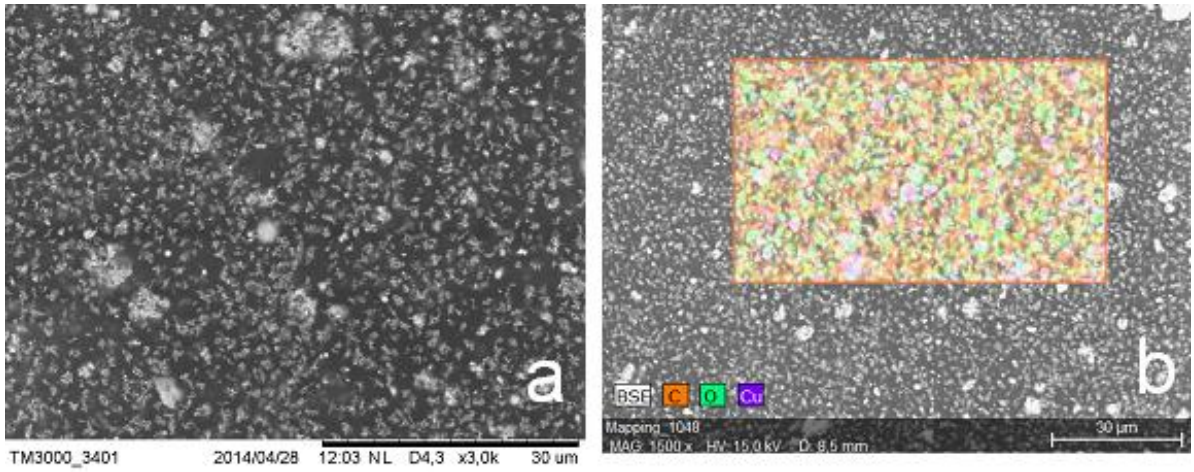


Figure 9. BMK-5-10 wt % Cu NPs composite film with deposited 25 nm carbon layer at different magnifications: a – BSE image, b – BSE image with EDX map

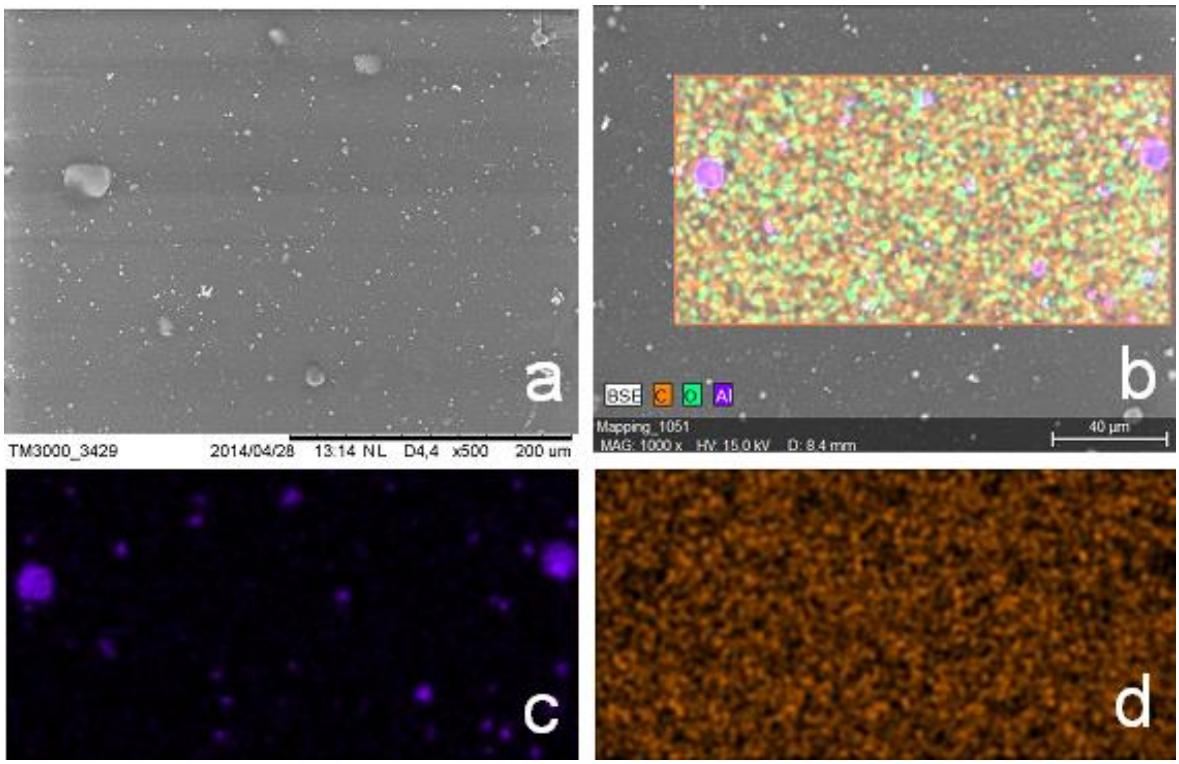


Figure 10. BMK-5-3.3 wt % Al NPs composite with carbon deposited layer of 25 nm at different magnifications: a – BSE image, b – BSE image with EDX map, c – Al EDX map confirms that the NPs consist of pure aluminium , d – C corresponding map confirms the position of Al NPs

There is no doubt that apart from the efforts in the development of the theoretical methods directly linked to the ability of quantitative description of interfacial layers around NPs, in which properties of the surface phase differ from the properties of the bulk polymer phase the experimental techniques revealing the structure of the polymer-NPs materials should be further developed. Our next objective was to insure the possibility of application of developed SEM protocol to the evaluation of the structure of composite with different concentration of metallic filler and different degree of aggregation. Figure 11 shows SEM images of BMK-5-Ni composites for 10 and 30 wt. % Ni weight fractions in aggregated and de-aggregated states. De-aggregated structures look like rather uniform but

irregularly shaped aggregates show rather large distribution of sizes: from the size close to that of a single particle up to the aggregates of 30 microns average size. The difference in filler content is better appreciated in the de-aggregated composites.

Another interesting feature confirming the uniformity of obtained material comes from the magnetic measurements. Magnetic hysteresis loops of BMK-5-10 wt % Ni NPs deaggregated composite measured in plane of the composite in two perpendicular directions showed no measurable magnetic anisotropy. In the case of aggregated composites the average size of the aggregates and their size distribution are most appropriate parameters for the description of structural features but in the case of de-aggregated samples the average size and size distribution of free volume seems to be more appropriate. Although at present there is no software for automatic evaluation of the composite structure it seems to be possible to adapt the existing metallographic protocols with minimal modifications. In recent years, magnetic field assisted structuring of polymer composites filled with magnetic NPs attracted special attention. Their magnetic and microwave properties are critically dependent on the structural peculiarities (Kurlyandskaya GV 2006; Barcikowski S 2015). We therefore have prepared BMK-5-10 wt % Ni NPs composite film dried in the presence of external magnetic field of 70 Oe applied in the plane of the composite during dry process. NPs formed well defined chains oriented approximately in the direction of the field application.

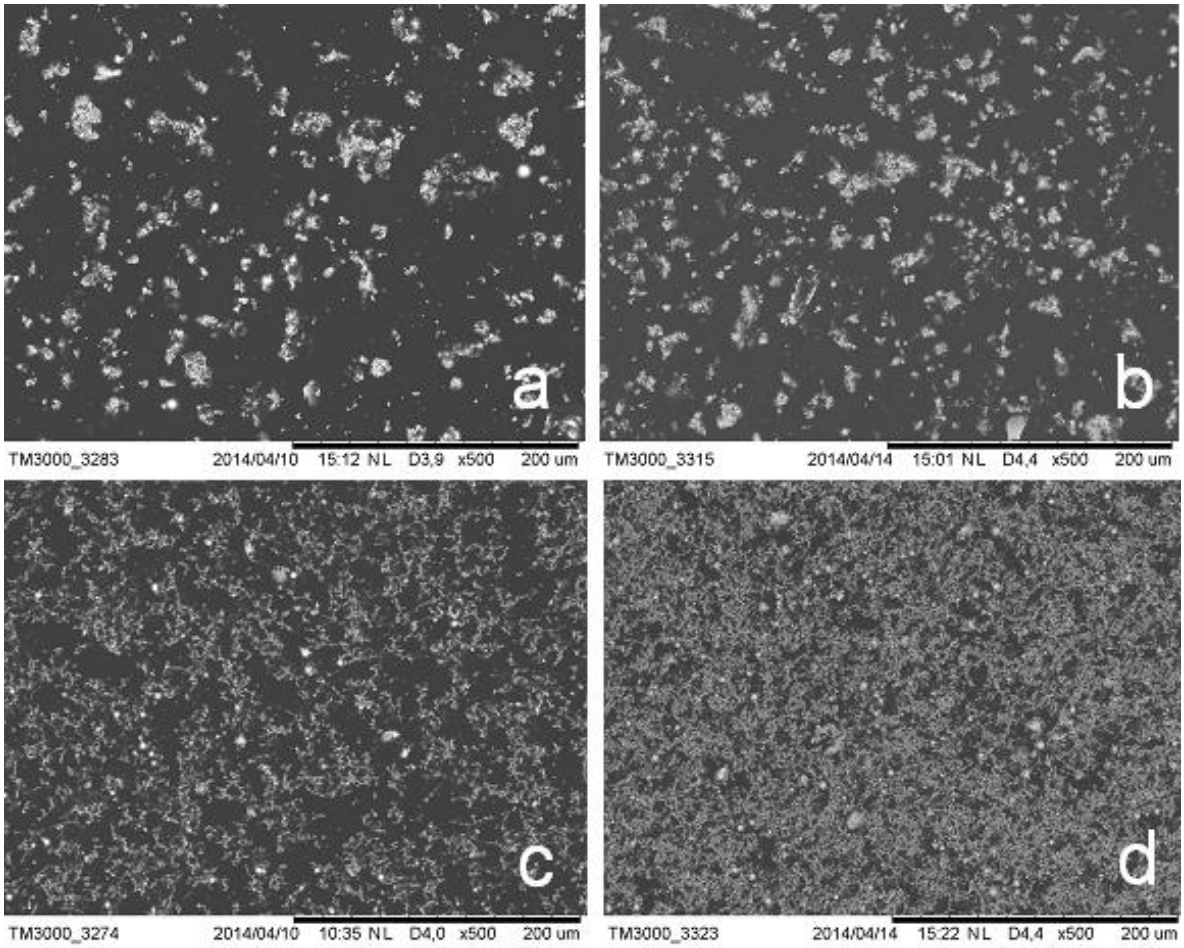


Figure 11. Scanning electron microscopy images: a- aggregated BMK-5-10 wt % Ni NPs composite, b - aggregated BMK-5-30 wt % Ni NPs composite, c- de-aggregated BMK-5-10 wt % Ni NPs composite, d – de-aggregated BMK-5-30 wt % Ni NPs composite

Figure 12 shows SEM images of such composites at different scales. Obtained reasonably uniform (at the millimetre scale range) material has structural anisotropy defined by the field orientation. One interesting feature is very clear – large particles are always incorporated into long chains and large particles of the same chain are separated from each other. Again, for high magnifications and long observation time the charge accumulation affects the image quality. For example, Figure 12 d contains dashed red curve indicating the area with clear problem of electric charge accumulation. Figure 13 is an example of the elemental analysis of BMK-5-10 wt % Ni NPs composite film dried in the presence of external magnetic field – Ni EDX map confirms that the chains are formed by nickel NPs and allow quantitative estimation of average structural parameters. Figure 13 a (left border in the centre) contains rectangular charged area corresponding to Figure 12 d observation due to partial destruction of the carbon layer by incident electron beam.

Finally we have prepared cycloolefine TOPAS 5013-Ni NPs composites with different filling factor. Cyclopolyolefine is a popular in microfluidic and biosensor applications polymer well known due to very good thermal stability, resistance with respect to aggressive chemicals. Cyclopolyolefine films also exhibit 92% light transmittance and enhanced brightness (Garcia-Arribas A 2011). Figure 14 shows an example of de-aggregated TOPAS 5013-40 wt % Ni NPs composite film covered by sputtered 25 nm carbon film. Overall structure is quite uniform at the millimetre scale. For high magnifications (Figure 14 b) the average size of free volume locations and their size distribution can be calculated. Again development of appropriate software might be useful for better image processing. One can notice the absence of the overcharging of the composite even at quite high magnifications.

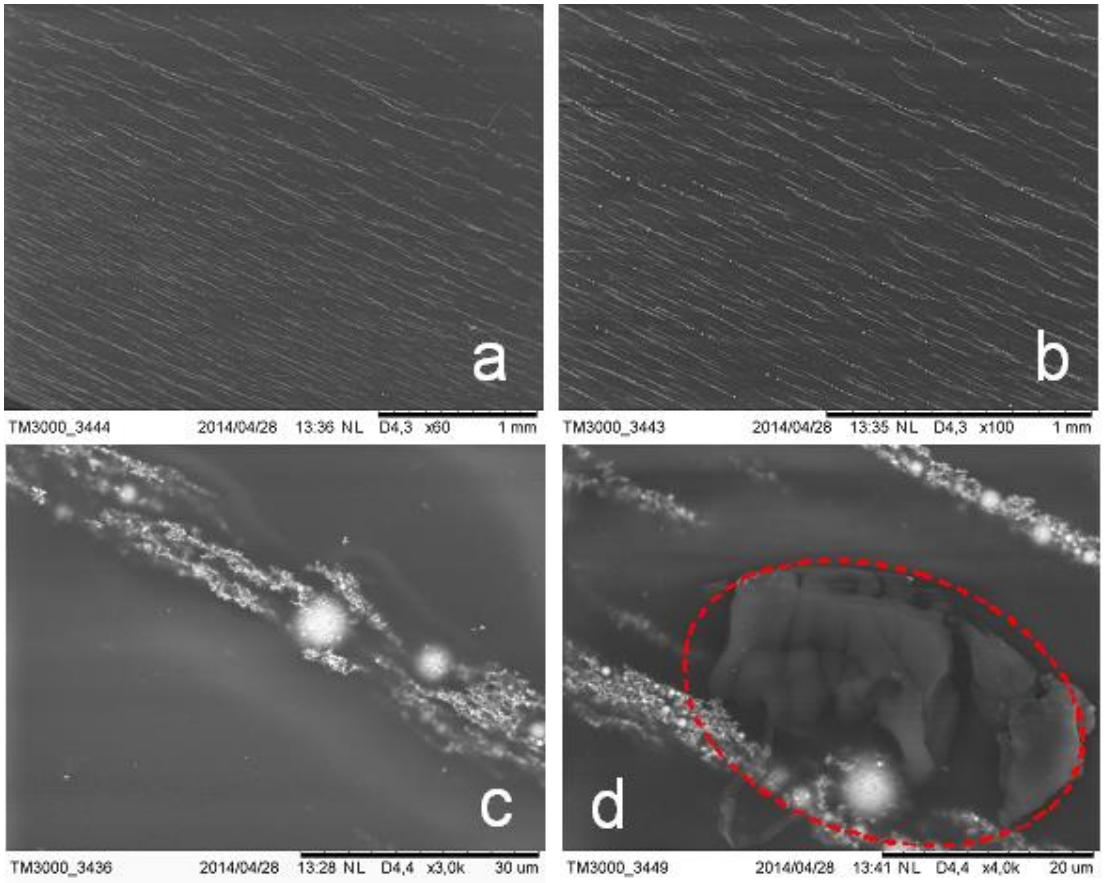


Figure 12. Scanning electron microscopy images of BMK-5-10 wt % Ni NPs composite dried in the presence of external magnetic field at different magnifications. NPs chains are oriented approximately in the direction of the field application. Dashed red curve (part d) indicates the area with clear charge accumulation problem due to carbon layer destruction by the incident electron beam

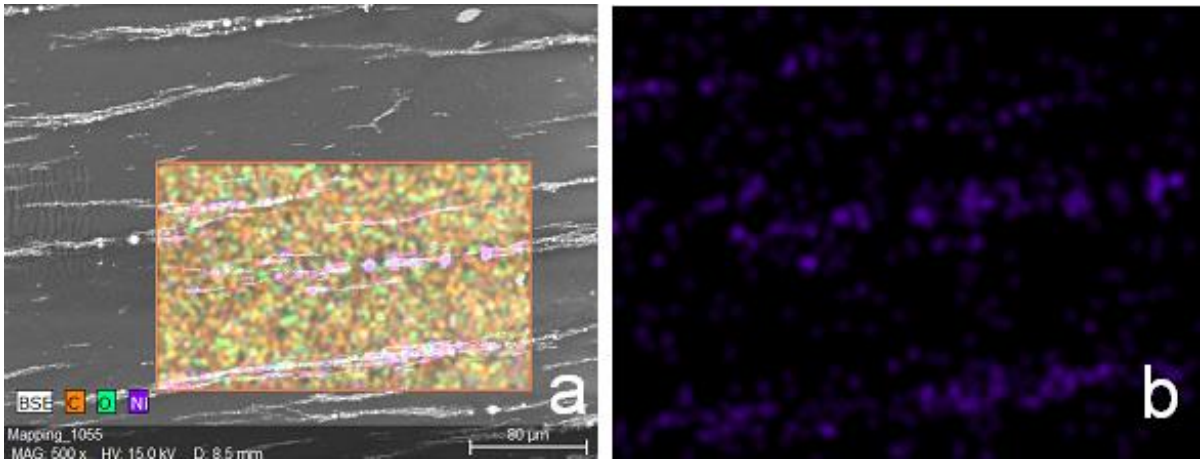


Figure 13. Electron microscopy image of BMK-5-10 wt % Ni NPs dried in the presence of external magnetic field composite with carbon deposited layer of 25 nm: a – BSE image, b – BSE image with EDX map, b – Ni EDX map confirms that the chains are formed by nickel NPs

As a consequence the obtained images are very sharp. Making a supposition that the way of the NPs rearrangement does not depend on the direction we can very roughly estimate (Figure 14 d) the information depth of the method: it seem to be close to 2-3 microns.

Despite the promising impression of the proposed simple protocol the main problem of the structural evaluation remains clear. We are able to visualize the surface of the composite for 2-3 microns depth only. In the present study for selected cases we have compared the structure of from the both surfaces of a composite film (one was initially exposed to air, another was formed in contact with glass substrate) and did not find a pronounced difference but more careful studies are still necessary with this respect. It means that for polymer composite we are able to obtain the structural information for about 5 microns of its thickness. It is acceptable thickness for selected applications but many other require thicknesses of the order 100 microns. In the latter case one can use the fine slicing techniques usually employed for the preparation of the biological samples followed by the deposition of carbon layer. However, the last option would be more expensive and more local.

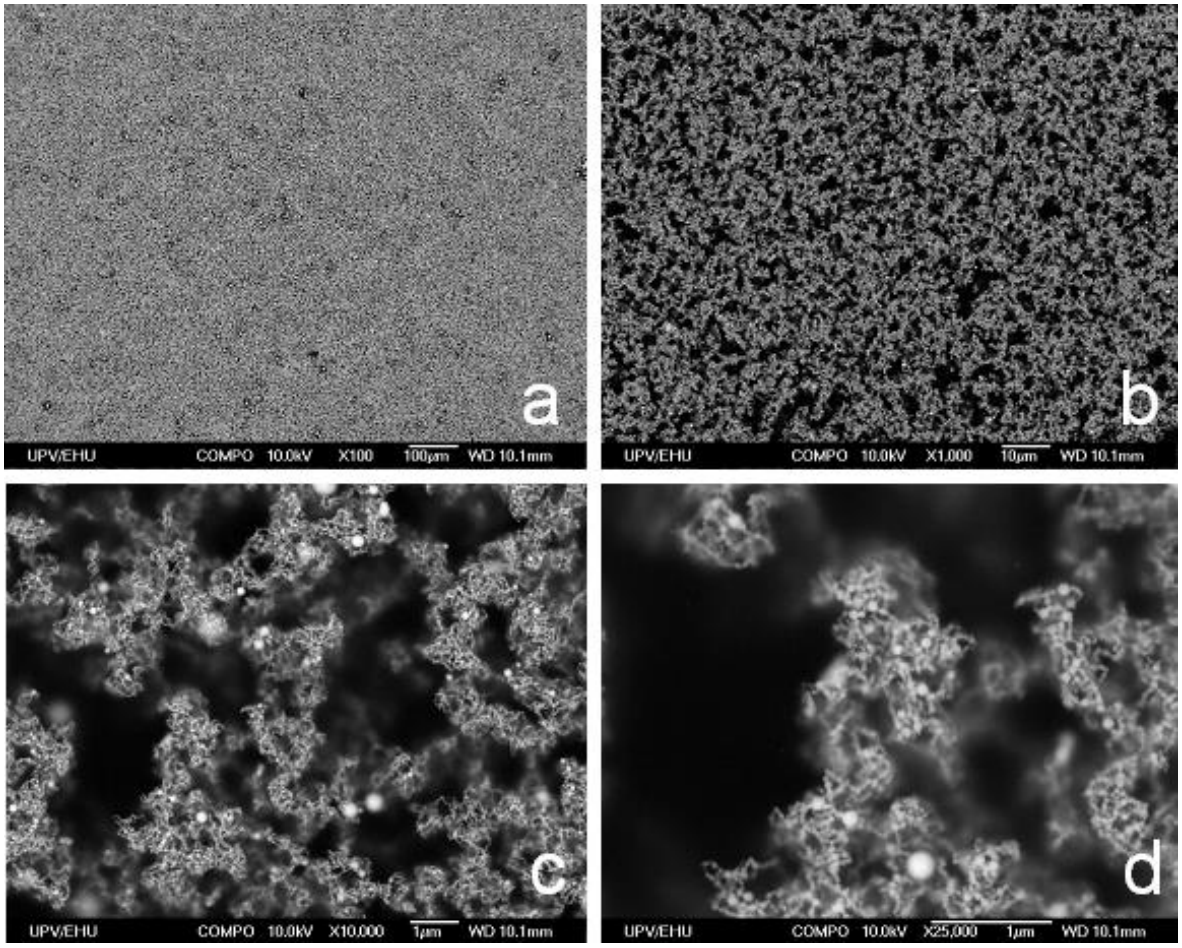


Figure 14. Scanning electron microscopy of CO - 40 wt % Ni NPs composite with carbon deposited layer of 25 nm at different magnifications

Final remark should be made with respect to employed electron microscopes. JEOL JSM-640 is a complex instrument requiring maintenance, air conditioning and operation by highly qualified technician specialized in SEM studies. TM3000 Hitachi is a versatile table instrument which can be used by the personnel after the short training. For example, in a Group of Magnetism and Magnetic Materials of the University of the Basque Country UPV-EHU it is included as part of laboratory exercises of the Master and even bachelor diploma students in physics. At the stage of the development of methodology we used both instruments for comparison and confirmation of the obtained results and find very good agreement between both groups of the data. It means that the proposed method can be useful at the stage of the development of functional composites even if just a simple table SEM instrument is available for routine monitoring of the structure of fabricated composites.

3. CONCLUSIONS

$Fe_{45}Ni_{55}$, Ni, Cu and Al NPs were prepared by the electric explosion of wire technique and their structural and magnetic properties were studied. Butylmethacrylate resin, poly(4,4'-oxydiphenylene-pyromellitimide and cycloolefine polymers were used for fabrication of NPs composites with different filler content and aggregation features. Both aggregated and de-aggregated composites were prepared, including the composites formed under the application of 70 Oe in-plane external magnetic field. We designed and developed very simple methodology for the evaluation of up to 3 micrometer surface layer structure of composite based on scanning electron microscopy applied to relatively large

scanning areas of a few millimetres order. This technique was efficient and successful for aggregated and de-aggregated composites based on different kind of polymers filled both with magnetic and non-magnetic nanoparticles.

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