kinds of details spread in all the matrix: some brighter areas with a circular shape, many dark particles with an almost rectangular shape, and few dark and round particles (Figure 6a).

The bright circular areas appear like "bubbles" in all the polymer matrix. They are clearly visible with a darker contrast with respect to the matrix also in the HAADF STEM images and are less dense than the other inclusions. This result should be due to the deposition process, especially to the use of water as the solvent for the suspension. During the deposition, electrolysis of water can occur and some bubbles can result trapped in the coating for the resulting gas evolution at the electrode (Besra and Liu, 2007).

The dark details, marked as MMT in Figure 6a, are homogeneously distributed in all the matrix. These particles are very similar in shape to the original clay tactoids, as appear before the EPD deposition. A particle of pristine MMT is shown in Figure 6b. Its nature can be defined also through HAADF STEM images, where they are shown as bright details because their Z number is higher than that of the polymer matrix. Their chemical nature is also confirmed by the EDS spectra (Figure 6c), collected by focusing the electron beam on a MMT particle, where the characteristic peaks of the typical elements of nanoclays (Si, Al, O, and Mg) are present.

Other dark particles, but with a very different shape with respect to MMT particles, are also clearly visible. In Figure 7a there is a BF TEM image of some MMT particles, while in Figure 8a some almost circular details are visible. In order to investigate on their nature, many EDS spectra were acquired and compared to

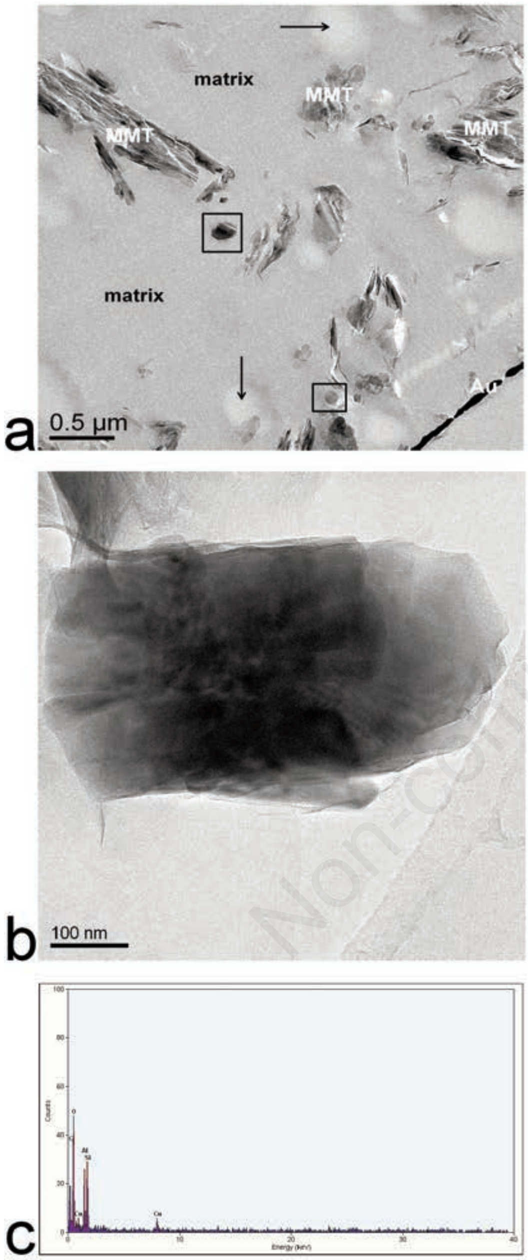

Figure 6. **a) BF TEM image of the epoxy nanocomposite coating: the black arrows mark the brighter circular details, while in the black square there are round black particles. b) TEM image of a single pure MMT particle. c) A typical EDS spectrum collected with the beam focused on a rectangular particle. Cu peak is due to the support grid.**

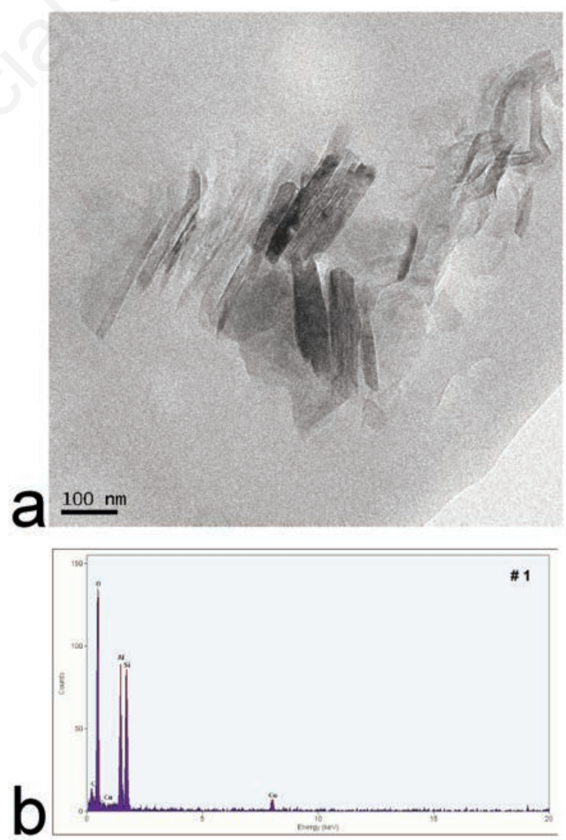

Figure 7. **a) BF TEM image of some MMT particles in the coating. b) EDS spectrum obtained with the electron beam focused on the MMT particle.**

those collected from the MMT nanoparticles. In Figure 7b and Figure 8b there are typical EDS spectra acquired with the electron beam focused on MMT particles (#1) and on the round details (#2), respectively. In the last case, a noticeable amount of Ti was recorded, so it is possible to attribute these features to the pigments present in the polymer matrix since they were also detected in some polymer coatings prepared without the MMT.

As far as MMT fillers, they are formed by regularly stacked clay platelets, identified with the (001) layers. A deeper observation was conducted to analyse the distribution of MMT in the epoxy based coating. Figure 9 shows a BF TEM image at higher magnification, where some MMT particles are visible. Few dark layers, well visible and corresponding to (001) planes of MMT, shown in a square, are intercalated with the epoxy resin. The distance between two of them, as measured from BF TEM images, ranges from 2.5 nm to 6.2 nm, which is definitely wider than the interplanar distance of 1.2 nm typical of pristine MMT. Very few layers of MMT particles are exfoliated, as shown in Figure 10.

These findings suggest that this EPD process, in particular the preparation of the suspension, was successful to produce suitable polymer nanocomposite coatings with an intercalated dispersion of the clay layers. The appropriate alternating steps of sonication and rest of the mixture of MMT particles and water was fundamental to allow the swelling of the nanoclay particles without any chemicals (De Riccardis *et al*., 2011; Yebassa *et al*., 2004; Jia and Song, 2014).

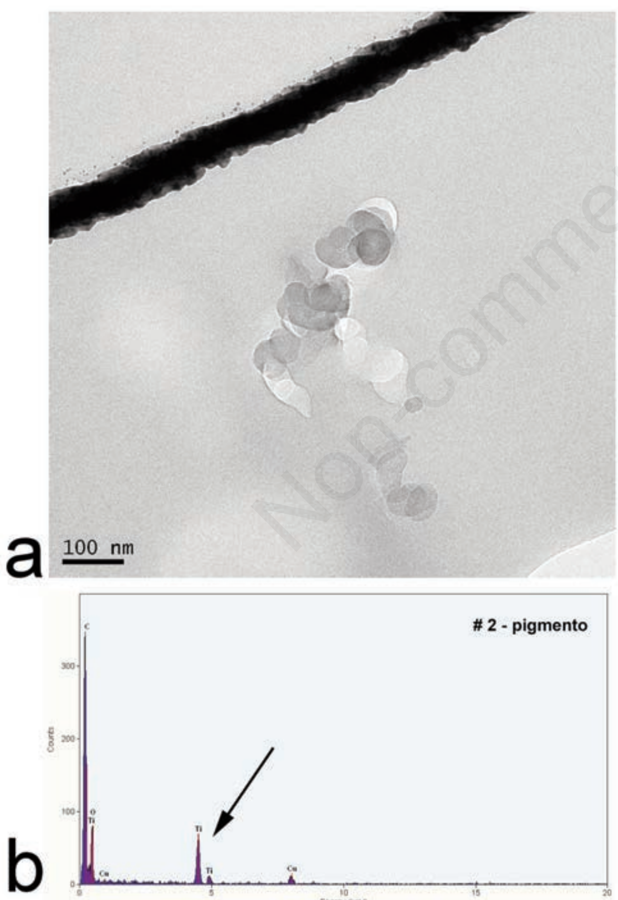

Figure 8. a) BF TEM image of some round details in the coating. b) EDS spectrum obtained with the beam focused on the round black detail present in the coating.

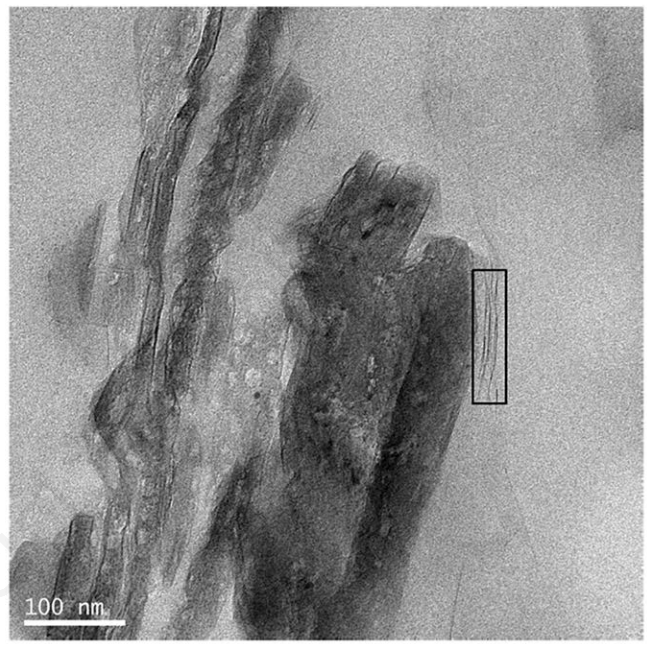

Figure 9. A BF TEM image of some MMT particles at higher magnification; in the black square some intercalated platelets.

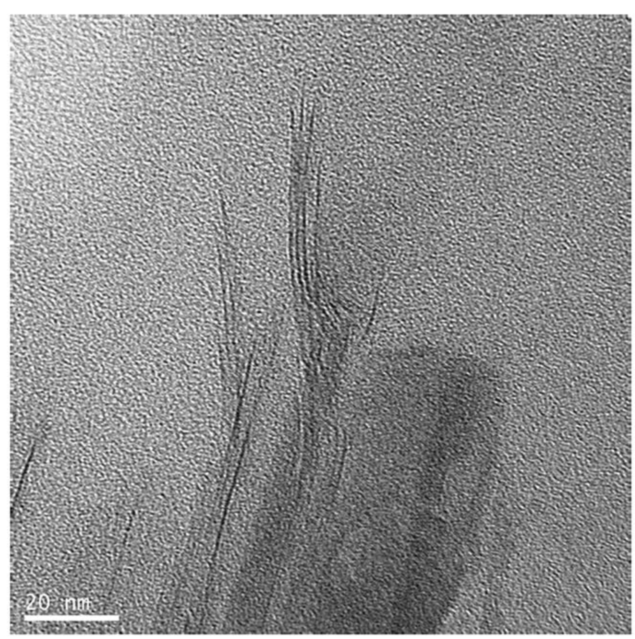

Figure 10. A high resolution TEM image of some exfoliated layers.

Conclusion

TEM investigation has proved to be an invaluable technique for analyzing structural characteristics of EPD nanocomposite polymer coatings. In this case, a proper procedure was optimized in order to prepare thin sections suitable for TEM observation by ultramicrotomy, by using an "ad hoc plastic substrate" with mechanical properties similar to those of the polymer coating of the nanocomposites. Therefore, the TEM characterization allowed highlighting all the characteristics of the nanofillers inside the coatings.

References

Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng R Rep 2000;28:1-63.

Azeez AA, Rhee KY, Park SJ, Hui D. Epoxy clay nanocomposites–processing, properties and applications: a review. Compos B Eng 2013;45:308-20.

Besra L, Liu M. A review on fundamentals and applications of electrophoretic deposition (EPD). Prog Mater Sci 2007;52:1-61.

Bhattacharyya A, Joshi M. Functional properties of microwave-absorbent nanocomposite coatings based on thermoplastic polyurethane-based and hybrid carbon-based nanofillers. Polym Adv Technol 2012;23:975-83.

Boccaccini AR, Keim S, Ma R, Li Y, Zhitomirsky I. Electrophoretic deposition of biomaterials. J R Soc Interface 2010;7:S581.

Chen S, Zhu J, Zhou T, He B, Huang W, Wang B. Preparation and properties study of polyaniline conductive anti-fouling coatings. Int J Electrochem Sci 2012;7:8170-84.

Conradi M, Kocijan A, Zorko Mand Verpoest I. Damage resistance and anticorrosion properties of nanosilica-filled epoxy-resin composite coatings. Prog Org Coat 2015;80:20-6.

Cury Camargo PH, Gundappa Satyanarayana K, Wypych F. Nanocomposites: synthesis, structure, properties and new application opportunities. Mat Res 2009;12:1-39.

De Riccardis MF, Martina V, Carbone D, Re M, Pesce E, Terzi R, Bozzini B. Incorporation of montmorillonite in epoxy to obtain a protective layer prepared by electrophoretic deposition. Mater Chem Phys 2011;125:271-6.

De Riccardis MF. Ceramic coatings obtained by electrophoretic deposition: fundamentals, models, post-deposition processes and applications. In: F. Shi, Editor. Ceramic Coatings - Applications in Engineering. InTech Open; 2012. p. 43-68.

Fiorini Baldissera A, Leite de Miranda K, Bressy C, Martin C, Margaillan A, Ferreira CA. Using conducting polymers as active agents for marine antifouling paints. Mat Res 2015;18:1129-39.

Fratoddi I, Venditti I, Cametti C, Russo MV. Chemiresistive polyaniline-based gas sensors: A mini review. Sens Actuator B-Chem 2015;220:534-48.

Frigione M, Lettieri M Recent Advances and Trends of Nanofilled/Nanostructured Epoxies Materials 2020;13:3415.

Giannelis EP, Krishnamoorti R, Manias E. Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes. Adv Polym Sci 1999;138:107-47.

Grim RH. Clay mineralogy. McGraw-Hill, 1953.

Guadagno L, De Vivo B, Di Bartolomeo A, Lamberti P, Sorrentino A, Tucci V, et al. Effect of functionalization on the thermo-mechanical and electrical behaviour of multi-wall carbon nanotube/epoxy composites. Carbon 2011;49:1919-30.

Hang TTX, Truc TA, Olivier M-G, Vandermiers C, Guérit N, Pébère N. Corrosion protection of carbon steel by an epoxy resin containing organically modified clay. Surf Coat Technol 2007;201:7408-15.

Jia F, Song S. Exfoliation and characterization of layered silicate minerals: a review. Surf Rev Lett 2014;21:1430001.

Jia ZR, Gao ZG, Lan D, Cheng Y-H, Wu G-L, Wu HJ. Effects of filler loading and surface modification on electrical and thermal properties of epoxy/montmorillonite composite. Chin Phys B 2018;27:117806.

Kabeb SM, Hassan A, Mohamad Z, Sharer Z, Mokhtar M, Ahmad F. Exploring the effects of nanofillers of epoxy nanocomposite coating for sustainable corrosion protection. Chem Eng Trans 2019;72:121-6.

Kaur G, Adhikari R, Cass P, Bown M, Gunatillake P. Electrically conductive polymers and composites for biomedical applications. RSC Adv 2015;5:37553-67.

Khostavan S, Fazli M, Ghorbanzadeh Ahangari M, Rostamiyan Y. The effect of interaction between nanofillers and epoxy on mechanical and thermal properties of nanocomposites: theoretical prediction and experimental analysis. Adv Polym Technol 2019;2019:8156718.

Li J, Zhang G, Zhang H, Fan X, Zhou L, Shang Z, Shi X. Electrical conductivity and electromagnetic interference shielding of epoxy nanocomposite foams containing functionalized multi-wall carbon nanotubes. Appl Surf Sci 2018;428:7-16.

Luo J, Li H, Xian G. Electrically conductive nanocomposite coating for strain and health monitoring. in: Proceedings CICE 2010, he 5th International Conference on FRP Composites in Civil Engineering 2010, Beijing. Available from: https://www.iifc.org/proceedings/CICE_2010/for+pub/Vol%20I/05%20Smart%20FRP%20Structures/092_Electrically_Xian.pdf

Merachtsaki D, Xidas P, Giannakoudakis P, Triantafyllidis K, Spathis P. Corrosion protection of steel by epoxy-organoclay nanocomposite coatings. Coatings 2017;7:84.

Morgan AB, Gilman JW. Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: a comparative study. J Appl Polym Sci 2003;87:1329-38.

Mostafaei A, Nasirpouri F. Preparation and characterization of a novel conducting nanocomposite blended with epoxy coating for antifouling and antibacterial applications. J Coat Technol Res 2013;10:679-94.

Muralishwara K, Achutha Kini U, Sharma S. Epoxy-clay nanocomposite coatings: a review on synthesis and characterization. Mater Res Express 2019;6:082007.

Paul DR, Robeson LM. Polymer nanotechnology: Nanocomposites. Polymer 2008;49:3187-204.

Piazza D, Lorandi NP, Pasqual C I, Scienza LC, Zattera AJ. Influence of a microcomposite and a nanocomposite on the properties of an epoxy-based powder coating. Mater Sci Eng A 2011;528:6769-75.

Rezwan K, Chen QZ, Blaker JJ, Boccaccini AR. Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering. Biomaterials 2006;27:3413.

Suarez-Martinez PC, Robinson J, An H, Nahas RC, Cinoman D, Lutkenhaus JL Polymer-clay nanocomposite coatings as efficient, environment friendly surface pretreatments for aluminium alloy 2024-T3. Electrochim Acta 2018;260:73-81.

Tjong SC. Structural and mechanical properties of polymer nanocomposites. Mater Sci Eng R Rep 2006;53:73-197.

Tomić MD, Dunjić B, Likić V, Bajat J, Rogan J, Djonlagić J. The use of nanoclay in preparation of epoxy anticorrosive coatings. Prog Org Coat 2014;77:518-27.

Ur Rehman MA, Ferraris S, Goldmann WH, Perero S, Bastan FE, Nawaz Q, et al. Antibacterial and bioactive coatings based on radio frequency co-sputtering of silver nanocluster-silica coatings on PEEK/bioactive glass layers obtained by electrophoretic deposition. ACS Appl Mater Interfaces 2017;9:32489-97.

Vaia RA, Liu W, Koener H. Analysis of small-angle scattering of suspensions of organically modified montmorillonite: implications to phase behavior of polymer nanocomposites. J Polym Sci B Polym Phys 2003;41:3214-36.

Van Olphen H. An introduction to clay colloid chemistry. New York: Interscience; 1963.

Vovchenko L, Perets Yu, Ovsienko I, Matzui L, Oliynyk V, Launetz V. Shielding coatings based on carbon–polymer composites. Surf Coat Technol 2012;211:196-9.

Yebassa D, Balakrishnan S, Feresenbet E, Raghavan D, Start PR, Hudson SD. Chemically functionalized clay vinyl ester nanocomposites: effect of processing parameters. J Polym Sci A Polym Chem 2004;42:1310-21.