Transmission electron microscopy (TEM) characterization of MMT-Epoxy nanocomposite coatings obtained by electrophoretic deposition process

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SUMMARY

Epoxy-nanoclay composite coatings are particularly attractive for their application in many technological areas, such as anticorrosion coatings on metal substrates and protective barriers. By adding layered silicates, having typically a structure formed by platelets with regular interspaces, it is possible to achieve an improvement of the specific properties of epoxy, even with surprising results. This is due to the penetration of polymer matrix between the silicate layers, inducing a dispersion of nanoplatelets at different degrees. In order to maximize the positive effect of the added silicate on the properties of the epoxy matrix, it is of primary importance to optimize the coating preparation process. To this aim, transmission electron microscopy (TEM) is an invaluable characterization technique, essential to obtain complete information on how much and how the nanoplatelets are distributed in the polymer matrix. For TEM observations it is necessary to find the right way to prepare a section of the sample by ultramicrotomy, without introducing artefacts. In this paper, we report TEM studies of montmorillonite epoxy (MMT-epoxy) coatings obtained by electrophoretic deposition (EPD).

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Introduction

Polymer nanocomposites are a very interesting class of materials because the lightweight and the ductile nature of the polymer can be combined with suitable nanofillers in order to properly design or improve many physical characteristics, such as electrical and thermal conductivity, mechanical strength, heat and impact resistance, and flame retardancy (Cury Camargo *et al*., 2009). In the literature there are many examples of their applications in several technological fields: as barrier and anti-corrosion coatings, as membranes for gas separation, as UV screens, as coatings for abrasion resistance or for flammability resistance, as electromagnetic interference shielding (EMI) coatings, as gas sensors, as antifouling paints, as electrodes for supercapacitors, and in biomedical applications. (Vovchenko *et al*., 2012; Fratoddi *et al*., 2015; Fiorini Baldissera *et al*., 2015; S. Chen *et al*., 2012; Mostafaei and Nasirpouri, 2013; Kaur *et al*., 2015; Bhattacharyya and Joshi, 2012; Ur Rehman *et al*., 2017; Tjong, 2006).

Epoxy resin is one of the most commonly used polymers as a nanocomposite matrix, because of its excellent resistance to chemicals, durability, stability even to severe environments, low shrinkage upon curing process, excellent adhesion to various supports, light weight, besides a relatively high mechanical and impact strength. Its weaknesses are low values of toughness, low thermal and electrical conductivity, high coefficient of thermal expansion. In metal corrosion protection, it is used in form of a coating, but its drawback is the not negligible adsorption and permeability to water vapour molecules, which can diffuse to the interface between the epoxy coating and the substrate, where the corrosion of the metal can easily start, especially in wet conditions. The introduction of nanofillers, with the proper chemical composition, shape, size and distribution in the epoxy matrix can induce not only an improvement of the original properties of the polymer but also new characteristics (Frigione, and Lettieri, 2020; Khostavan *et al*., 2019; Conradi *et al*., 2015; Luo *et al*., 2010; Guadagno *et al*., 2011, Li *et al*., 2018; Piazza *et al*., 2011; Kabeb *et al*., 2019).

One kind of the most studied fillers is the class of layered silicates, such as montmorillonite (MMT), which is environmentally friendly and readily available in large quantities at a relatively low cost. MMT is a 2:1 layered silicate, with a crystalline structure formed by an inner octahedral sheet of aluminium or magnesium oxide between two silicate tetrahedral sheets to which it is fused by the tip and its oxygen ions belong also to the tetrahedrons (Figure 1). Each group of these three sheets forms a single platelet. Within this layer some of the aluminium (Al^{3+}) can be replaced by magnesium (Mg^{2+}) and the negative charge distributed within the plane is balanced by positive ions, usually sodium ions, located in the galleries between two platelets (Alexandre et Dubois, 2000; Van Olphen, 1963; Grim, 1953). The platelets are stacked together in tactoids with a regular van der Walls gap between them, the so called "gallery". Since the bond between two successive platelets is weak, when MMT fillers are introduced in the matrix, polymeric molecules can penetrate among them and the clay platelets can be dispersed more and less homogeneously in the matrix. The nanoplatelets, constituting the second phase in these polymer nanocomposites, have high aspect ratio and high surface area, fundamental peculiarities to ensure a wider area of interaction with the matrix.

When the platelets are well dispersed individually in the polymer matrix, their distribution influences many specific properties of epoxy-nanoclay composites, that show better thermo-mechanical characteristics, electrical properties, flame retardant behaviour, and especially corrosion resistance, and wear resistance (Muralishwara *et al*., 2019; Zi-Rui *et al*., 2018; Pilar *et al*., 2018; Merachtsaki *et al*., 2017; Hang *et al*., 2007; Azeez *et al*., 2013; Tomić *et al*., 2014). As far as the mechanical behaviour, the propagation of microcracks can be deflected into a tortuous path by these layers, so resulting in an improvement of the toughness of the nanocomposite with respect to that of the pure epoxy. As regards the barrier and corrosion protection properties, well dispersed platelets act as barriers to corroding agent, by increasing the diffusion length into the coating, limiting or preventing the diffusion of water vapour molecules, so reducing the typical permeability and adsorption of the epoxy. For this reason, the amount and the distribution of the nanoplatelets in the matrix are fundamental parameters in the preparation of epoxy-nanoclay composite.

At nanoscale it is possible to distinguish two morphologies of nanoclay-polymer composites, depending upon the degree of nanoplatelets dispersion: "exfoliated" (or "delaminated") nanocomposites, and "intercalated" nanocomposites. In the first case, the complete separation of the individual clay layers into the polymer matrix occurs, obtaining a homogenous nanocomposite. In intercalated nanocomposites, the polymer chains result inserted into the nanoclay layers, producing an increased interspacing between the platelets, without inducing a loss of the layered morphology of the nanoclay. On the contrary, when the polymer chains are unable to intercalate between the clay layers, the second phase is well separated from the matrix (in form of tactoids) and the properties are those of traditional microcomposites (Alexandre and Dubois, 2000).

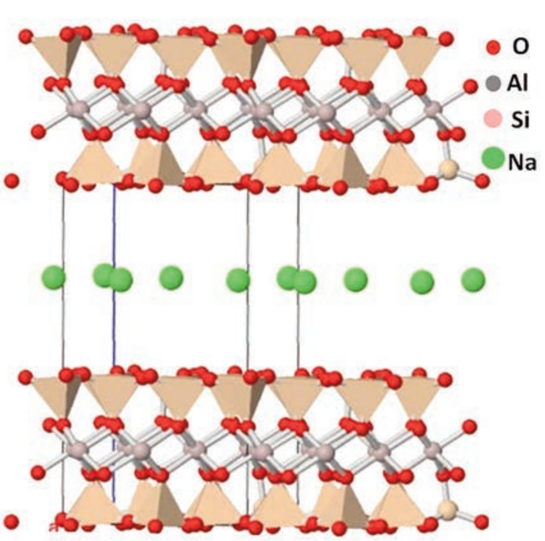

Figure 1. Crystalline structure of MMT; Si tetrahedrons are marked.

The above differences in morphology lead to significant variations in physical and mechanical properties of polymer nanocomposites. For this reason, the study of the distribution of the clay platelets in the epoxy matrix is invaluable in order to evaluate the effect of the preparation process of the coating on the nanofillers and their interaction with the matrix.

In order to study epoxy-nanoclays composites, X-ray diffraction (XRD) is the characterisation technique used as first, as it can rapidly detect the presence of periodically stacked MMT layers of tactoids. In a X-ray diffractogram, the diffraction peaks are related to the characteristic MMT interlayer spacing, in particular corresponding to the (001) planes. The structure of the intercalated layers can be easily identified because the characteristic peak is displaced as the d-spacing is increased by the presence of polymer chains in the galleries. When disordered (bunched together but not parallel to one another) or exfoliated layers are present, diffraction peaks are no longer visible either because of a large spacing between the layers or because the nanocomposite does not present any ordering (Giannelis *et al*., 1999). The results obtained from XRD can be misleading, because are averaged over the entire sample volume and because sometimes the amount of nanofillers is too small and the technique sensitivity may not be sufficient to distinguish low intensity peaks. Moreover, very often there is a coexistence of different kinds of dispersion (Morgan and Gilman, 2003), not always detected by XRD, but however influencing the final properties of the epoxy-clay nanocomposite. An example of XRD spectrum of epoxy-MMT compared with pure epoxy and with pure MMT is in Figure 2 (De Riccardis *et al*., 2011).

Transmission electron microscopy (TEM) is a characterisation technique of widely recognized importance for the study of all kinds of nanocomposites since it allows to obtain information on the spatial distribution of the nanofillers in the matrix, on their shape and size in localized areas. Indeed, it is a direct way to visualize the nanocomposites morphology. Besides, by observing many different regions at different magnifications it is possible to have a descriptive representation of the nanocomposites. For this reason it provides useful information and details that complete the overall description resulting from XRD characterisation (Paul and Robeson, 2008; Morgan and Gilman, 2003; Vaia *et al*., 2003).

In order to observe polymers by TEM, ultramicrotomy and cryo-ultramicrotomy are the most used techniques to get samples well representative and without artifacts. When a polymer nanocomposite is deposited in form of a coating on a substrate with very different mechanical properties with respect to the film, it is essential to prepare samples suitable for TEM observations carefully. In this work, the TEM characterisation of nanoclay-epoxy coatings deposited by electrophoretic deposition (EPD) is reported, after having optimized the procedure for preparing suitable TEM cross-section samples through ultramicrotomy.

Materials and Methods

In order to obtain MMT-epoxy coatings, EPD process was used. This simple technique allows an excellent control of the thickness and the morphology of the film through a fine tuning of the deposition parameter, is characterised by high rates of deposition employing low cost equipment, and permits to coat substrates with a complex shape (Boccaccini *et al*., 2010; Rezwan *et al*., 2006; De Riccardis, 2012). To deposit MMT-epoxy coating, an aqueous suspension based on a commercial epoxy resin (Cathoguard 325, BASF, Germany) was prepared by adding 0.1 wt% unmodified nano-MMT (Dellite HPS, Laviosa S.r.l., Livorno, Italy). The experimental details on suspension preparation and deposition parameters are reported otherwhere (De Riccardis *et al*., 2011).

For TEM investigation of polymer nanocomposite coatings, ultramicrotomy is usually the best method to prepare sections thin enough to be transparent to the electron beam. The main difficulty in the sectioning is due to the different mechanical properties of substrates and polymeric nanocomposite coatings. Therefore, to obviate these drawbacks, an "ad hoc plastic block" was used as a substrate, where the EPD coatings of MMT-epoxy were deposited. In this way, the differences in cutting between the strength of the coating and the substrate were minimized.

The plastic blocks were made by low viscosity "Spurr resin", put in a typical rubber embedding mould (Figure 3), and polymer-

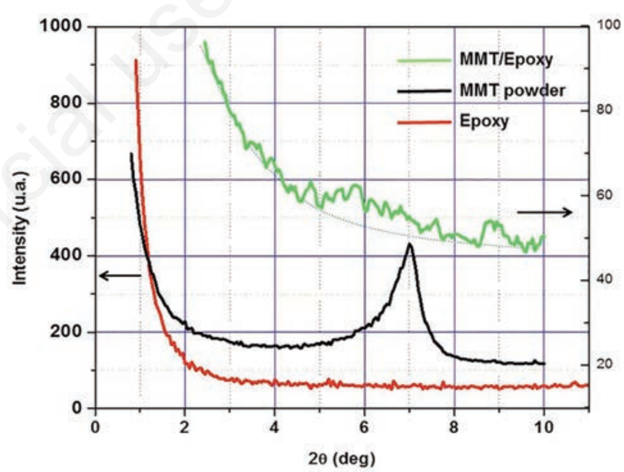

Figure 2. XRD spectra of epoxy-MMT, pure MMT and pure epoxy (from De Riccardis et al., Mater Chem Phys 2011;125:271-6; with permission).

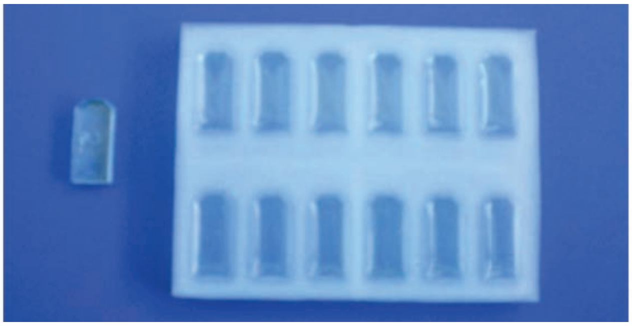

Figure 3. Image of the resin block used as substrate after the deposition of Au thin layers on the surface.

ized in oven at 70°C overnight. Then, these supports were coated with a thin Au layer in order to have a conductive surface, suitable for EPD process. After the deposition of the MMT-epoxy coating, another similar Au layer was deposited on EPD epoxy based coatings to mark the polymer nanocomposite coating and to identify it from the polymeric block, since they should have the same contrast in conventional TEM images. In Figure 4 there is a schematic picture of the final sample consisting of the resin substrate and the MMT-Epoxy coating between two Au thin layers. Thin slices were cut in the cross-section geometry, along the dashed plane z in Figure 4, by ultramicrotome (TOP-ULTRA 170A, Pabisch) at room temperature by using a diamond knife, and then collected on Cu grid. The solid section in the foreground of Figure 4 is how the cross section should appear.

Pristine MMT was also observed by dispersing some particles and then dropping the solution on a Carbon coated Cu grid for comparison with MMT in the nanocomposite coating.

The polymer nanocomposite samples and pristine MMT were observed by a TEM TECNAI G2 F30, equipped with a Schottky Field Emission source and a STEM attachment with Bright Field, Dark Field and High Angle Annular Dark Field Detectors (HAADF), at an acceleration voltage of 300 kV and with a resolution of 0.205 nm in TEM mode, at low-dose, in order to avoid electron-beam damaging of the sample.

Conventional TEM Bright Field (BF) images were obtained from many areas of the samples in order to analyse the coating morphology, such as its quality, size and distribution of the second phase. At higher magnification it is possible to distinguish MMT nanoplatelets in the nanocomposite coating as darker lines, so information about their dispersion, that is how and if they are dispersed in the epoxy matrix can be obtained; besides distance between two of them can be measured and compared to the characteristic distance of the (001) planes of pristine MMT.

STEM HAADF images gave invaluable information about the different composition of the characteristic details thanks to their Z contrast sensible to the local chemistry and thickness of the observed region. Besides, X-ray spectra were obtained by focusing the electron beam on the area of interest and collected by an Energy dispersive Spectrometer (EDAX, solid state detector with an ultra-thin window) for qualitative chemical analysis.

Results and Discussion

Thin slices of MMT-epoxy coatings with different nominal thickness were cut in order to define the best condition which should be a compromise between an electron-transparent sample and with a well-handling specimen with no artefacts. The best nominal value for these samples was found equal to 50 nm.

Many BF TEM images were obtained at low magnification, some of them (*not reported*) showing all the cross-section of the nanocomposite coatings, well defined by the two Au layers. A region of the coating is shown in a BF TEM image and in HAADF STEM image in Figure 5a and 5b respectively. In both of them, the Au layer deposited on the resin block before the EPD is well visible as a black layer in Figure 5a and as a white layer in Figure 5b. As it can be seen, this Au layer can help to distinguish the epoxy-based coating from the polymer block of the substrate since they have similar contrast in TEM images.

Inside the polymer nanocomposite coating, there are three

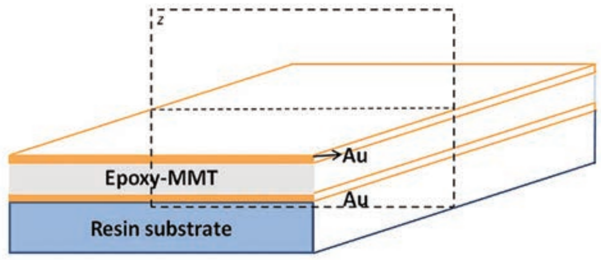

Figure 4. Schematic picture of the sample for TEM preparation. On the ad hoc resin substrate, there are a thin layer of Au, then Epoxy-MMT coating by EPD and another thin layer of Au. Along the dashed plane z thin cross-section were cut.

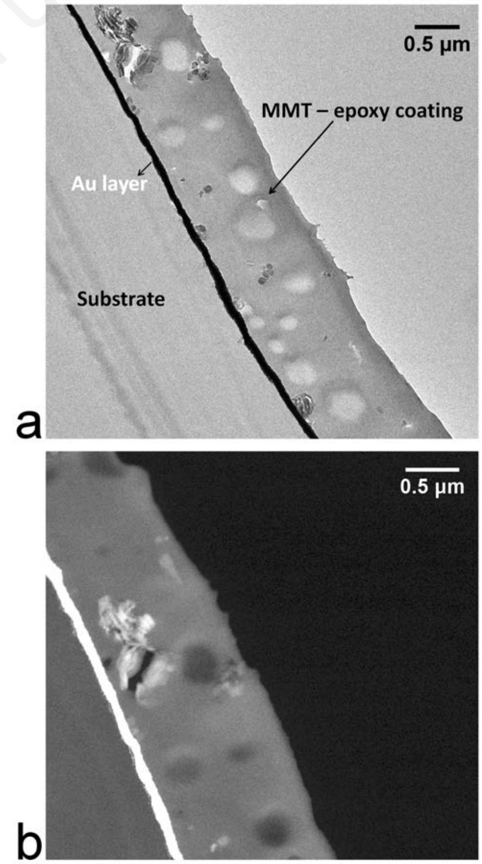

Figure 5. a) BF TEM image of a region of the MMT-epoxy coating at low magnification. b) HAADF STEM image of a similar area where the bright thin layer delimited the resin block and the epoxy nanocomposite coating.

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

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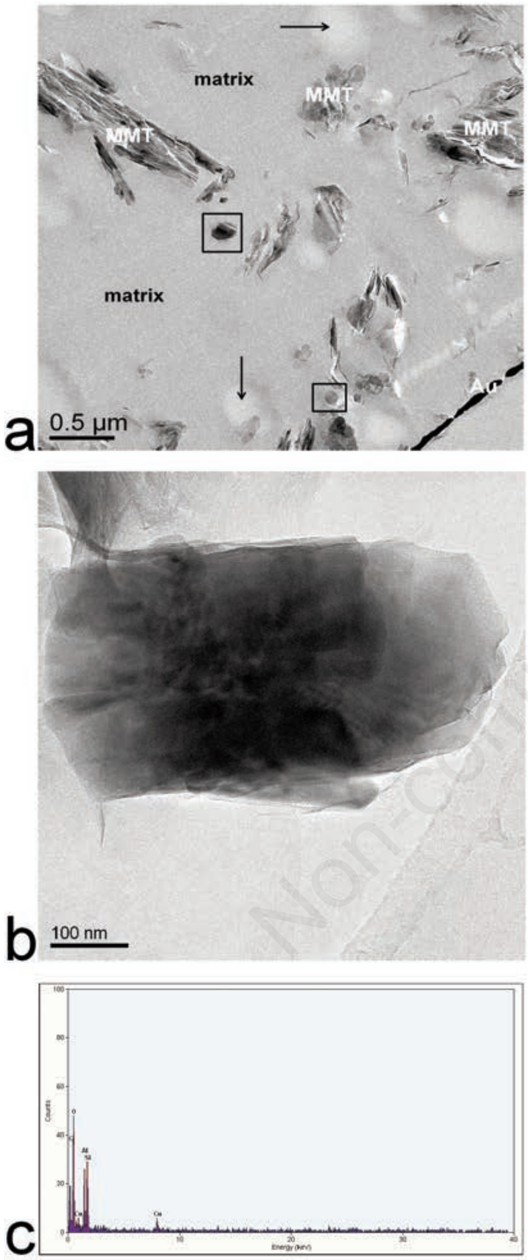

Figure 6. a) BF TEM image of the epoxy nanocomposite coating: the black arrows mark the brighter circular details, while in the black square there are round black particles. b) TEM image of a single pure MMT particle. c) A typical EDS spectrum collected with the beam focused on a rectangular particle.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

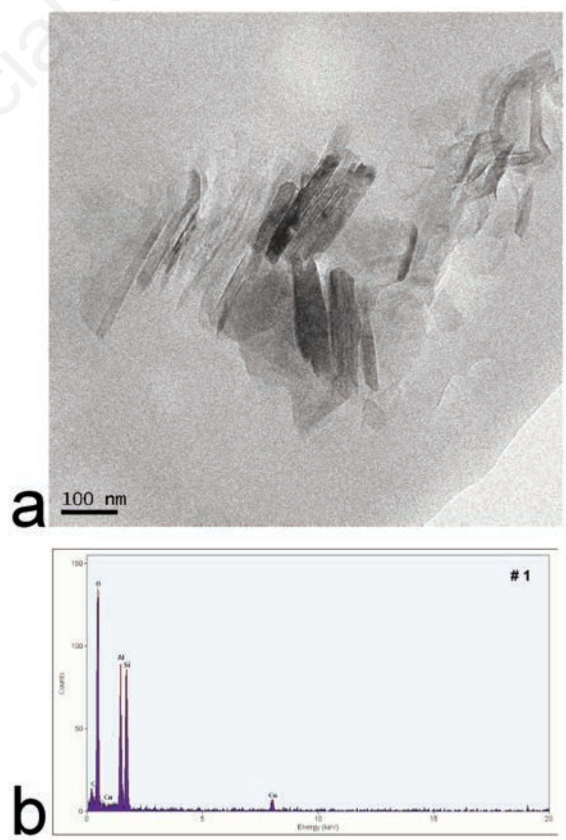

Figure 7. a) BF TEM image of some MMT particles in the coating. b) EDS spectrum obtained with the electron beam focused on the MMT particle.

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).

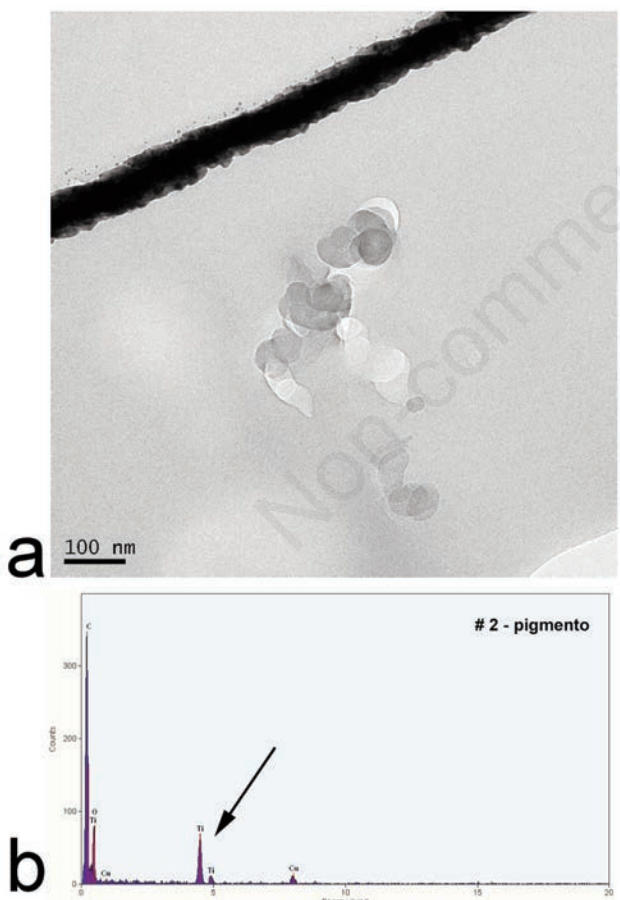

Figure 8. **a) BF TEM image of some round details in the coating. b) EDS spectrum obtained with the beam focused on the round black detail present in the coating.**

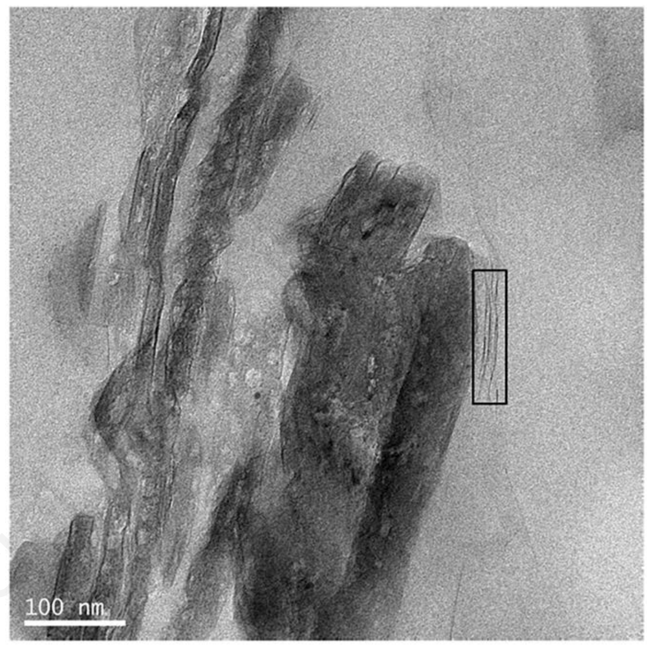

Figure 9. **A BF TEM image of some MMT particles at higher magnification; in the black square some intercalated platelets.**

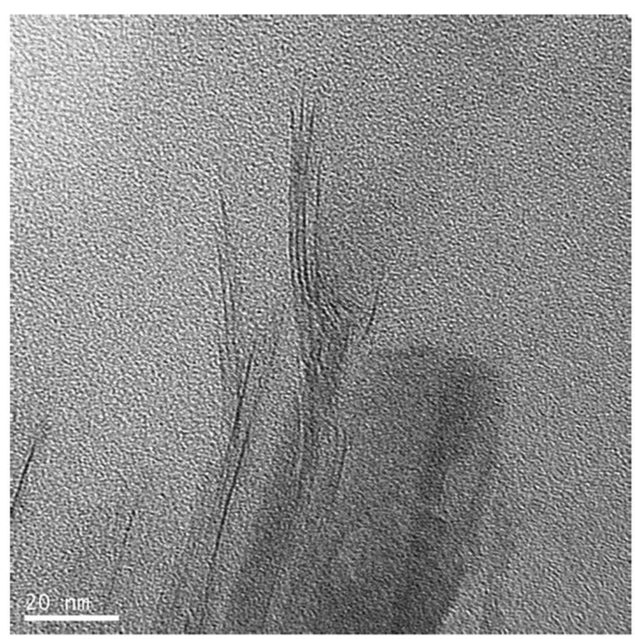

Figure 10. **A high resolution TEM image of some exfoliated layers.**

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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.

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