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PROOF-OF-CONCEPT EXPERIMENT REPORT

INVESTIGATION ON POLYMERIC TEETH DEFECTS

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ISTITUTO OFFICINA DEI MATERIALI

Proof-of-Concept experiment details

Received sample: stock of artificial teeth

Description by customer: the samples consist in artificial teeth made of a matrix of PMMA resin containing dyes. The customer identified different types of visible defects, classified for colour and size.

Planned analysis:

1st step: optical microscope analysis, with recording of the high magnification images of the defects/inclusions.

2nd step: polishing

3rd SEM and EDS in order to understand the nature of the material generating the defect.

Sample preparation: for the first step, no preparation is required. For the second step polishing of the teeth surface has been necessary (see dedicated paragraph in the report)

Measurement author, dates and place: the optical microscope images, the SEM (Zeiss) and EDS (EDAX) measurement of the sample has been performed by dr. Simone Dal Zilio at Istituto Officina dei Materiali- CNR. The polishing of the samples and the imaging with SEM (JEOL) has been performed by Mojca Vrčon and Mattia Fanetti, University of Nova Gorica, Materials Research Laboratory.

These measurements are performed within the framework of NANOREGION project, following the POC proposal submitted on 02/09/2020 and approved on 13/10/2020.

Main aim of the proposal: investigation of samples to understand the composition of the defects.

Optical microscope imaging

Imaging: Nikon optishot 150 microscope . Except where differently specified, all the images have been collected with 20X objective lens.

Morphology

In the next picture we report one example image for each investigated defect.

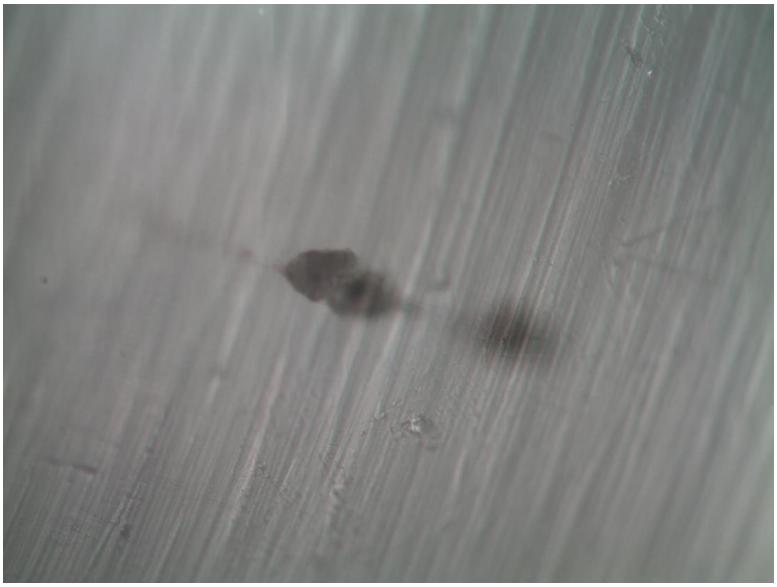


Figure 1 Black agglomerate.

Figure 2 Blue agglomerate.

Figure 3 Red spot.

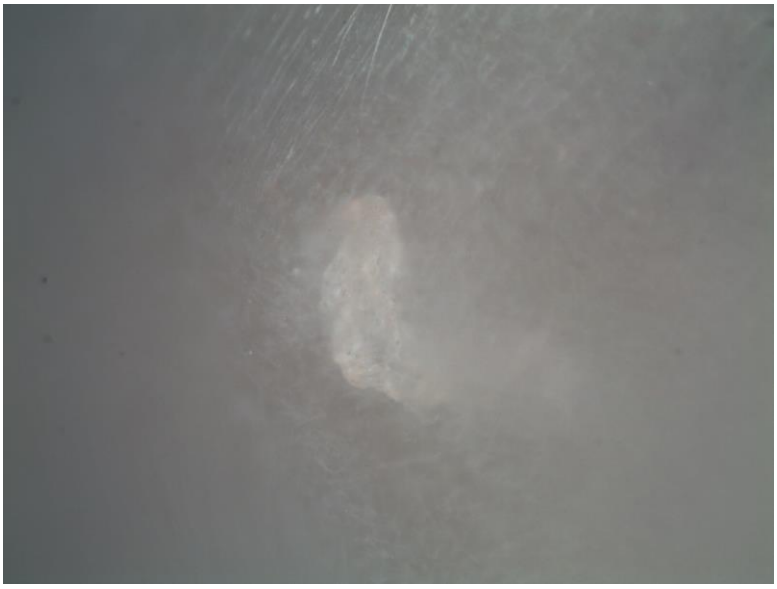


Figure 4 white spot.

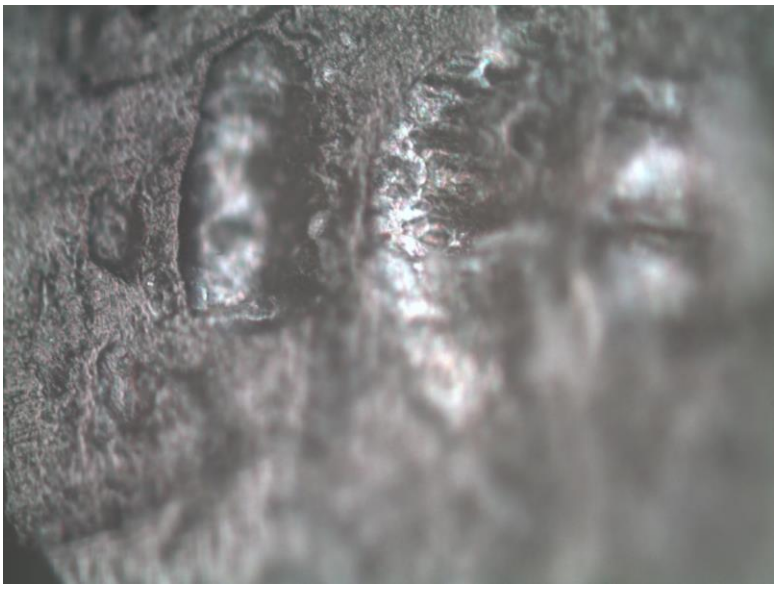


Figure 5 white block (10X).

Figure 6 undefined defect.

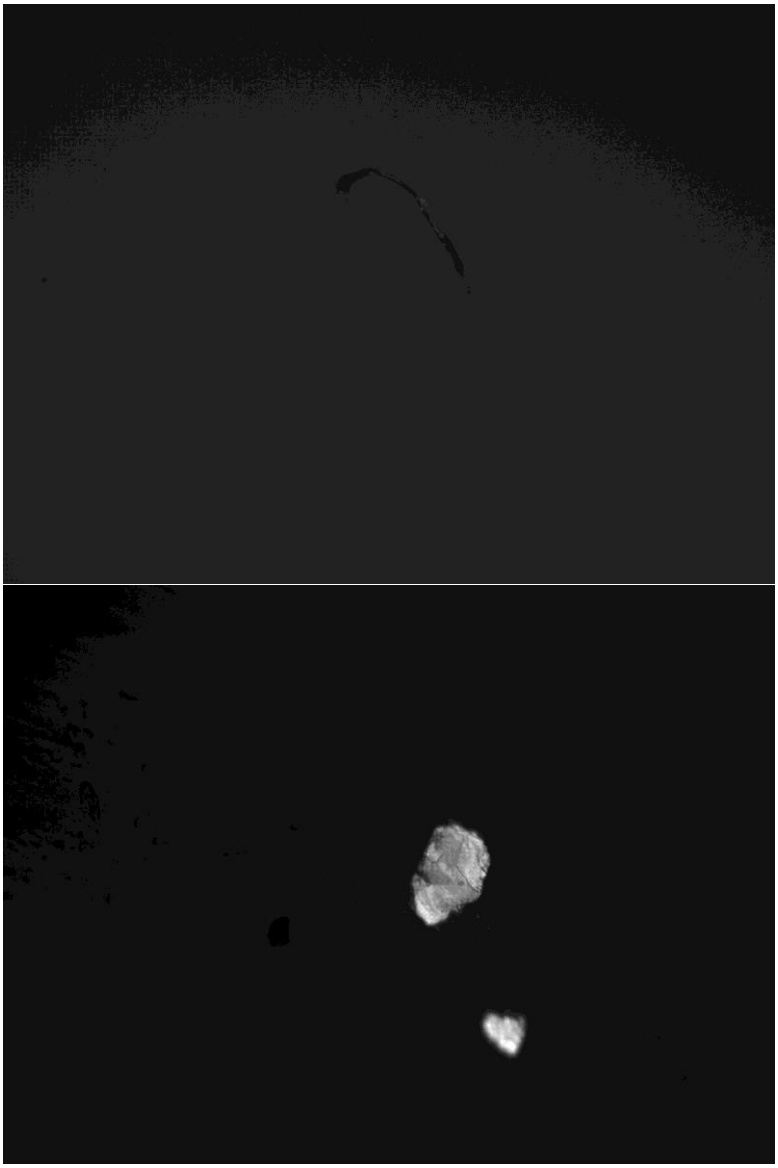


Figure 7-8 Fiber defect: the fiber is clearily inside the PMMA matrix. In the fig. 8, the presence of other cluster inside the polymeric matrix.

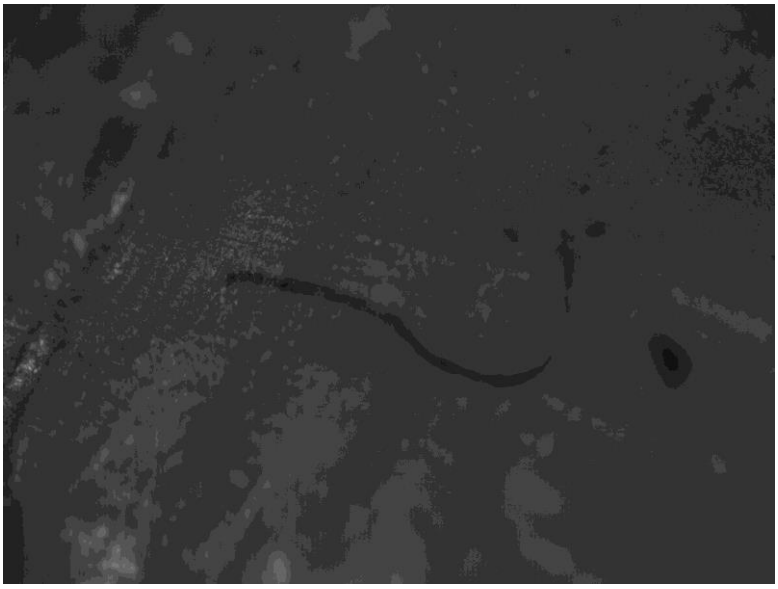


Figure 9 Fiber hair defect: it looks very similar to the fig.7 defect

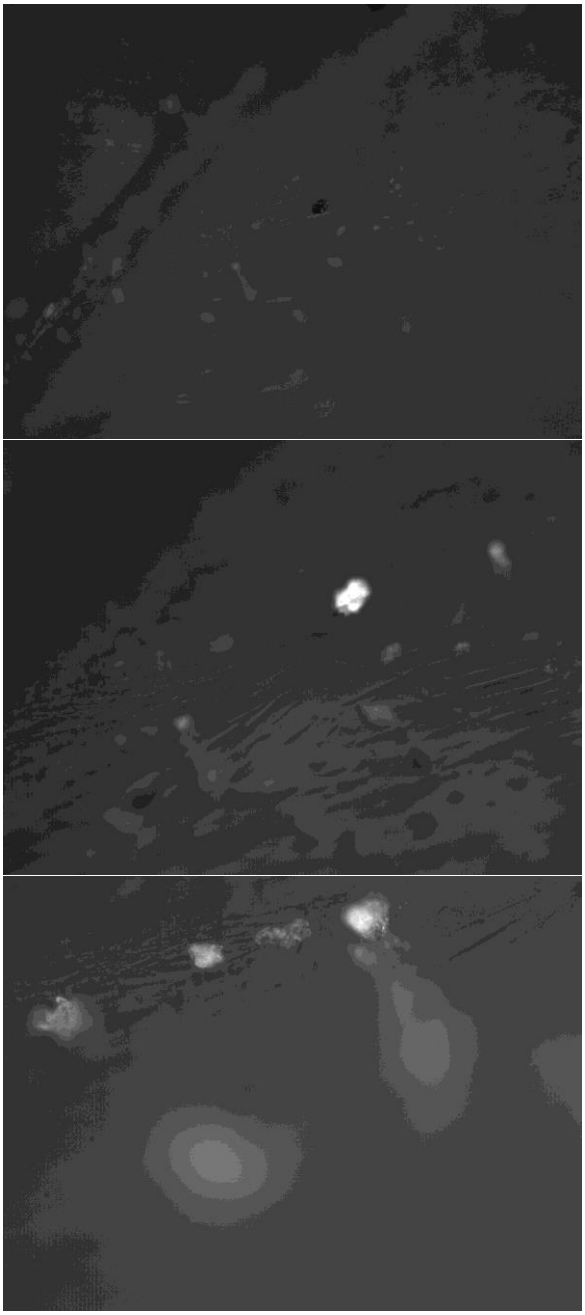


Figure 10-11-12 some of the metal *defects. IN some cases they looks white, in other cases black spots.*

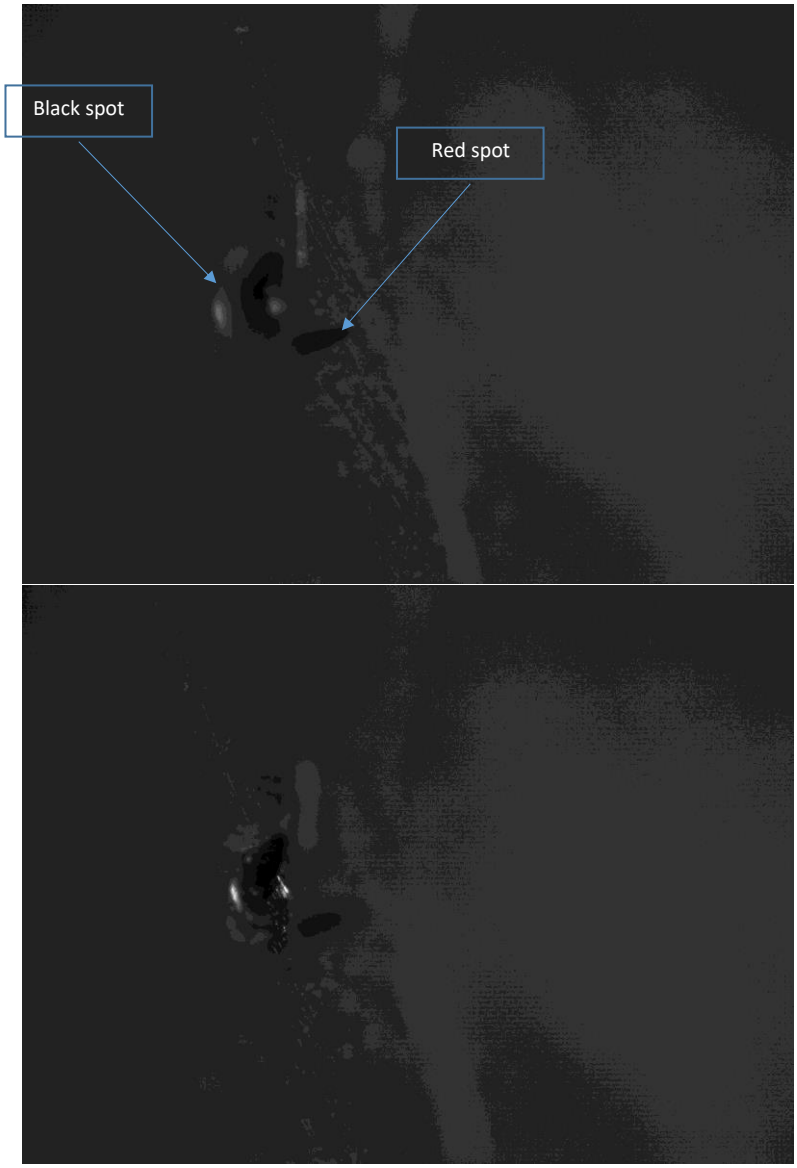


Fig. 13-14 Metal *defect after removal of PMMA. The defect is composed of 2 particles: one looks black/dark, the other one is red. (same different, images collected with different focal leght in order to highlight both the particles)*

Some general considerations on all the samples can be made following this first observation:

- the defects are all clusters or inclusions of foreign material.

- these defects are all found within the material, and not on the surface, as they can be focused at a depth of about 10-20 µm below the surface focus.

- the white spots and blocks have the appearance of crystals or any other material in crystalline form; they look very similar, just different in size.

An initial rough removal of the resin with a scalpel or abrasive paper has been tried to fully expose the defect, but it is difficult to be able to remove only the material above the defect. Below are some pictures of the attempts made.

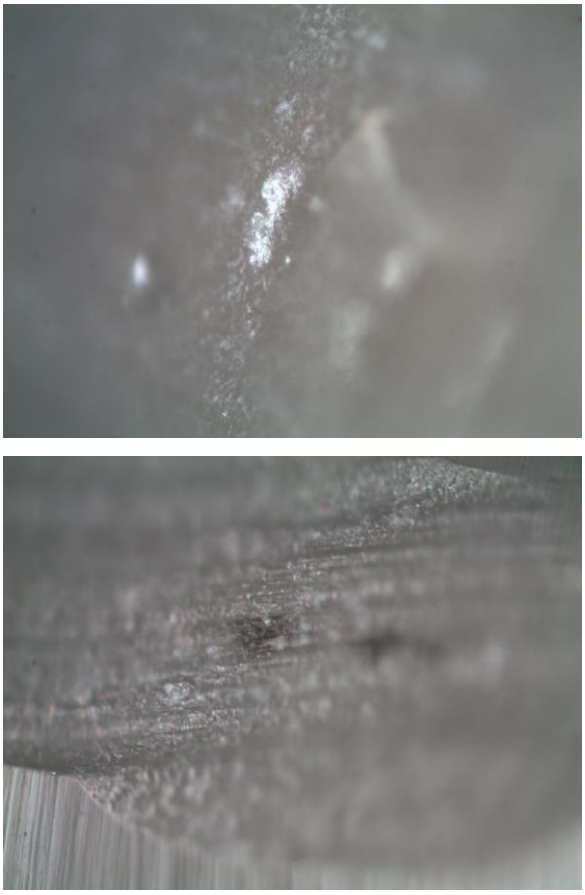


Figure 14-15 optical images of the defect after the removal of pmma resin by blade or abrasive paper.

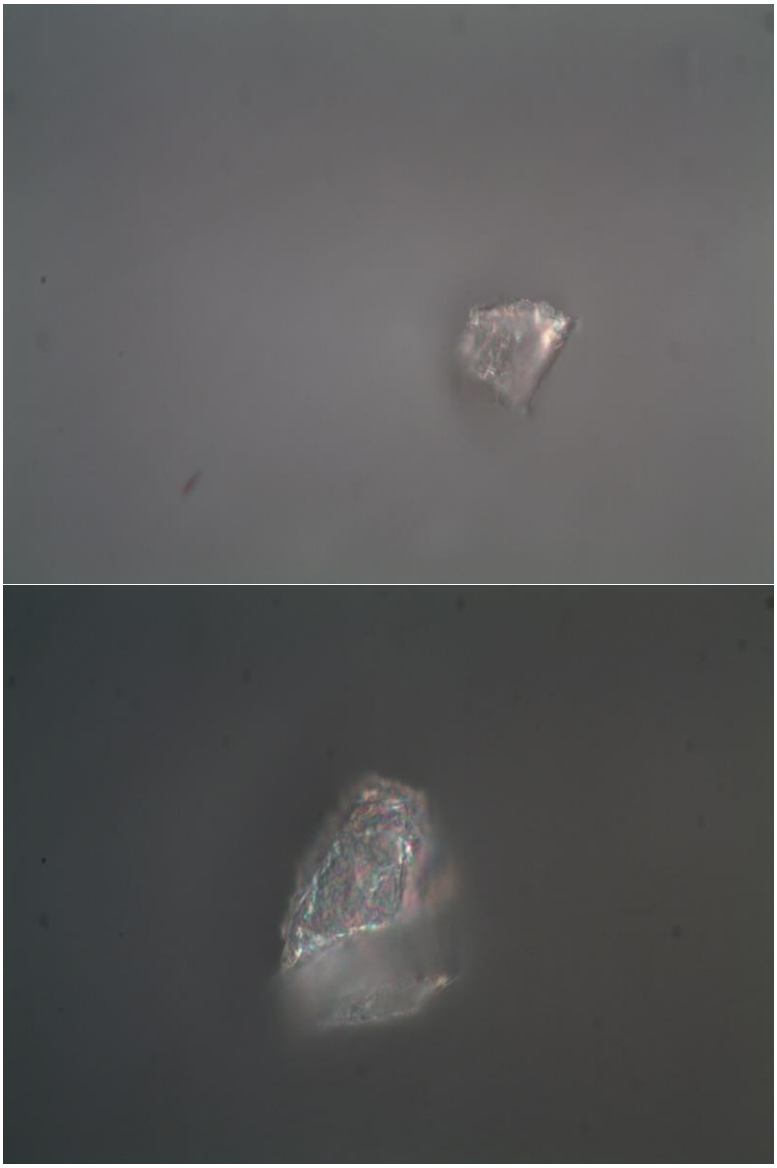
To proceed with the SEM and EDS analysis, it is therefore necessary to dedicate particular care to the polishing procedure.

Lapping procedure and SEM/EDS analysis

Different attempts have been tried to polish the polymeric teeth until the exposition of the target defect. In the end, the use of fine sandpaper (Struers, SiC paper, grit 2000) has been found a reasonable solution. The finishing has been performed by polishing with 50 nm Alumina nanoparticles-coated polishing paper, which results in a mirror-like polished surface. After polishing, sonication in absolute ethanol for 10-20 seconds has been performed, to remove the polishing residual.

The embedding of the prosthesis in transparent supporting polymer (Struers, ClaroCit) allows for a better handling during polishing, but it is not strictly necessary. Very frequent checks by optical microscope during the polishing process are necessary to stop the process when the defect is exposed at the surface.

An interesting observation from the polished sample is the presence of other defect, such as crystals, inside the tooth bulk, as visible from the optical microscope image (fig.9). We suppose the defects visible on the teeth (at least the white ones) are the ones close to the surface, but they are largely present also inside the matrix of the sample.



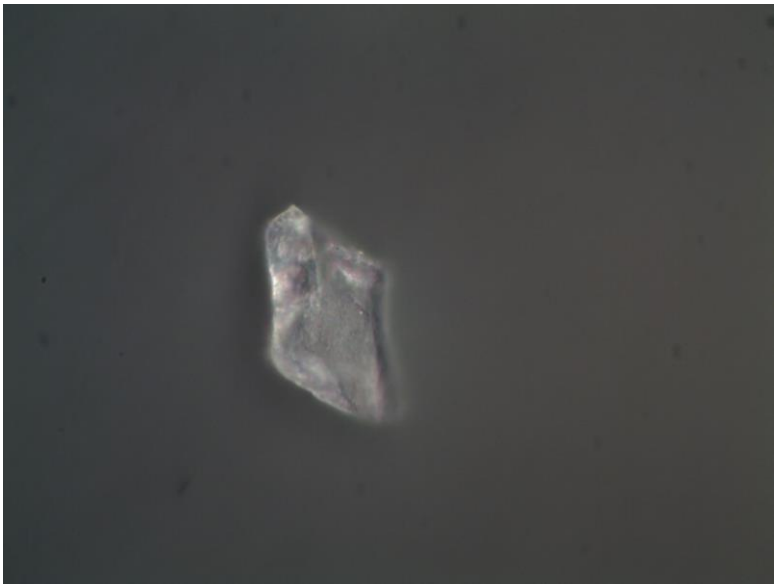


Figure 16-17-18 optical images of the defects after the removal of pmma resin by polishing. All the defects were present in the same sample. Mag: 50X

SEM and EDS Analysis

SEM analysis:

Two microscopes have been used for SEM imaging

1) ZEISS LEO 1540 XB (@IOM-CNR). Measurement conditions: Acceleration Voltage:15KV, aperture size: 30um, WD: 10mm. Two detectors are used: a) InLens; b) Secondary electrons
2) JEOL JSM 7100f (@UNG). Measurement conditions: Acceleration Voltage:15KV, WD: 6.4 / 10.7mm. Two detectors are used: a) Back-scattered electrons; b) Secondary electrons

We found that the choice of the detector is fundamental for better detection of the defects in the PMMA matrix. With ZEISS microscope, the secondary electron detector provides a better recognition of the defects with respect to Inlens. In fact, with the latter all the surface morphology features (scratches, holes, …) are very bright, and hinder the localization of the defects.

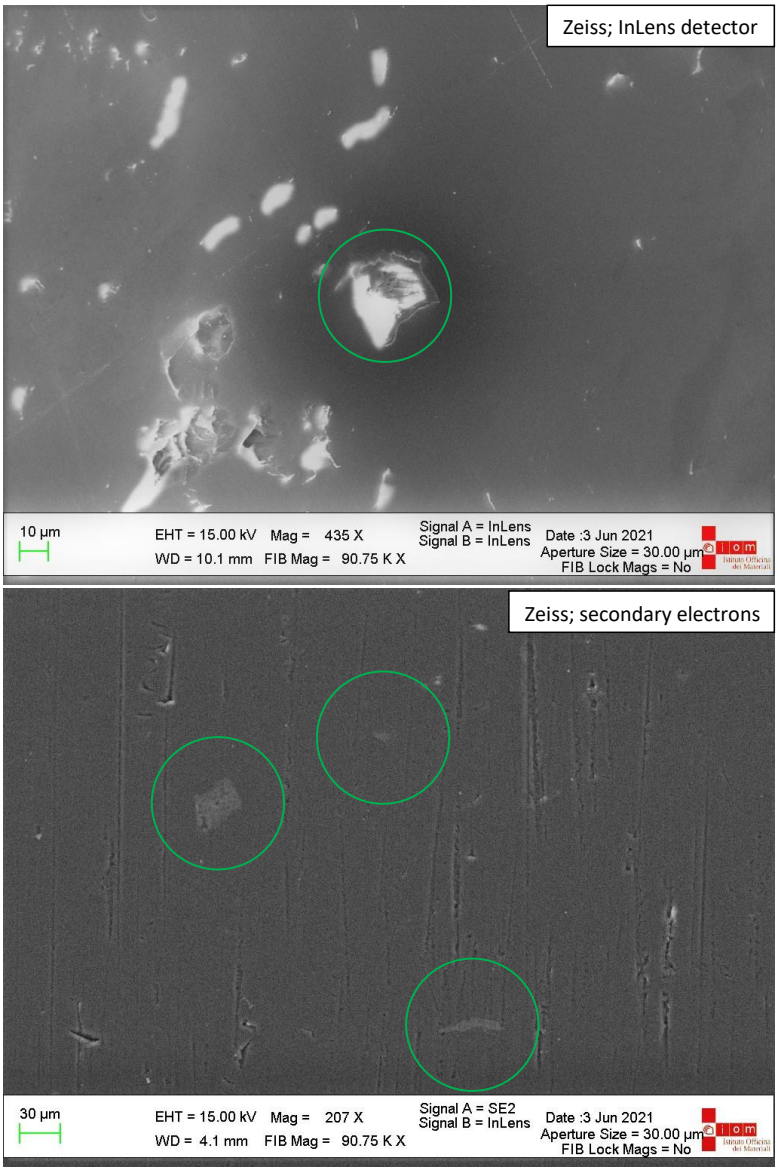


Figure 19-20 SEM image of two defects (»unclassified defect« sample). Defects are indicated by green circles.

With JEOL microscope, it was possible also to try with the backscattered detector, which is the more suitable for phase recognition, due to the Z-contrast (i.e. the sensitivity to the material density) and the low sensitivity for surface features.

In the following, the secondary and backscattered images of the same defects imaged in fig.10 are shown:

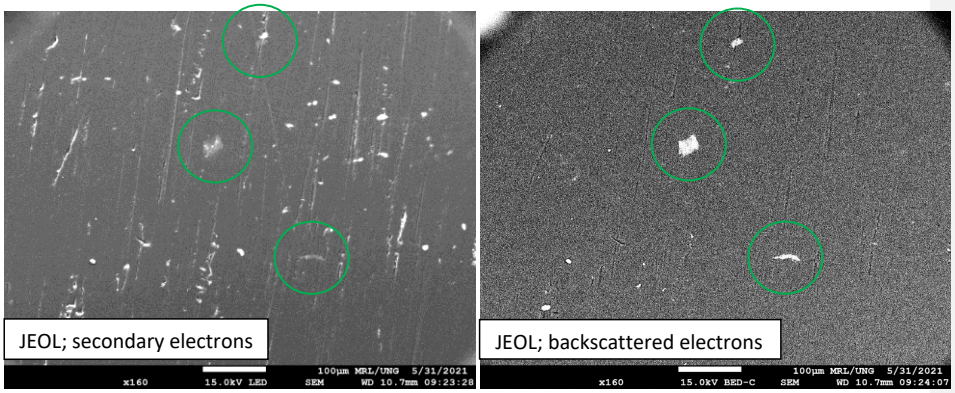


Figure 21 SEM image of the same defect imaged in fig.9, with secondary electrons (left) and backscattered electrons (right).

The defects are visible with the secondary electrons, but the contrast is higher with the backscattered electrons, which confirm the different composition of the defects with respect to the PMMA matrix.

With the backscattered electron detector, the defects are localized even when they are not really at the surface, but slightly below it. In the next images (both acquired on the same area), the defect is not visible with secondary detector (left image), but it is clearly localized with backscattered (right).

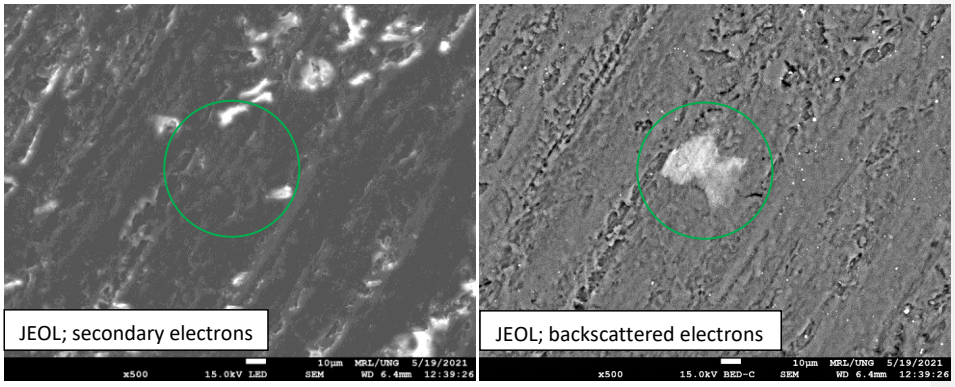


Figure 22 SEM image of the same area acquired with secondary electrons (left) and backscattered electrons (right).

EDS analysis:

For EDS analysis we used the SEM at IOM-CNR, i.e. ZEISS LEO 1540 XB (@IOM-CNR). Measurement conditions: Acceleration Voltage:15KV, aperture size: 30um, WD: 10mm. EDS spectrometer: EDAX PV7716, active area 10mm^2

From the SEM observation, few crystals have been identified and analysed by EDS. Inlens detector allowed a sufficient contrast, but in any case, the quality of the collect images permits to just detect the presence of a different material (respect the polymeric matrix surrounding the particles). IN the figure 13, an example of the collected SEM images and the correspondent EDS map of Silicon.

From the EDS analysis, we just measured the signal of Si and O, no other elements can be found. We suppose, if present, the amount of contaminant is below the detection limit.

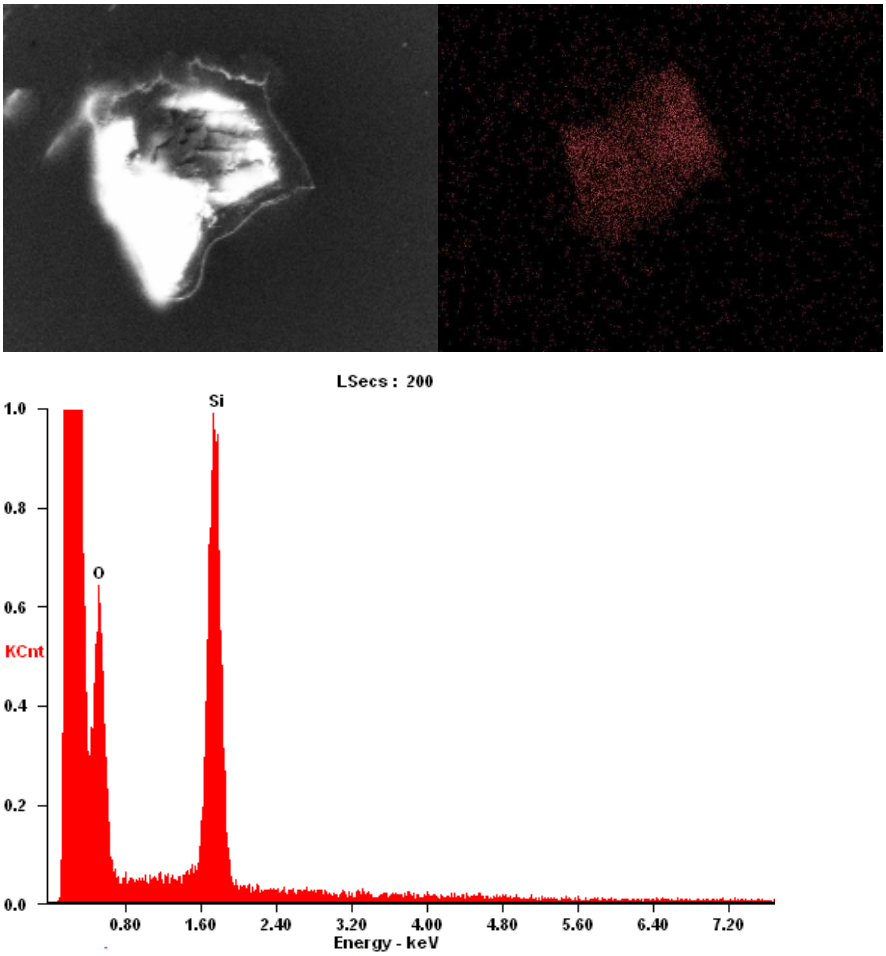


Figure 23-24 SEM image of a defect, correspondent EDS maps of Si and EDS spectrum of a difect after polishing. Beside the C from the PMMA matrix, the only detected elements are Si and O.

Conclusions and final remarks

The defects present in the samples provided by the company, have been characterized by optical microscope, SEM and EDS analysis. From optical microscopy, we can deduce that the visible defects

are incorporated in the polymeric matrix, at a depth in a range of about 5-15 µm. The origin of the different colouring of the defects is not clear, even after the EDS analysis, which highlighted the presence of Si and O in the regions where the defects are present. From the polishing of some samples, it is clear that the number of inclusions inside the polymer matrix is higher than that visible from the initial sample, but only the defects present near the surface are visible to the naked eye.

For the polishing process, fine SiC sandpaper (grit 2000) is suitable. Finishing with 50 nm alumina paper results in a flat surface appropriate for analysis. Sonication in absolute ethanol allows for removal of polishing residuals.

For SEM imaging, the more effective detector to localize the defects is the backscattered electron detector, first because of Z-contrast (i.e. density contrast, since the density of (Si,O) defects is higher than then the density of PMMA matrix) and second because its lower sensitivity to surface morphology. Defects which are slightly (few micrometers) below the surface can still be visualized by backscattered electron detector.

This report has been written on 28 august 2021