Italian National Agency for New Technologies,
Energy and Sustainable Economic Development

NANOCOMPOSITES EFFECT ON LASER ABLATION RATE OF TREATED MARBLE SAMPLES

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OVERVIEW

ABLATION OF POLYMERIC FILMS DOPED WITH NANOPARTICLES

- RESEARCH OBJECTIVE
  - Check the removal power of the pure and doped polymer film
- MATERIALS
  - PEMA + SiO_2 , TiO_2 Nanoparticles coated on Carrara marble
- INSTRUMETATION
  - Laser
- RESULTS
- CONCLUSIONS

INTRODUCTION

LASER ABLATION OF POLYMERIC MATERIALS

- Nanomaterials are used to improve:
  - Mechanical strenght
  - Hydrophobicity
  - Photo resistance

- Applications of laser ablation:
  - Removal of thin protective layers from artwork surfaces
  - Preservation of architectural and cultural heritage surfaces

MATERIALS

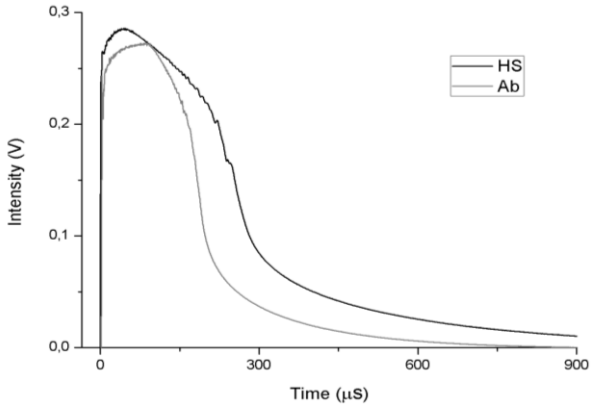
- The selected polymer is a copolymer of methyl and ethyl-methacrylate (PEMA)
- Commercial name: Paraloid B72
- Nanoparticles: SiO_2 and TiO_2 synthesize by CO_2 laser pyrolysis using tetraethoxysilane and Titanium isopropoxide as reagents
- Nanoparticles dispertions in solvent by ultrasonic bath
- Substrate of Carrara Marble

SAMPLE	POLYMER	NPS	SUBSTRATE
C1	-	-	Gray Carrara marble
C2	Paraloid B72	SiO_2 (1%) +TiO_2 (0,1%)	Gray Carrara marble
C3	Paraloid B72	SiO_2 (1%)	Gray Carrara marble
C4	Paraloid B72	TiO_2 (0,1%)	Gray Carrara marble
C5	Paraloid B72	SiO_2 (0,1%)	Gray Carrara marble
C6	Paraloid B72	-	Gray Carrara marble

INSTRUMENTATION

Ho:YAG LASER

- LitHo system (Quanta System) with 2100 nm emission
- Laser pulses are delivered by optical fibre (600 µm)
- Gaussian beam profile



"Pulse temporal profiles for the LitHo regimes selected for ablation tests"

OPERATION MODES

Hard Stone (HS)

prr	E per Pulse	Pulse duration	Mean fluence	Peak fluence
3 Hz	0.5 J	330 µs	$1{,}19e2\,\frac{W}{cm^2}$	$1{,}33e5\,\frac{W}{cm^2}$

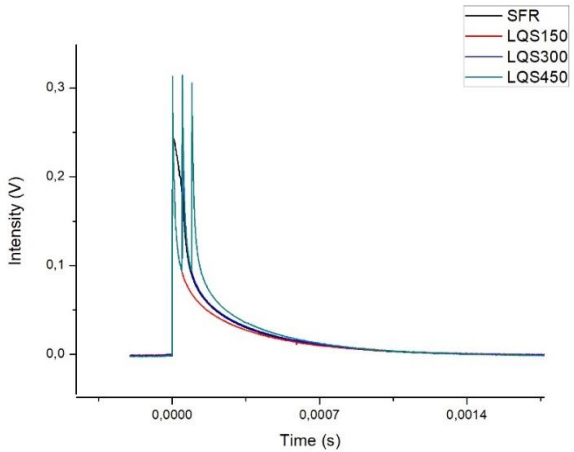
Ablation (Ab)

prr	E per Pulse	Pulse duration	Mean fluence	Peak fluence
8 Hz	0.5 J	200 µs	$3{,}19e2\,\frac{W}{cm^2}$	$1{,}99e5\,\frac{W}{cm^2}$

INSTRUMENTATION

Nd:YAG LASER

- EOS COMBO (El.En. S.p.A.)
- Wavelenght: 1064 nm



"Pulse temporal profiles for the EOS COMBO regimes selected for ablation tests"

OPERATION MODES

- EOS COMBO combines two temporal regimes
- Beam delivering: two 1000 μm optic fibers, 3 and 10 m long
- Beam profile: Homogeneus
- Aiming beam: diode laser 3 mV (635 nm)

Short Free Running (SFR)

prr	E per Pulse	Pulse duration
Selectable	2 J	30 – 110 μs

Long Q-Switch (LQS)

prr	E per Pulse	Pulse duration
Selectable	150 mJ	100 ns

INSTRUMENTATION

Nd:YAG LASER

- Opolette™ 355 LD, turn-key tunable laser system
- Pulsed
- Tunable

OPERATION MODES

Pump Laser Specifications

Pump Wavelenght	prr	Pulse Lenght	Beam Diameter	External Trigger
355 nm	20 Hz	7 ns	3 (4) mm	Flashlamp and Q-Switch

OPO Parameters

Wavelenght Tuning Range	Access to residual 355 nm	Peak OPO Energy
410 - 2200 nm	6 (12) mJ	4.3 (9)* mJ

REFLECTANCE AND COLORIMETRY

INSTRUMENT

- *ColorLite sph850 contact spectrophotometer illuminated with D65 standard illuminant*

- System calibrated with a reference measurement using the BAM white, performed on samples with a probe with a diameter spot of $3.5\ \mathrm{mm}$
- The measure reflectance is the average reflectance on the total treated area

PROFILOMETRY

- Mechanical 2D profiler
- Contact profiler **KLA-Tencor D-10** equipped with a scanner with a diamond stylus (tip radius of $2\ \mu\mathrm{m}$)
- The resulting trace represents a cross-sectional view with high vertical and spatial resolution (scan speed of $5\ \mu\mathrm{m/s}$, vertical range equal to $327\ \mu\mathrm{m}$)

LIF (Laser Induced Fluorescence)

LiDAR fluorosensor experimental apparatus developed at the Diagnostic and Metrology Laboratory of the ENEA centre of Frascati

Light source: compact pulsed, diode pumped, solid state lasers, emitting at $266\ \mathrm{nm}$ (UV region)

Set of **optics** for the transmission of the exciting radiation and the reception of the scattering and fluorescence signals from the target

Filter ($\mathrm{HR}\ @\ 266\ \mathrm{nm}$) to cut out unwanted laser light

CCD detector in the spectrometer permits to record the overall spectral emission with $2.5\ \mathrm{nm}$ resolution in the range from $200\ \mathrm{nm}$ up to $900\ \mathrm{nm}$

- For every sample a set of measurements are acquired in different points of the surface in order to take into account material inhomogeneities.
- For the acquisition ($1\ s$ long) no temporal delay was applied
- Laser energy was set at $1\ \mathrm{mJ}$ for the laser at $266\ \mathrm{nm}$

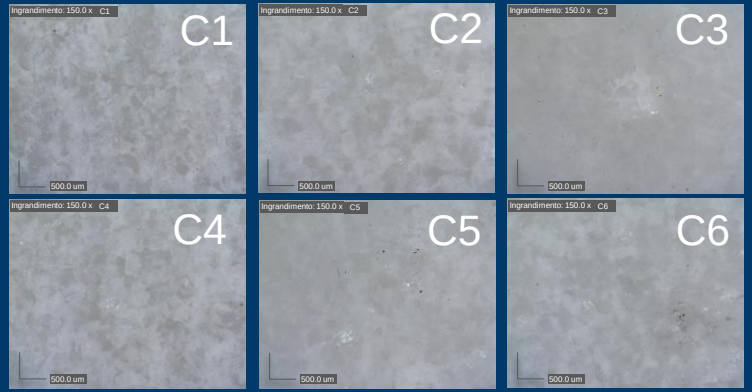
RESULTS AND DISCUSSION

M.O.

- In the first image (C1) a no-treated area of the sample is shown, in the other images the areas subjected to treatment in different conditions are shown
- It is possible to notice that in the sample covered only with PEMA, even the more severe laser conditions used were not sufficient for the removal of the polymeric film. In fact, in all the treated points it was not possible to detect any removal of the material. The only effect obtained was a chromatic variation of the area undergoing treatment.
- On the other hand, it possible to notice that the presence of Silica nanoparticles in the polymeric film allows, with the same laser conditions, the removal of the polymeric film in its entirety.

SAMPLE	POLYMERIC FILM
C1	-
C2	B72 + SiO_2 (1%) +TiO_2 (0,1%)
C3	B72 + SiO_2 (1%)
C4	B72 + TiO_2 (0,1%)
C5	B72 + SiO_2 (0,1%)
C6	B72

Sample C3 after laser treatment



On samples, near the areas under consideration, some photos were taken with an optical microscope (Dino-Lite Edge AM4515ZT) to observe the differences before and after laser treatment (150x magnification)

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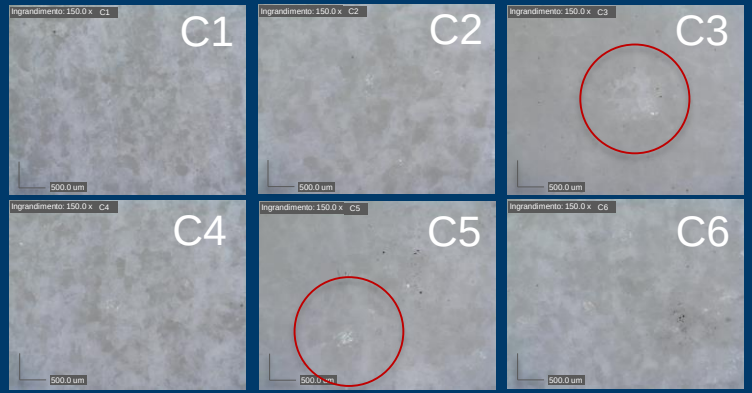

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RESULTS AND DISCUSSION

LIF measurements

LIF measurements were carried out before and after laser treatments.

- PEMA fluorescence signal centred at 340 nm

➢ For C6, treated with LitHo, the PEMA fluorescence band is still present also after laser ablation, indicating that the polymeric film was not removed

➢ Same results also for other LASER

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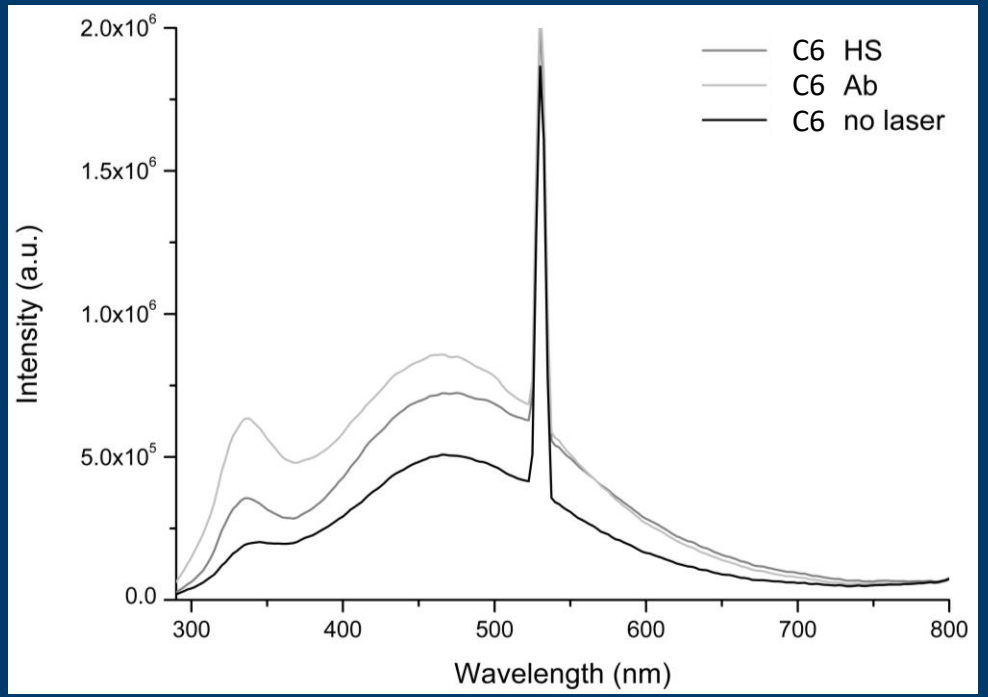
C6	B72



"LIF spectra on C6 sample before and after laser ablation tests"

RESULTS AND DISCUSSION

LIF measurements

- In presence of nanoparticles we observed the disappearance of nanocomposite fluorescence band and that all the Ho:YAG operation modes tested cause similar effects.

- The spectra after ablation test are very similar to untreated marble spectra (not reported), suggesting that laser always exceeded damage threshold of the surface.

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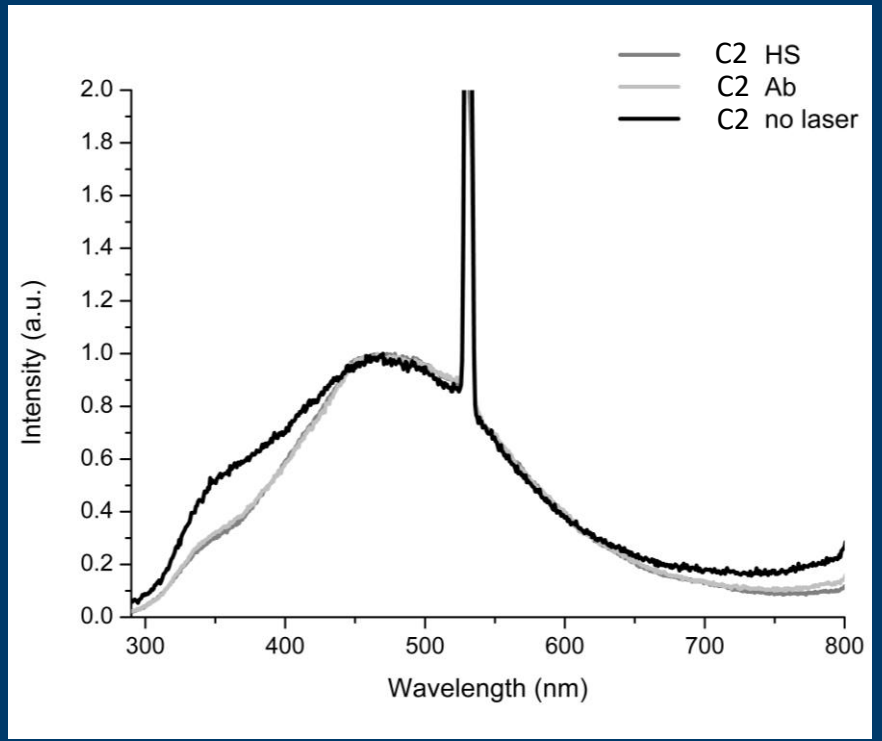
C1	-
C2	**B72 + SiO_2 (1%) +TiO_2 (0,1%)**
C3	B72 + SiO_2 (1%)
C4	B72 + TiO_2 (0,1%)
C5	B72 + SiO_2 (0,1%)
C6	B72



"LIF spectra of C2 sample before and after laser ablation tests"

RESULTS AND DISCUSSION

LIBS

- Yellow spectrum: 12 mJ
- Purple spectrum: 27.5 mJ
- Single shot

Detected peaks:
- Ca (I),(II)
- Ti (I)

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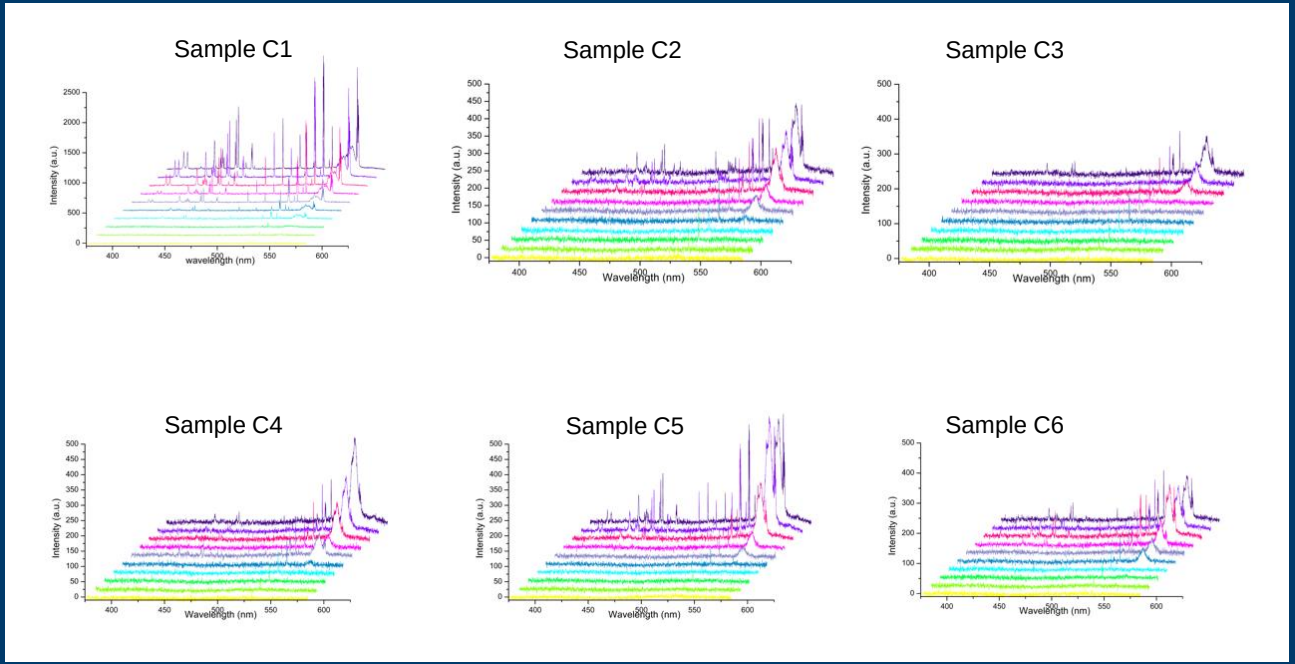
C5	B72 + SiO_2 (0,1%)
C6	B72

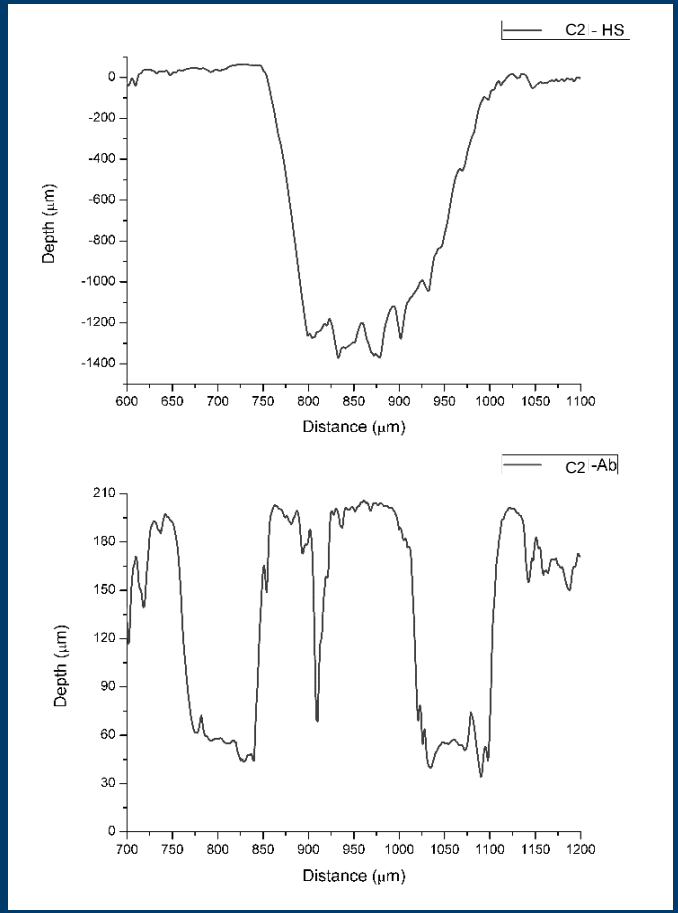


RESULTS AND DISCUSSION

Profilometry

Surface profiles after single shot with different laser regimes on the samples put in evidence that there is a much lower effect in the same conditions on the film of pure polymer.

- No craters can be detected by profilometry on the surface of the sample C6
- Craters due to ablation tests have well defined profiles on sample C2, as shown in figure
- It was possible to individuate a trend in the ablation rate, that decreases from HS (craters about 1300 μm deep and 250 μm large) to Ab (craters about 150 μm deep and 120 μm large)
- The thickness of PEMA and nanocomposite films: in the order of tens of μm
- Depth of the craters on MG11 is greater that this thickness value, both for HS and Ab regimes, confirming the exceeding of damage threshold of the surface



"Crater profiles for samples C2 after single pulse ablation tests in HS (top) and Ab (bottom) conditions"

CONCLUSION

The scattering power of nanoparticles affects transmission, absorption and reflection of the film applied on marble surfaces. Consequently, effects of their presence can be noticed also on the laser irradiation response. All the technique used suggest that the presence of SiO_2 nanoparticles induces higher ablation rates of the polymeric matrix in which they are embedded. This effect does not seem to be affected by the differences in laser operation parameters.

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Thank you for your attention!