

## Finest High-quality Natural and synthetic polymer substrates and fibers innovative plasma treatments for fashion MUSA Project- Spoke 5 Fashion



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DEGLI STUDI MILANO BICOCCA

- State of the art
- Fabrication of Graphene Oxide
- Characterization techniques
- Results
- Plasma treatment on Polymers
- Deposition of GO on Polymers
- Discussion
- Future Aspects



#### **Motivation**

Textiles going beyond clothing, actively contributing to well-being and comfort.

Reshaping textiles through nanoscale surface modifications and plasma treatment.

Introducing GO, rGO, and rGOQD's coatings to adapt textiles to diverse applications (UV protection, antistatic, antibacterial, thermoregulating, photoluminescent finishes, improvement of mechanical properties, flexible supercapacitors, sensors) *Nascimento et al. 2021*[1].

Revolutionize **antibacterial** and **comfortable** (thermoregulating) textiles for clothing, paving the way for applications in healthcare, sportswear, and beyond.



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## State of the Art

## **Innovation in Textile Industry: Weaving the future**

- "Traditional textiles face challenges—limited durability, suboptimal wettability, and a lack of specialized functionalities. These challenges demand innovative solutions to propel textiles into the future.
  - Plasma Treatment on textiles
  - Coating on Textiles
- Different Textile materials respond uniquely depending on structures.

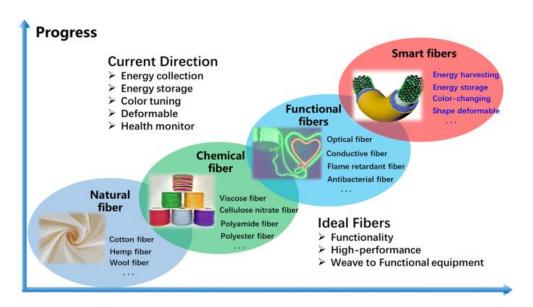


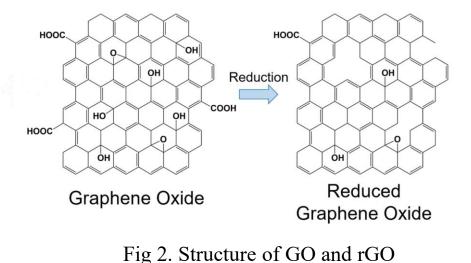
Fig 1. Innovation in textile industry



## State of the Art

# Graphene Oxide (GO), rGO, rGO-QD's: As a coating material

- Graphene Oxide, formerly called graphitic oxide, is a compound of carbon, oxygen, and hydrogen, obtained by treating graphite with strong oxidizers
- Structurally, GO can be visualized as a graphene sheet with its basal plane decorated by oxygen-containing groups.
- GO can be reduced to acquire rGO. Reduction eliminates the majority of the carbonyl, carboxyl, hydroxyl, and epoxy groups on the GO sheets



### State of the Art

#### Graphene Oxide (GO), rGO, rGQD's: As a coating material

rGO-QDs, as a new type of zero-dimension quantum dot, have become one of the hottest interests compared to graphene form due to their unique properties originating from the quantum confinement effect

rGO-QDs have non-toxicity, chemical stability, excellent photostability and biocompatibility



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### State of the Art

#### Methods:

- Modified Humers Method ---- for fabrication of GO
- Simple Dipping Method ----- for deposition

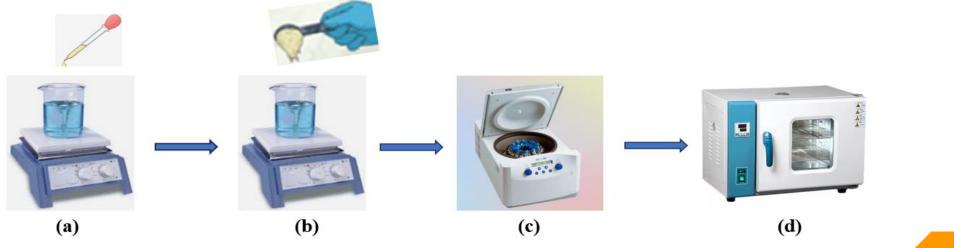


Fig. 3 Modified Humers Method (a) Stirring condition (b) Stirring condition adding powders (c) Centrifugation (d) Drying in Oven



## Fabrication of Graphene Oxide

- Modified Humers Method Zaaba. et.al 2017[2]
- 27 ml of sulfuric acid ( $H_2SO_4$ ) and 3 ml of phosphoric acid ( $H_3PO_4$ ) (volume ratio 9:1) were mixed and stirred for several minutes.
- 0.225 g of graphite powder was added into the mixing solution under stirring condition
- 1.32 g of potassium permanganate ( $KMnO_4$ ) was then added slowly into the solution.
- Stirred for 6 hours until the solution became dark green.
- To eliminate excess  $KMnO_4$ , 0.675 ml of hydrogen peroxide  $(H_2O_2)$  was dropped slowly and stirred for 10 minutes
- 10 ml of hydrochloric acid (HCl) and 30 ml of deionized water (DIW) were added and centrifuged 3 times each for 10 minutes
- The washed GO solution was dried using the oven at 90 °C for 24 hours to produce the powder of GO





At Stirring condition The solution became dark green





Fabricated GO at weight balance

GO after drying



## **Fabrication of Graphene Oxide**

Prepared 4 batches of Graphene Oxide
Each batch contains 4 days of fabrication.

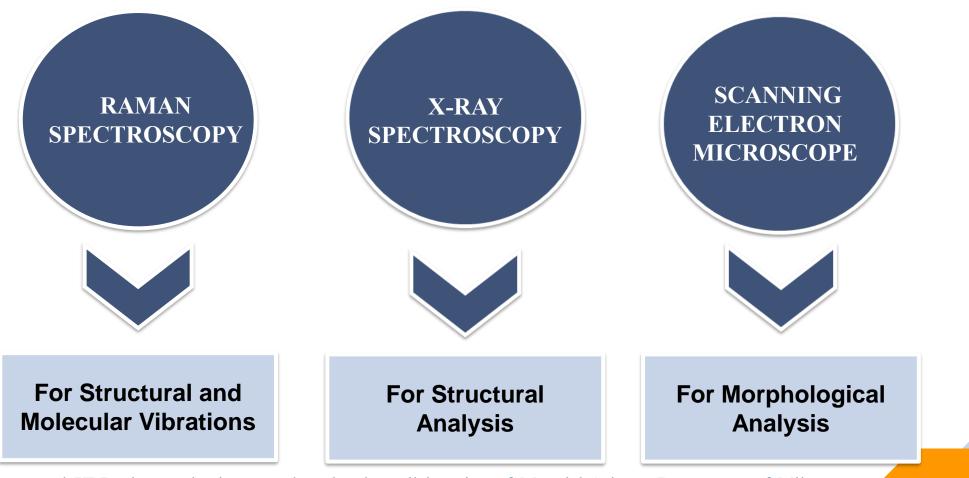
 Table 1: Weight and characterizations done of fabricated graphene oxide

	1	2	3	4
gram	0.290	0.220	0.295	0.246
XRD	$\checkmark$	$\checkmark$		
RAMAN	$\checkmark$	$\checkmark$		
SEM	$\checkmark$	$\checkmark$		





### **Characterization Techniques**



\* Raman and XRD characterization was done by the collaboration of Material Science Department of Milano Bicocca and SEM was done by the collaboration of the Centre of Microscopy.

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#### Results

#### **Raman Spectroscopy of GO**

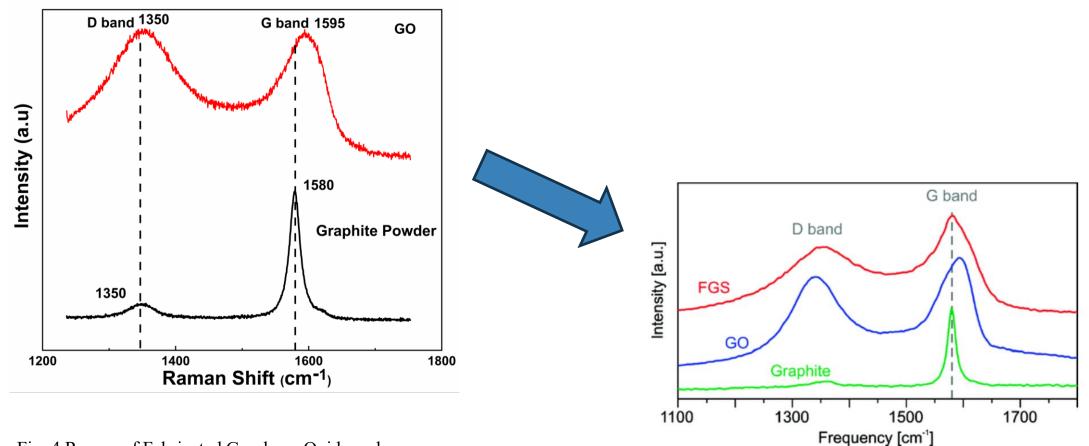


Fig. 4 Raman of Fabricated Graphene Oxide and Graphite Powder

Fig. 5 Raman of Graphite Powder and Graphene Oxide in Literature. *Kudin et al. 2008* [2]



#### **Results**

#### **X-ray Spectroscopy of GO**

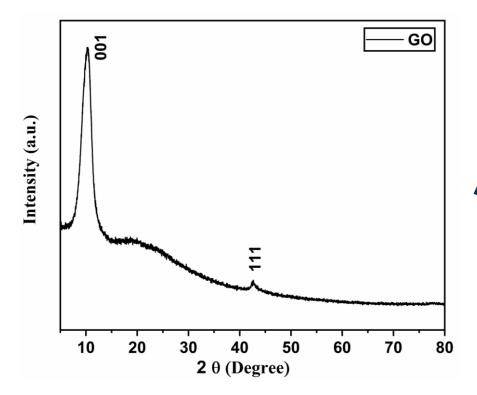


Fig. 6 XRD of Fabricated Graphene Oxide

Table 2: Crystallite size, lattice strains, and dislocation density calculation for GO

S.No	hkl	d- spacing (nm)	2θ(degr ees)	FWHM	Crystall ite size (nm)	Lattice Strain	Dislocat ion density
1	001	0.84	10.3	0.16	50.2	0.808	0.0003
2	111	0.21	42.6	0.1	92.7	0.111	0.0001

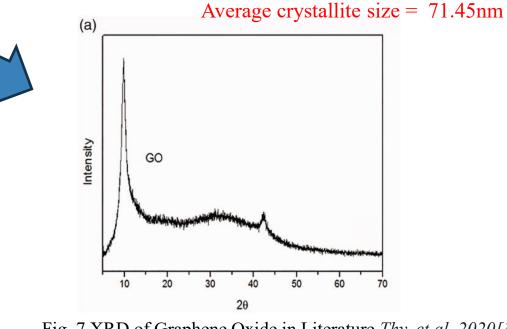


Fig. 7 XRD of Graphene Oxide in Literature Thy, et al. 2020[3]



#### **Results** Scanning electron microscope (SEM) of Graphite powder and GO

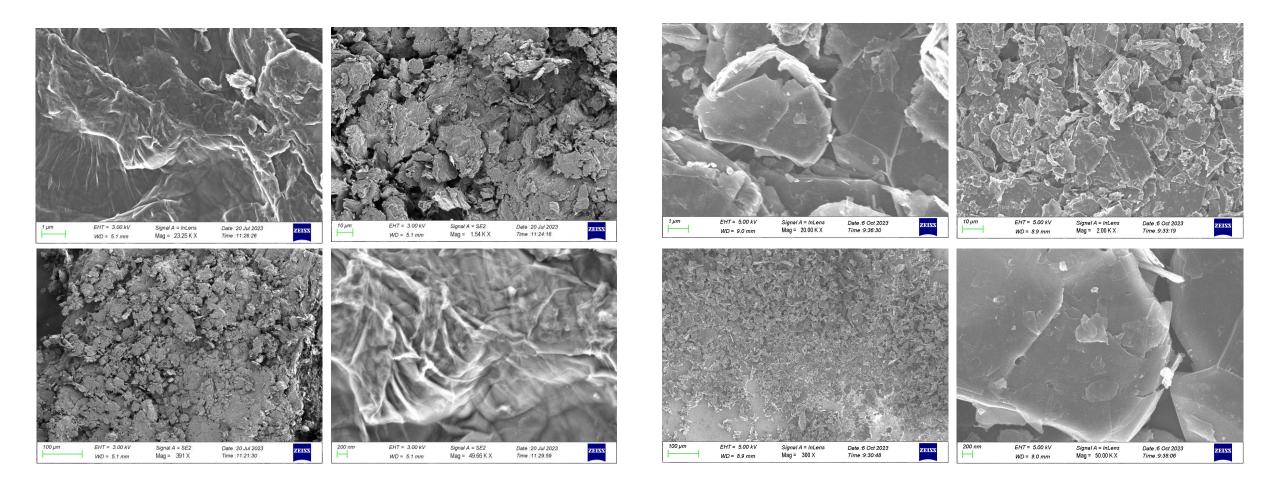


Fig. 8 SEM images of Graphene Oxide at 1  $\mu$ m, 10  $\mu$ m, 100  $\mu$ m, and 200nm

Fig. 9 SEM images of Graphite Powder at 1 μm,10 μm, 100 μm, and 200nm 13



### Plasma Treatment Setup

Plasma treatments were carried out to enhance surface area and change the wettability by chemical etching.

On polymeric (PET, PP, Teflon, Polycaprolactone) fabrics

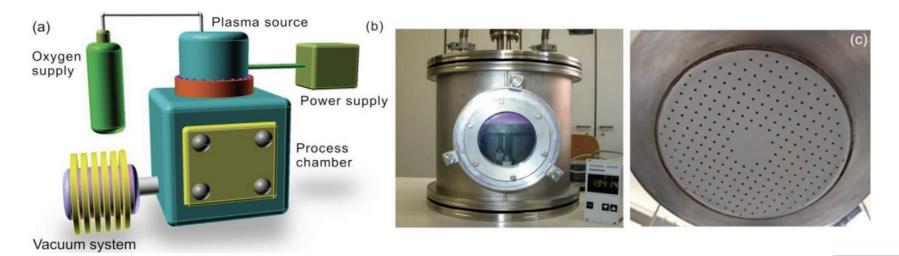


Fig. 8 a) General schematics of the experimental setup, b) photograph of the process chamber with ignited plasma and of the upper aluminum plate (upper electrode) with about c) 250 holes of 2 mm diameter spaced at a distance of 10 mm



## Plasma Treatment on Polyethylene tereftalato (PET)

- The Oxygen-Plasma was performed by an inductively coupled generator with an output power of 100W at 13.56MHz.
- The Pressure was assessed by a vacuum gauge of  $1.5 \times 10^{-1}$  mbar.
- The samples were placed in the discharge chamber, at a distance from the antenna between 2 and 5 cm, and treated for 2 min up to 30 min.



#### **SEM Results of Non-Treated and Plasma-Treated (PET)**

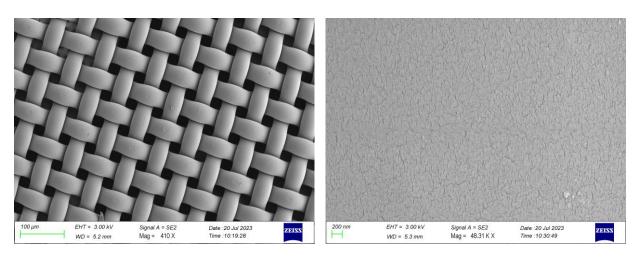


Fig 9. SEM images of non-treated PET Fabric at a) 100  $\mu m$  b) 200 nm

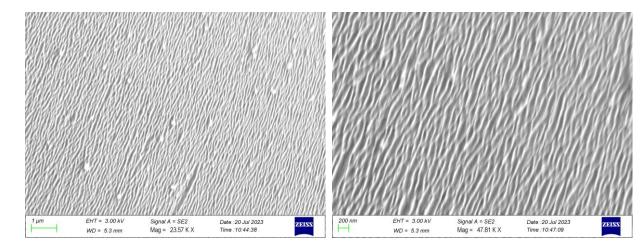


Fig 10. SEM images of 2mint Plasma-treated PET Fabric at a)  $1\mu m$  b) 200nm

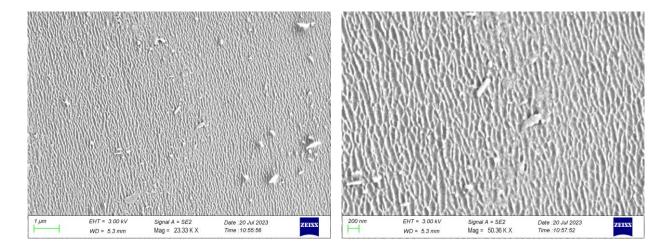


Fig 11. SEM images of 4mint Plasma-treated PET Fabric at a)  $1 \mu m b$ ) 200nm



#### Deposition of Graphite and GO on PET

- 0.5% of GO and Graphite Powder is dispersed in the DI water and it is sonicated for 60 min.
- The PET fabrics treated with plasma and non-treated are soaked in the solution of
  - Graphite Powder and GO for 30 min
- Fabrics are dried in a hot air oven at 80 °C for 30 min.
- This process is repeated for several times to increase the adsorption of Graphite and GO.
- Finally, the fabrics are washed to remove any unattached Graphite Powder and GO.
- Dried again in an oven and kept in the desiccators



Fig. 12 Coated PET



#### Water Contact Measurements

 Table 3: Weight of samples after deposition

 Table 4: Water Contact Angle Measurement of Samples

Samples	Weight deposition	g/m <sup>2</sup>	Samples	<b>Contact Angles</b>	Standard Deviation
	$(W_2 - W_1)$		P (untreated)	113.4°	6.09
			P2 (2 mins oxygen-plasma	75.86°	7.60
			treated),		
P(untreated) with	1.6 mg	4	P4 (4 mins oxygen-plasma	< 5°	-
Graphite Powder			treated),		
1	0.5	1.25	P (untreated) coated with	91.5°	7.04
P4 with Graphite	0.5mg	1.25	Graphite Powder		
Powder			P4 coated with Graphite	66.9°	4.79
P(untreated) with	0.9mg	2.25	Powder		
Graphene Oxide	C C		P (untreated) coated with	26.7°	4.5
1	0.0	2.25	Graphene Oxide		
P4 with Graphene	0.9mg	2.25	P4 coated with Graphene	57.9°	1.97
Oxide			Oxide (GO)		

- In the case of plasma treatment the GO deposition did not change the wettability
- Plasma changes the wettability while graphene will provide antibacterial, comfort, flexible supercapacitors, sensors, etc.
- Next studies on GO release in time will be done.



#### **SEM Results of Coating on PET Fabric**

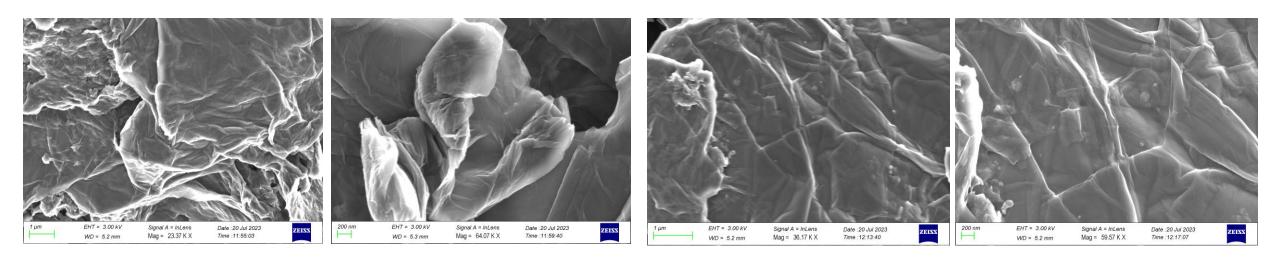


Fig 13. SEM images of non-treated PET Fabric coating with GO at a) 100 µm b) 200nm

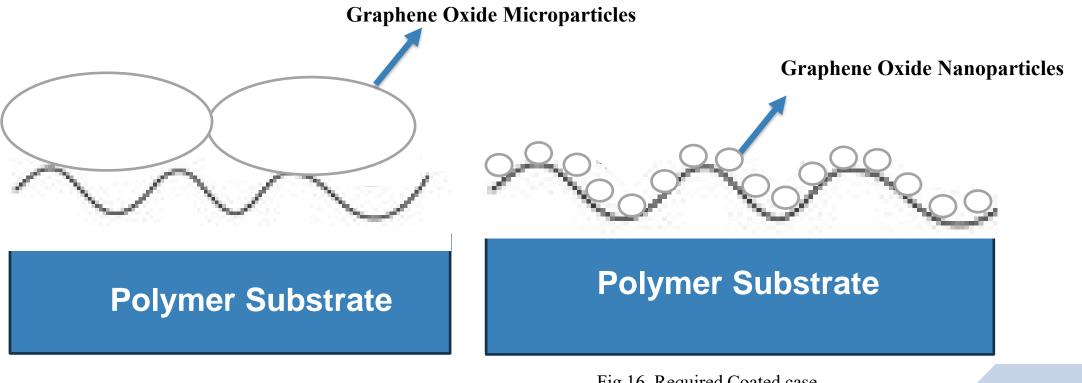
Fig 14. SEM images of 4mint Plasma-treated PET Fabric coating with GO at a)  $1\mu m$  b) 200nm

#### The coating of GO on PET covers almost all the fabric surface due to the particle size of Graphene Oxide. Next studies to reduce the GO size.



## Discussion

#### Sizing of GO





## Method to Reduce Particle Size

#### **Graphene Quantum Dots**

- I will use the hydrothermal method.
- For this I need a few things
  - Teflon-lined Autoclave
  - Dialysis bags
  - Microporus membranes
  - Some chemicals



#### **Future Aspects 1**

- In the Future Quantum dots will be used.
- Deposition of rGO QD's nanoparticles on different textile materials
- GO is an effective antibacterial agent. Antibacterial application will be used on rGO QDGO-coated textile materials



#### Future Aspects 2: plasma surface sizing

Study of Interaction of Plasma-Polymer by investigating the particle sizes in plasma gas and the polymer surface: correlation between surface roughness and the production of polymeric particles in plasma gas



Fig 17. Setup for Particle counter



# Future Aspects 3: Review on graphene applied to textile



Will work on a Review article on graphene-coated fabrics

With the aspect of

- Toxicity of Graphene Oxide
- Coating methods
- Substrate behaviours
- Applications of GO coated fabrics



#### **Conferences, Papers**

EPS 49th Plasma Physics Conference - Poster

**Proceedings**: Tunning the surface wettability of graphene-coated polymeric

substrates by plasma treatment, R.Maryam et al. 2023

Review article on Development of medical masks: performance, properties, and

prospects, Memon et al., 2023

	ility of graphene-coated polymeric sub: <u>R. Marvani</u> , E. Tucci <sup>1</sup> , C. Riccardi <sup>1</sup>	··· 💉	
Depar	tment of Physics University of Milano Bicocca, Milan 2012	i Iealy 🔨	
1. Introduction and Motivation	For deposition, 0.05 g of Graphene Oxide and Graphite powder were dispersed in the detoxized water and scretczied the solution for 30	The SEM was used to invarigate the change in the surface morpholog of automaid, polyayter fabric, and orcours-playing mathed polyayter	
Non thermal plasma technology <sup>2</sup> proposes in day, clean, and safe method for modifying the surface of different materials <sup>2</sup> without character their bulk	minutes, 2 × 2 cm <sup>2</sup> PET (dwice (P and P4) were dirend in the solution of	fabric at 2 mine and 4 mine. It is clearer that the untreated polyoster	
properties". This is particularly advantageous for heat-sensitive polymers	OO and Oraphile powder for 30 mine and then dried in an oven at 40 °C	surface in Figure 3 (a-c) is smooth. However, the 2 min orygen-	
commonly used in textiles, as non-thermal charman can be arehied without to	for 30 minutes. This presses is repeated three times to increase the	plasma meated polycoter Figure 3 (d) shows a doperate change in th	
thermal damaging materials?. Plasma processing inclusion grafting? of reactive	deparktion rate of GO and Graphite provder. After deparktion, the fabrics	polyestar surface. The small power and voids can be seen on the surface	
functional species, deposition of inequasic or organic <sup>4</sup> thin films and cleaning	were washed to remove the excess OO	of the polyester surface, these way he due to the eiching effect of th	
and exching. The different plasma processing can be tailored in order to	Table 1: Weight of samples after deposition	ygen plasma on the surface of the polyester. With the increase of	
engineering the polymeric metacos. The adhosion and efficiency of a coaring	Jumpin. Wight departion give <sup>1</sup>	plasma treatment on the surface, the structure can be changed more	
can be influenced by the earliest's level of its wetability?. By the treatment	Tarinard while the second seco	prominently, Figure 3 (c). Thus, this roughness is caused by the plasm	
of plasma, the chemical composition <sup>14</sup> , and physical structure <sup>34</sup> of a	Node 10	treatment and it is directed to the hydrophilic name of the polyost fabric. Undertaunidy, the fabric is not washed before the plasm	
material's surface will change, which in term can affect its ability to facilitate	Tjaninal/wikiloplase Ulag 231		
the adhesion of noise coarings as well as samoparticle inclusion.	Noiklaghachile Dag 231	trainent to in SIM images dust particles can be seen clearly. The route will be improved by washing the fabric with isopropared in	
In this work polymers are plasma treated in order to facilitate graphene	3. Results	spicate.	
coatings on their surfaces with the aim to control its thermal properties such	Raman spectroscopy was also performed on the Graphite powder and		
as thermal conductivity and heat transfer, is view of applications in the textile	OO to analyze the vibrational hands. The Raman spectrum of Graphite		
sector. In details the experiments concern the plasma treatment of polymens,	pender and GO is shown in Fig.3. The D and G hand is observed in Fig.	99999999999	
in a reactive oxygen gas, to enhance the surface wetability and the deposition	3 a) at 1330 cm <sup>-1</sup> and 1580 cm <sup>2</sup> respectively. While the D and G bands		
of graphene on the polymeric surfaces. Scanning electron microscope (SEM)	fig 3 b) showed at 1350 ${\rm cm^3}$ and 1598 ${\rm cm^3}$ respectively. The intensity		
on the polymeric surfaces for structural information, Raman spectroscopy for	of 10 band of both spectrums is different. The InTernato of graphite		
the control of graphene and substrate wetability analyses prior and after the	pender is 0.29 and for GO is 0.9.	10-1 2.12 2.12 2.12 2.12 2.12 2.12 2.12 (c) (c) (c) (c) (c) (c) (c) (c) (c) (c)	
graphene deposition are performed.	(2) = [100		
2. Equipment set-up	-		
Plasma matmate were carried out to hydrophilize the fabric. The	-	1. A.	
experiment was performed on polyosier (PET) libric material. The sample	- III		
vas cat into snall riscos of 5 > 6 cm <sup>2</sup> . The Owner-Plasma was built with			
an inductively coupled generator with an output power of 10070. The			
resource was assessed by a vacuum same of 1.5 > 10 <sup>4</sup> bar, and the power	Renar End per (	17" 11.12" AF145. 11.12"	
is supplied by a 13.56 MHz power generator. The surplies were placed in	(b) 00 00 00	Po.4 . HIM for an Treated samples at al (12 per b) Hyper of 200mm	
the discharge tabe and treated for 2 min and 4 min. SIM has been			
performed for samples to investigate the structure of the polynamic			
relatings. We used Zoiss 500 instrument for SEM androis. SEM androis.		Contraction of the Contraction of the	
which allows sample observations at different magnitudes.	·=/ \		
The hydroph licity was measured after plasma instruction by determining the	- ~		
water contact angle by using a demineralized water droplet of 344 volume.	Remark State and State		
An appentate conjugad with PC software SG420 was used for taking	Phys. 2 – a) Xannan, gyndrawr o f al Grophite Picarder (c) 200	[2. IN BU BUP ■][7 IN BU BUP ]	
measurements. For each sample, 5 measurements were taken in order to	Contact angle measurements show a decrease in angles after the plasma		
lower the statistical error. The droplet was dispensed on the surface of the	treatment with oxygen. The contact angle of P was 113.38". This is the	Po. 4 - UM for Pinana Tended 2 evin samples at a) (gas in) 200ers	
sample. Seven samples were measured P (universal), P2 (2 mins coxygen-	urituated sample, and it was clearly Hydrophobic. The value decreased vary	and the second	
plasma treated), and P4 (4 mine oxygen-plasma treated), P (unincated)	strapty with oxygen plasma instruent. The sample 72 was exposed to		
control with Graphite pender, P4 control with graphite pender, P	plasma for 2 mins and the value goes to 75.06". For the last sample, which is		
(unitrated) with GO, P4 coated with GO.	treated for 4 min with oxygen plasma, the droplet was dispensed and when	and the second se	
	it touched the surface it abruptly absorbed into the surface which is showing		
	reper <u>hydrophilicity</u> and a water contact angle is few than 57. Water contact angles were also performed on the costed samples with argefuls powder and	10- 111 FT 111 1117 1 17 111 FT 111	
	angles were also performed on the costed samples with graphite powder and GO3.	60 (51	
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The Darker with furnities the southful because of the state	Punround 91.5 7.94	graphite provider. Water contact angles also showed decreased ang	
For Orghene oxide formation, the modified humaness method was used. In this method, sufficie acid (27ml) and phosphoric acid (2ml). The sufficie	control with	without coated surface but the coating of graphite pewder and GO very effective. GO has hydrophilic names when it deposits to t	
and phorehoric acide were mixed in a %1 volume ratio and stimul for a	Draphic Powder 74 coated with 65.9" 4.73	very enceive. Go has systephric tante onto it appoint to relating surface k can increase the hydrophilic nature of the them	
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dorreise and stirred for a few minutes. At this state, the exchemnic	Sample P coated with graphic pewder shows 91.5'. Sample P4 with	Bandin, K. Lovelenin, T., Baronit, C. (2022) <b>J II applied Verse Memories</b> , 2 (4), pp. 4787- 4805.	
reaction occurred and the took for a few hours to cool down. Hultochloric	graphic coasing shows a 65.9° water contact angle due to the 4 min	<ol> <li>Zanini X.; Zana, Lawa; Della Propole R.; Nissarili, C.; Deploy and Gauriege Zation Age, 5 on 1711 (10) (2010).</li> </ol>	
Acid (10rd) and Delewined water (20rd) were added to the solution and	plasma treatment on this sample. Sampler P and P4 coated with GD	5. Zarini, E. Zuis, L., Dell'Iris, E. C., Nadollo, A., Vila, A. M., Panola B. Della Baccark	
washed raises a constituee of \$200 rms for 10 minutes. The immediate some	shows 26.7' and 57.9' angles. GO-coated sample on the universal	(2114) Monetak and Dargo, 103, pp. 201.001 d Daren B, Maran D, Nieta M, Doneta K (Donetak C (2018) Journal of Zalla V and Ameri Release 101.01	
washed using a commige a 5000 ppr for 10 minutes. The impartial write washed away and repeat and Graphite provder and then dried again in the	surface, the water droplet was absorbed alrophy on the surface, so it was	Drawn, 107171 T. Zanini, K., Golandi, M., Calonsin, C., Grinnald, K., Biransh, C. (2009). Zeragana Zigrind. Jz Z., 10171, pp. 110–101. R. Zanini, X.; Grinnaldi, K.; Calorsi, A.; Biransell, C., Agellad Japhan Datasar 1019, 201 – 202.	
even, this for 3 times. The washed solution was diad by using an own for	hydrophilic. And for the P4 sumple, the plasma treatment induced a		
24 hours at 90 °C to attain the proder of 00°.	negative charge on the surface and GO has a negative charge so GO is	(2019) A.H. Wildfilds C.L., Vanaro A., Zanini K., Janual and Zipsin- Cophenese Desit, 195(3), (21):03334 (2040). 11 June K., Zanin, J., Normi, C., Atlansar in Signal Classics, 2017, 2011.	
	not completely deposited on the surface, so it does not show hydrophilic		
	behaviour.	[11] Zanin, N. J., Foro, E. L., Hanimo, G., Tan, S. J., Lu, W. W., & Yoon, C. H. (2017) Apula of graphene scale undergrandified lasersers moduli aslowed influence. <i>Details's</i> argination, 245, 485-477.	
		anglowering 324, 100-217.	
- European Phy	sical Society • 49th Conference on Plasma Physics	3-7 July 2023	





Course: "New lignin-based sustainable materials science and technological aspects" Luca Zoia (DISAT), Ruggero Barni (DFO) and Carmen Canevali (SdM), 1CFU

- Course: **"Masterclass in Big Data within Science and Industry"** Dr. Elena Cuoco, Dr. Matteo Bregonzio, 1 CFU
  - Course: "Deep Learning for Physicists" Professor Stefano Giagu. 2 CFU





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