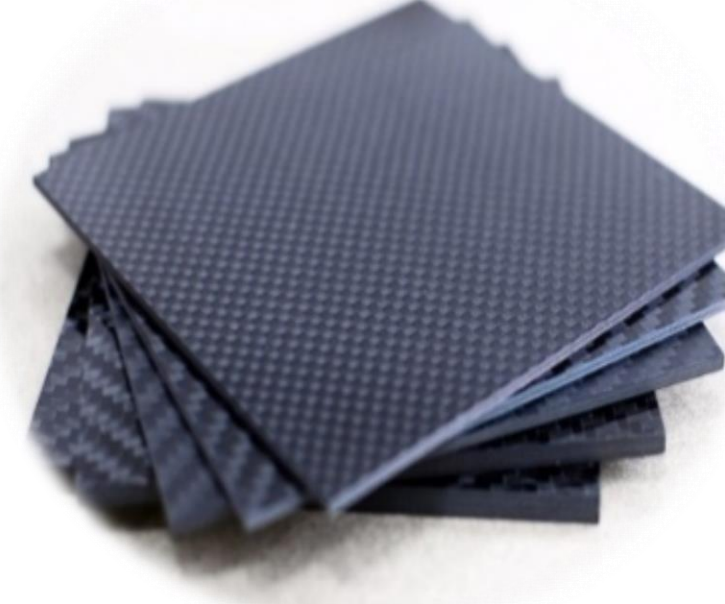


N. Ranger<sup>1-2</sup>, C. Jaoul<sup>2</sup>, P. Tristant<sup>2</sup>, T. Maerten<sup>1</sup>, S. Belveze<sup>1</sup>, S. Guimond<sup>3</sup>, M. Cavarroc<sup>4</sup>

<sup>1</sup>OERLIKON Balzers France, Limoges (FR) ; <sup>2</sup>IRCER, UMR CNRS 7315, Univ. Limoges (FR) ; <sup>3</sup>OERLIKON Balzers Liechtenstein, Balzers (LI) ; <sup>4</sup>SAFRAN TECH, Châteaufort (FR)

## Introduction

- Polymer based composites such as Carbon Fibres Reinforced Polymer (CFRP) are increasingly employed in aircraft industry because of their high specific resistance compare to metallic materials
- These materials are very sensitive to tribological wear (e.g. erosion) and the deposition of metallic or ceramic thin films on their surface can be a solution to increase their durability
- But adhesion of such films is low on polymer substrates [1]



## Objectives

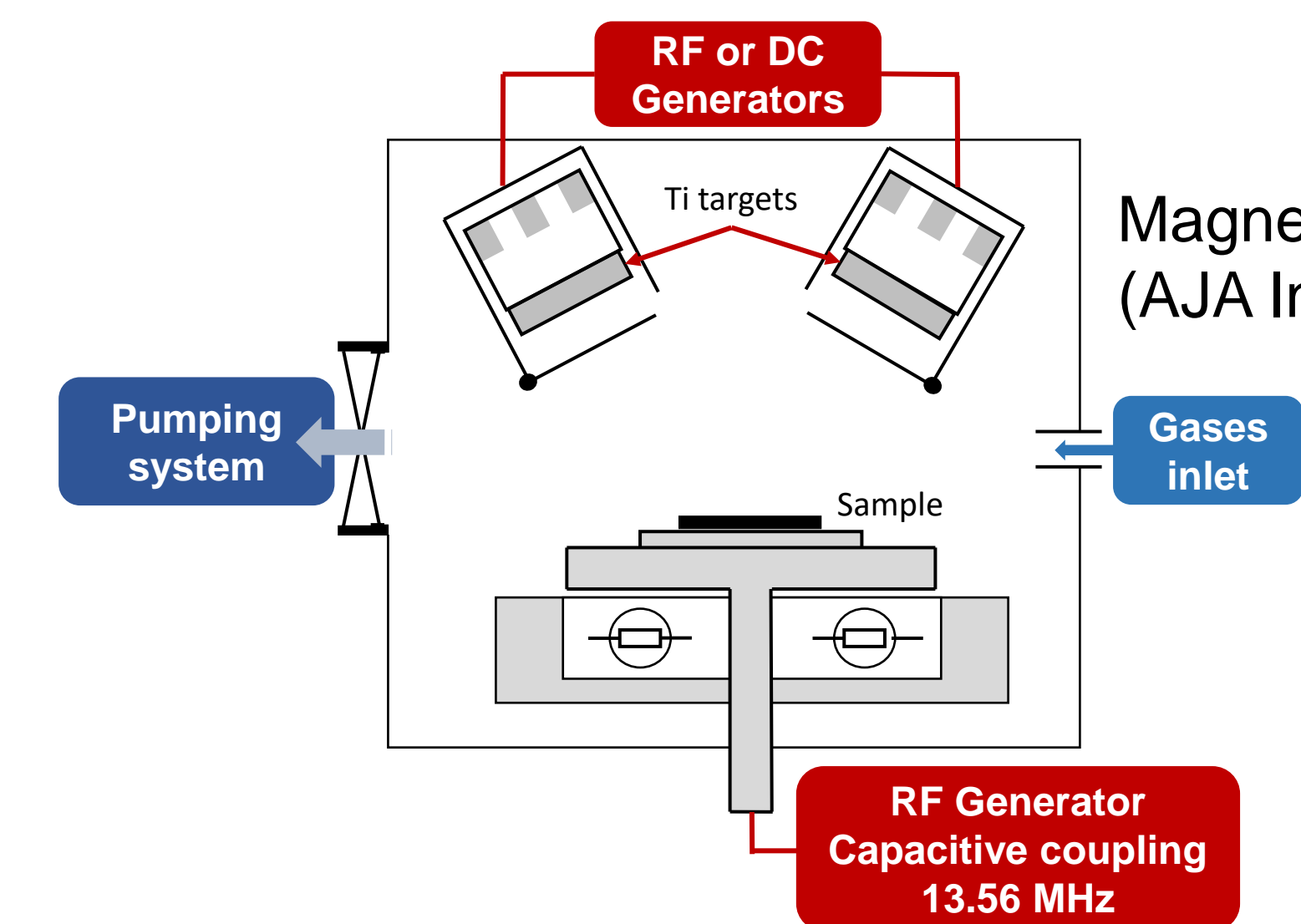
- Use plasma activation to increase adhesion of titanium thin films
- Understand the mechanisms associated for painted CFRP

## 1. Plasma activation of CFRP

### Samples

100 μm Polyamide epoxy based paint (spray painting + 1h curing at 80 °C)  
2D CFRP (amine epoxy matrix)

| Composition                 | Concentration (% w/w) |
|-----------------------------|-----------------------|
| Bisphenol A & F epoxy resin | 10                    |
| Polyamide amine             | 10                    |
| Trizinc bis(orthophosphate) | 10                    |
| Titanium dioxide            | 20                    |
| Others                      | 50                    |



Magnetron sputtering deposition chamber (AJA International)

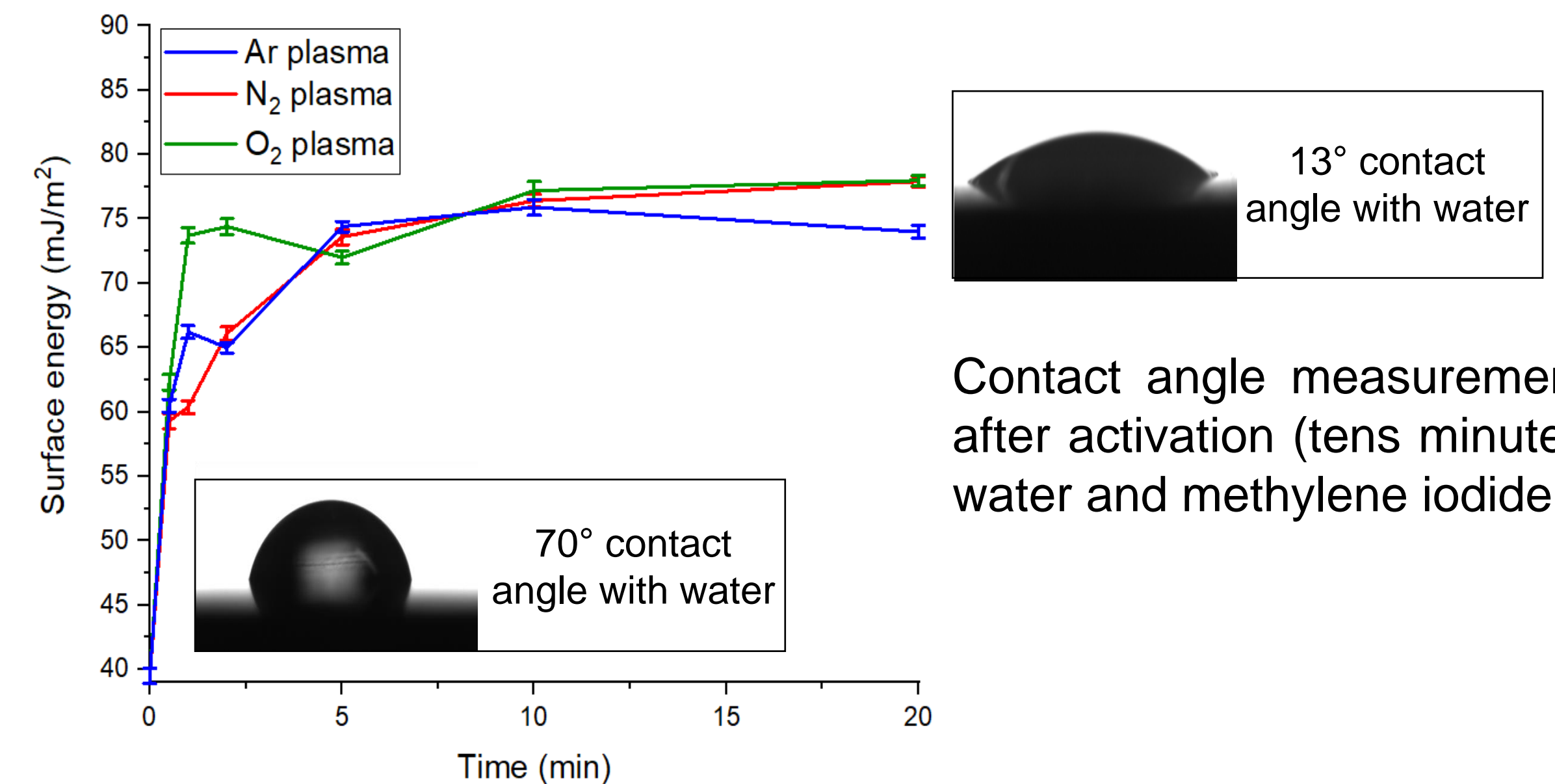
### Plasma treatment parameters:

- Chamber pressure set at  $9 \times 10^{-3}$  mbar
- Different gases: Ar, N<sub>2</sub>, O<sub>2</sub>
- Exposure times: 30 s to 20 min
- RF substrates biasing: -300 V
- Temperature < 77 °C

### Surface energy

Surface energy of epoxy based paint increases strongly with RF plasma treatment after 30 seconds and reaches a maximum value, about 76 mJ/m<sup>2</sup> after 5 minutes

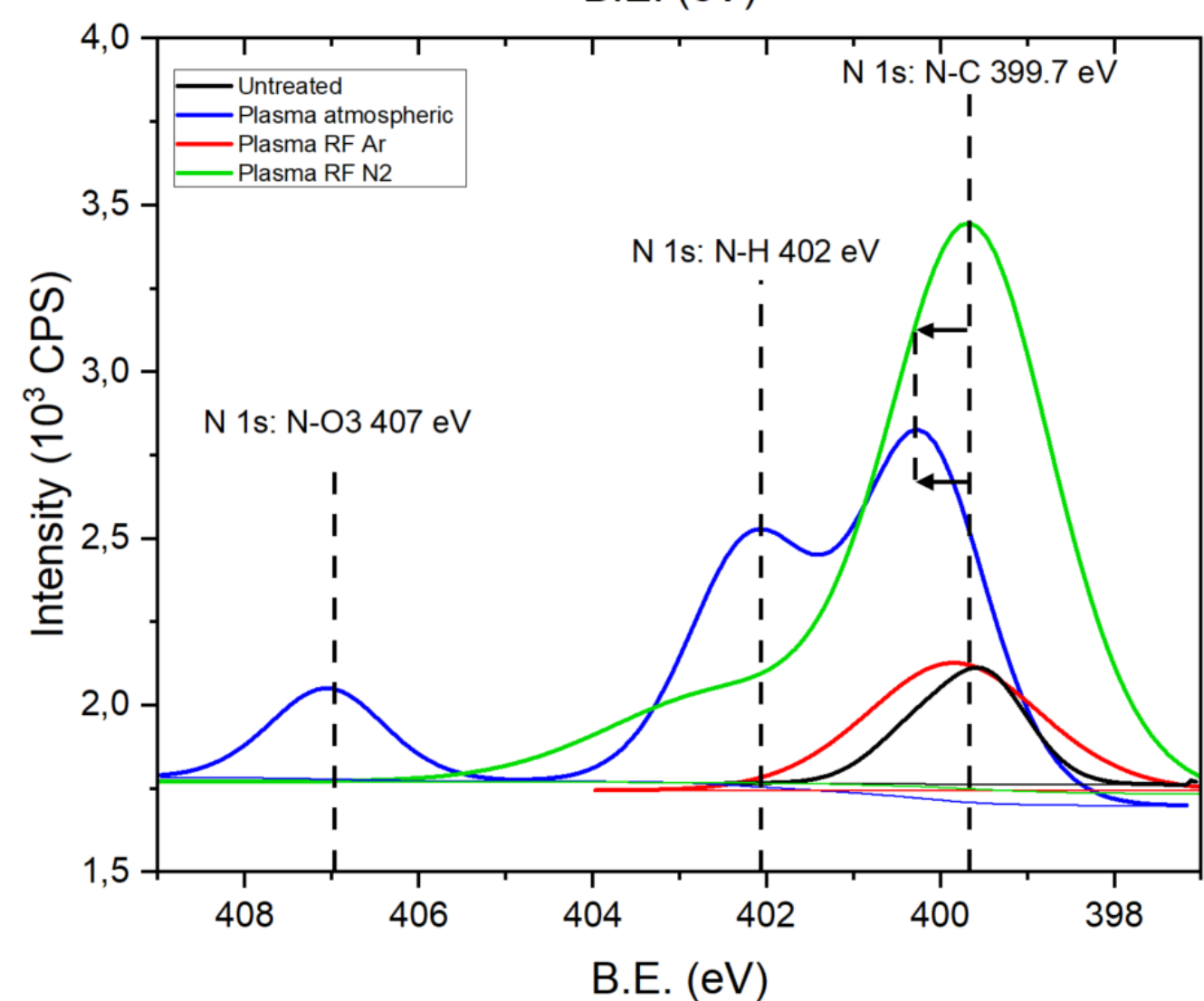
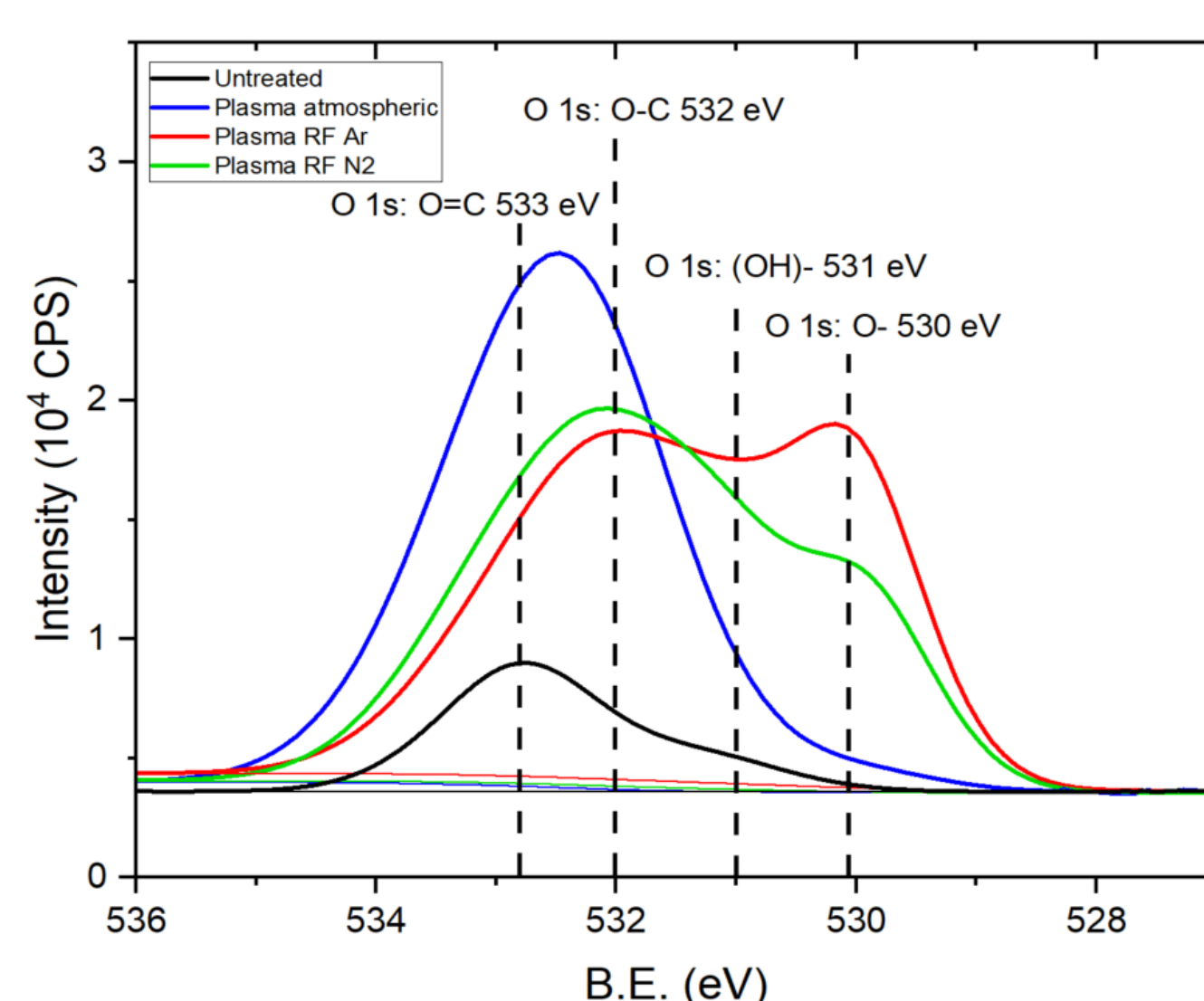
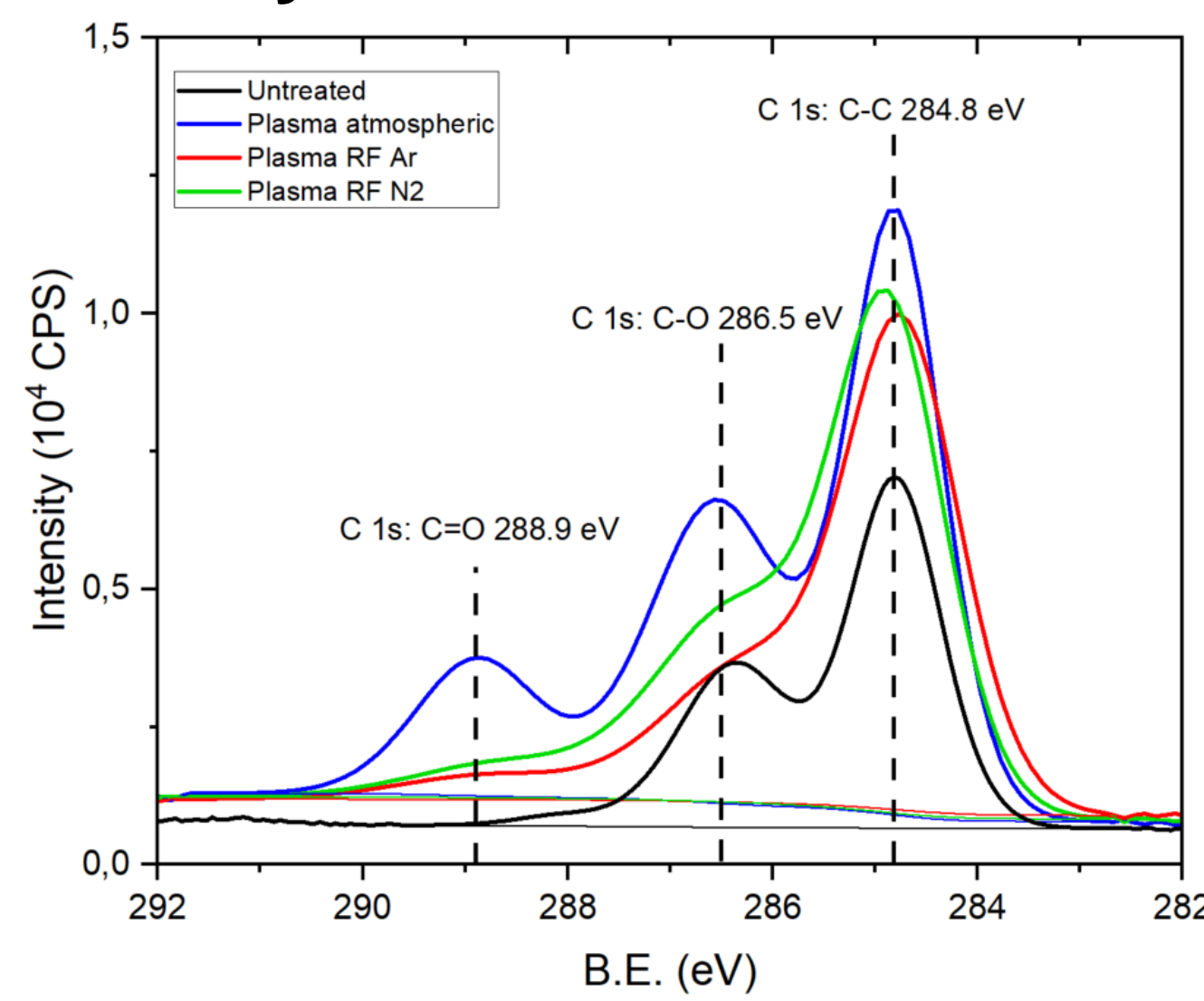
Values obtained are consistent with literature results on CFRP based epoxy matrix [2]



- ➔ Surface energy of epoxy based paint is increased by plasma treatment
- ➔ Maximum value is reached faster with oxygen plasma: after one minute

## 2. Mechanisms

### XPS analysis after 10 minutes treatment

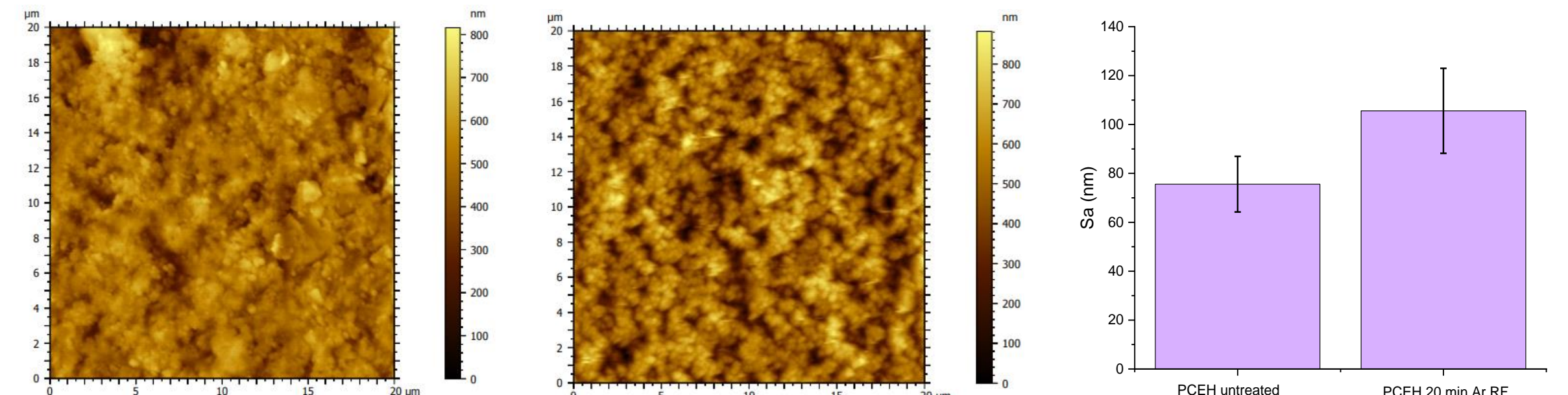


XPS analysis help to understand the improvement of surface energy by the creation or increase of polar chemical bonds at the surface of epoxy

These new chemical functions are created directly during the interaction with the plasma and/or after reaction with air after return to atmospheric pressure

### AFM scanning

AFM scans done after treatment (Ar plasma during 20 min), show a slight increase of the roughness from 76 nm to 106 nm



### Discussion

Plasma treatments are known to modify surface properties of polymer through energetic transfer between plasma-phase species and molecules at the surface

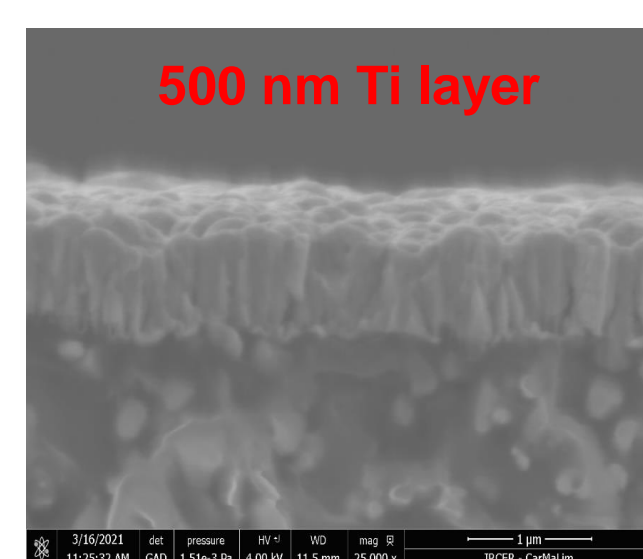
Four main effects are involved [3] :

- Etching
- Surface cleaning
- Crosslinking or branching of surface molecules
- Chemical modifications with formation of new functional groups

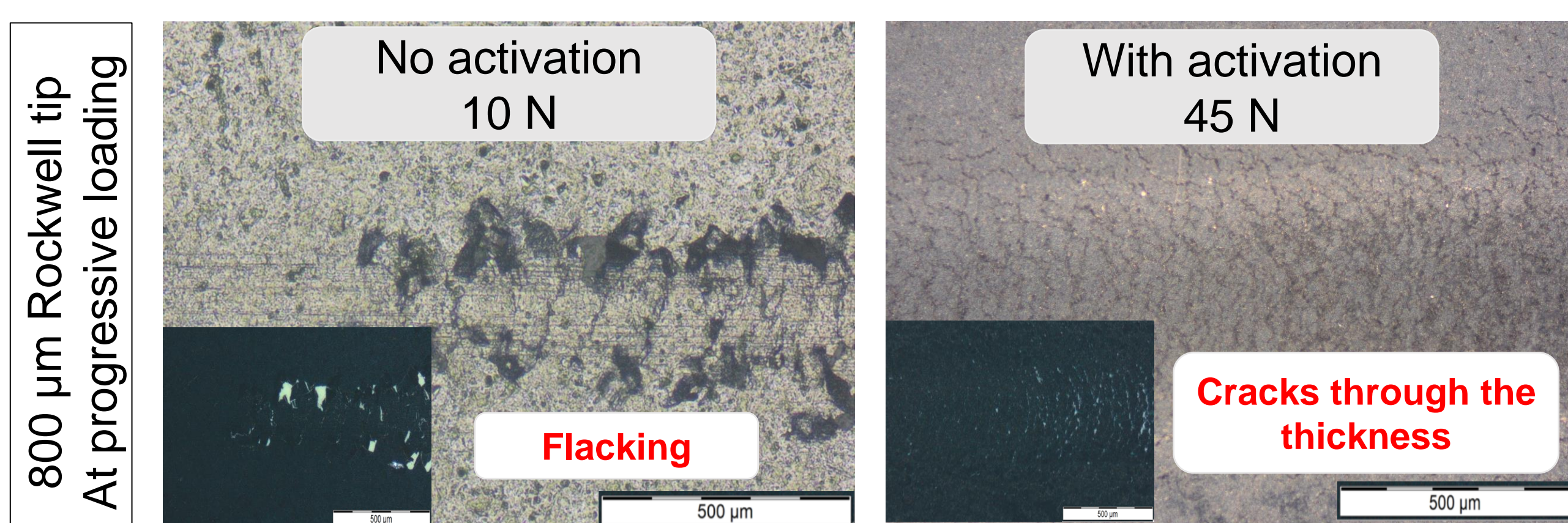
- ➔ Plasma treatment leads to surface chemical composition modification with formation and increase of polar groups (C=O, OH-)
- ➔ Roughness is slightly altered
- ➔ These modification explain the increase of the surface energy and thus, the higher reactivity of epoxy based paint after treatment

## 3. Titanium coating and adhesion

Results are given for 500 nm Ti layer deposited right after a 10 minutes plasma treatment with Argon (no return to atmosphere)  
Temperature < 132 °C



### Scratch test for adhesion measurement



- ➔ Higher reactivity of the surface means more chemical interfacial bonds with titanium atoms and thus, a better adhesion of the thin films

## Conclusion

- Epoxy based paint has been plasma activated under low pressure with a Ar, N<sub>2</sub> and O<sub>2</sub> gas discharge
- Main effect is chemical modifications with the increase and the formation of polar groups (C=O, OH-, N-H)
- These modifications increase the reactivity of the surface that enhances adhesion of Ti thin films

## Perspectives

- More investigations on effect of plasma treatment on surface roughness with SEM observation
- Comparison of Ti thin films adhesion with other gas discharge (O<sub>2</sub> and N<sub>2</sub>) and at intermediary treatment duration (30 seconds)
- Understand the evolution of adhesion of such thin films with plasma activation

### Acknowledgments

E.Laborde and V.Coudert (IRCER engineers) for XPS and AFM analysis  
Safran Composites  
ANRT (Association Nationale de Recherche et Technologie) for the financial support

### Reference

- [1] F. Awaja, M. Gilbert, G. Kelly, B. Fox and P. Pigram, "Adhesion of polymers," Progress in Polymer Science, vol. 34, no. 9, pp. 948-968, 2009
- [2] M. Pizzorni, E. Lertora, C. Gambaro, C. Mandolino, M. Salerno, M. Prato; Low-pressure plasma treatment of CFRP substrates for epoxy-adhesive bonding: an investigation of the effect of various process gases; The international journal of advanced manufacturing technology; vol. 102, pp. 3021-3035, 2019
- [3] E. M. Liston, L. Martinu and M. R. Wertheimer, "Plasma surface modification of polymers for improved adhesion: A critical review", Journal of Adhesion Science and Technology, vol. 7, pp. 1091-1127, 1993