

Context

Metal coatings on polymers are widely used in industries such as electronics, automotive, and packaging for their conductivity, barrier properties, and aesthetics. While strong adhesion between metal and polymer is typically beneficial, it poses a significant challenge for recycling. The separation of these layers is highly challenging (e.g., mechanical cleaning, burning, dissolving) and costly, often resulting in the disposal of such waste causing considerable environmental impact.

In this context, this study explores the use of plasma polymer films (PPF) as intermediate layers between metals and polymers to improve the recyclability. The PPF would ensure a strong adhesion with the metallic layer (i.e., Al) while weakening the interface with the polymer when exposed to a stimulus (e.g., heating). The PPFs are synthesized from a gas mixture of C₂H₄ and CO₂, known to generate PPF with a high content of carboxylic acid and alcohol functional groups¹ ensuring a strong interaction with aluminum coatings².

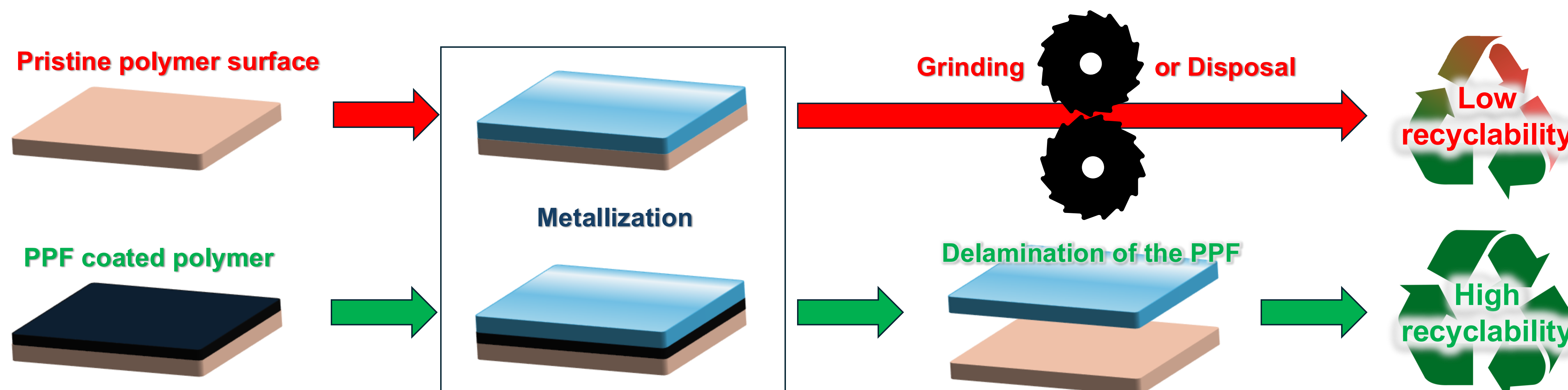


Figure 1 : Research strategy

Packaging



Automotive



Functionalization of the PPF

- Adding CO₂ in the precursor gas mix generates oxygen containing functional groups
- COOH and OH groups ensure a high adhesion of Al coatings² on the PPF

[CO₂] ↑ Oxygen content ↑

Power ↑ Oxygen content ↑

- Decrease of oxygen content at 150 W 80% CO₂
→ Etching of oxygen containing species takes over the deposition

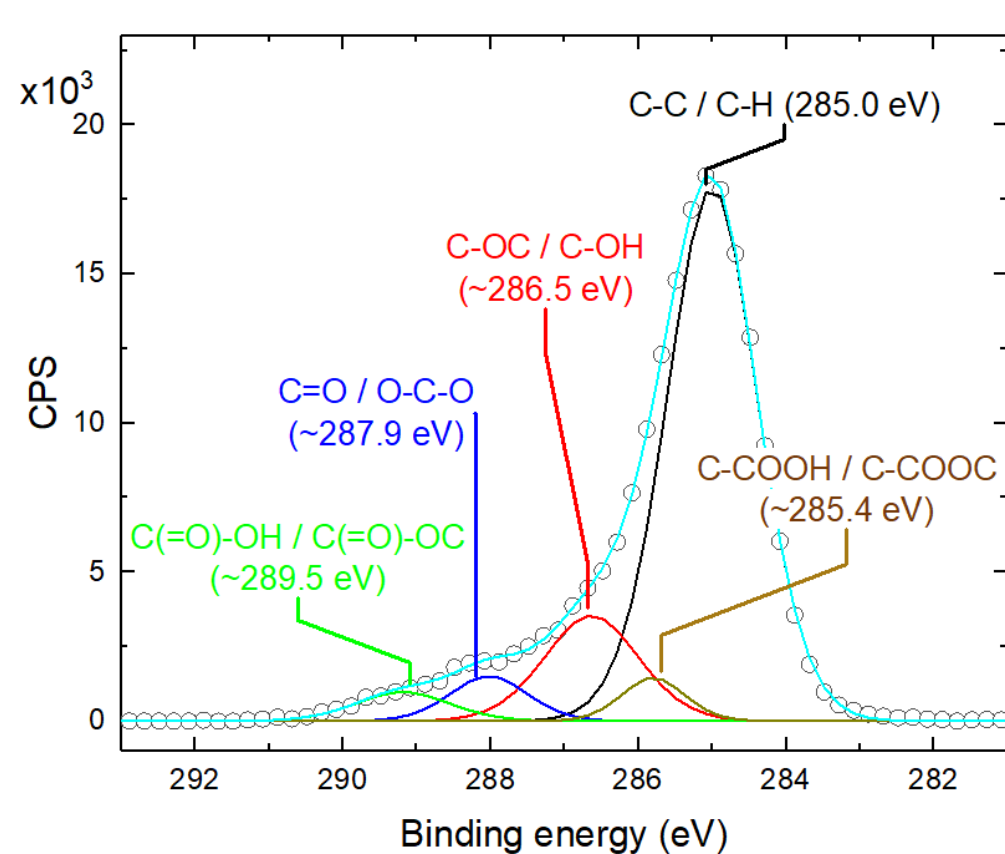


Figure 3 : Fitting of the C1s peak in XPS spectra

[CO₂] ↑ [-OR] ↑
[-COOR]

- Best production of -COOR at P_{RF} = 100 W [CO₂] = 80%

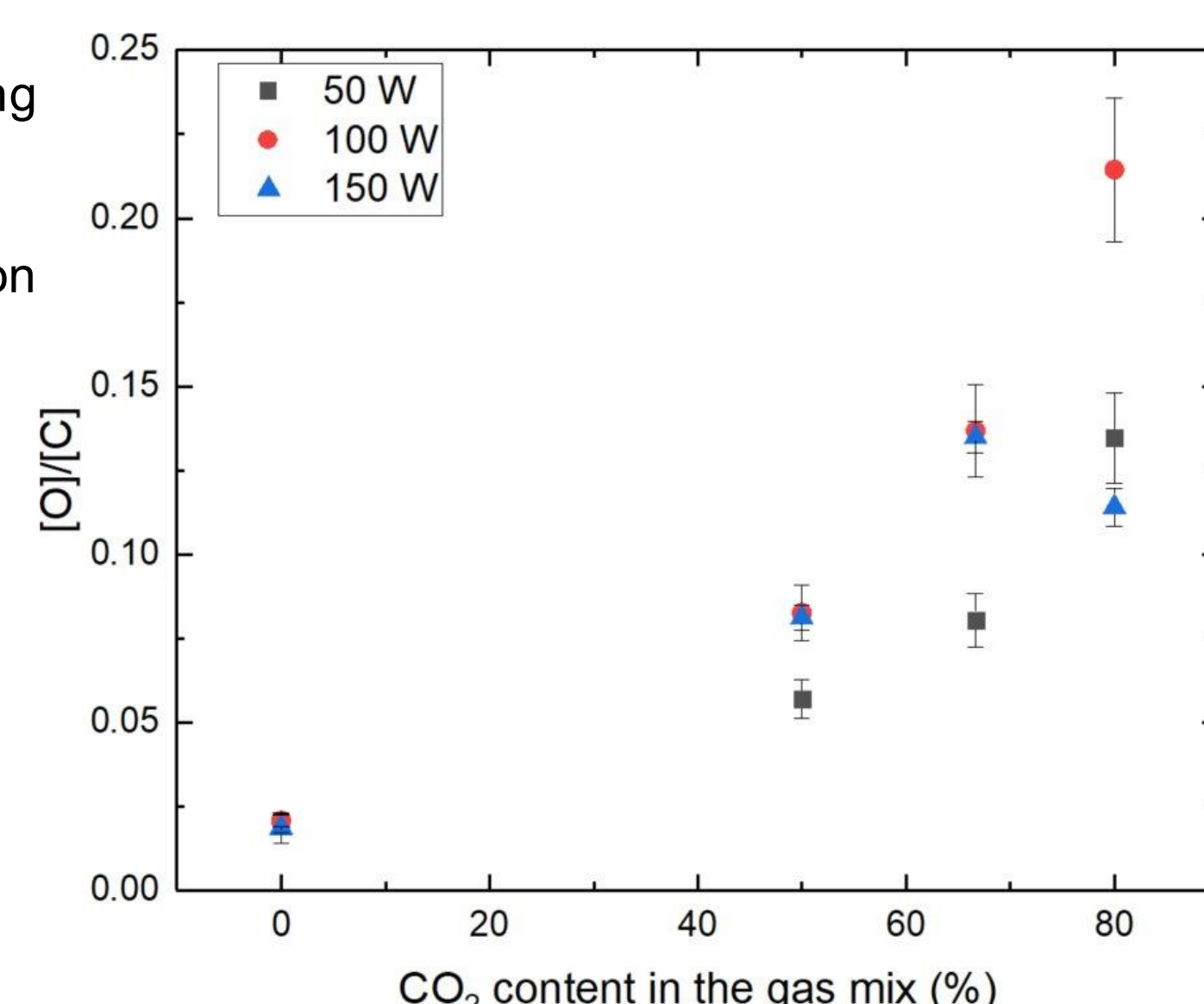


Figure 2 : Chemical content of PPF in function of [CO₂] and P_{RF} obtained by XPS

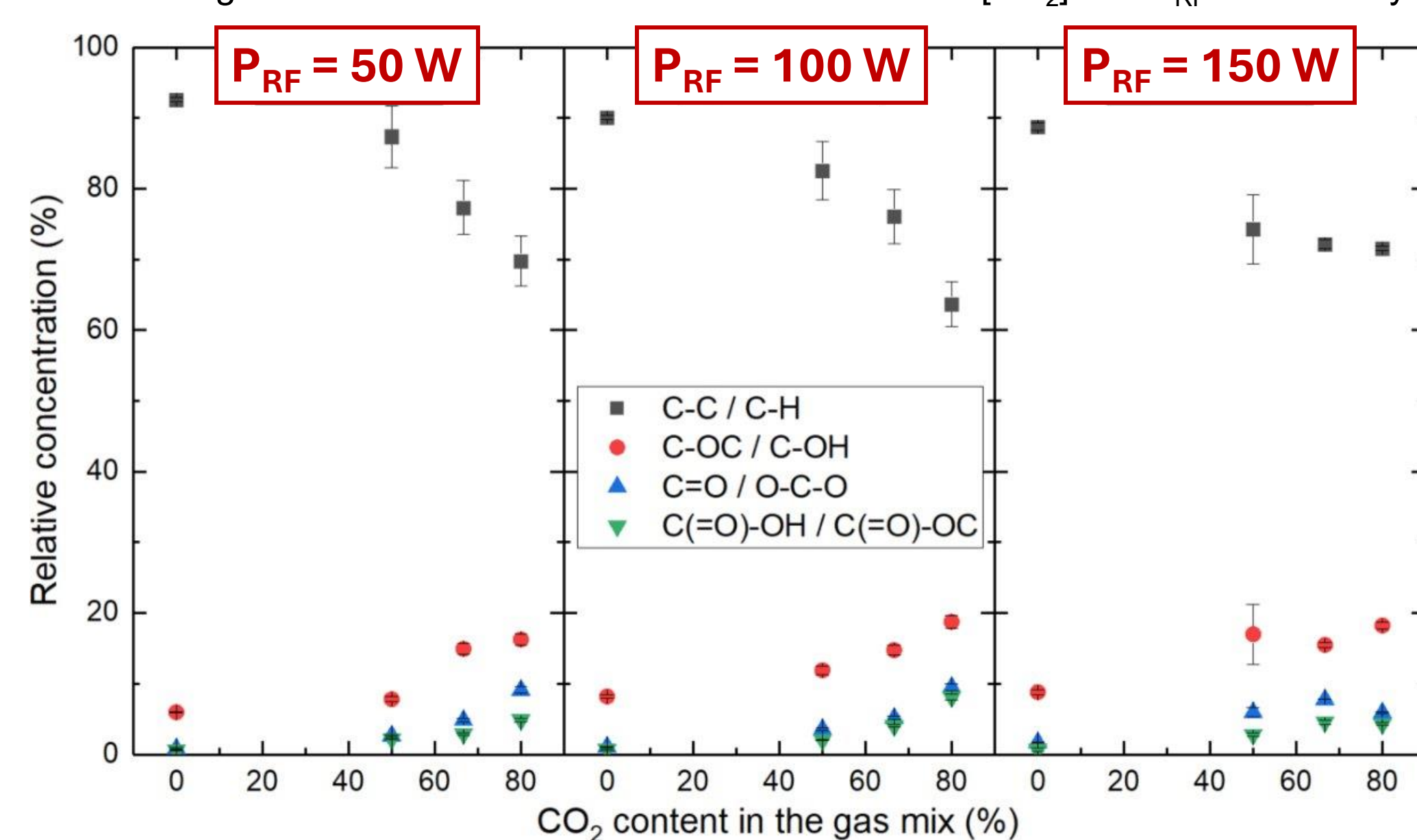


Figure 4 : Relative concentration of functions present in PPF in function of [CO₂] and P_{RF}

Delamination using water

The delamination process which was assessed for the PPF is the immersion of the material in water. The thickness of the PPF is compared before and after immersion to analyze the resistance of the films to the stimulus. The objective is to obtain the highest loss of thickness after the immersion in water.

[CO₂] ↑ Thickness loss ↑

Power ↑ Thickness loss ↑

→ Follows the same trend as oxygen content

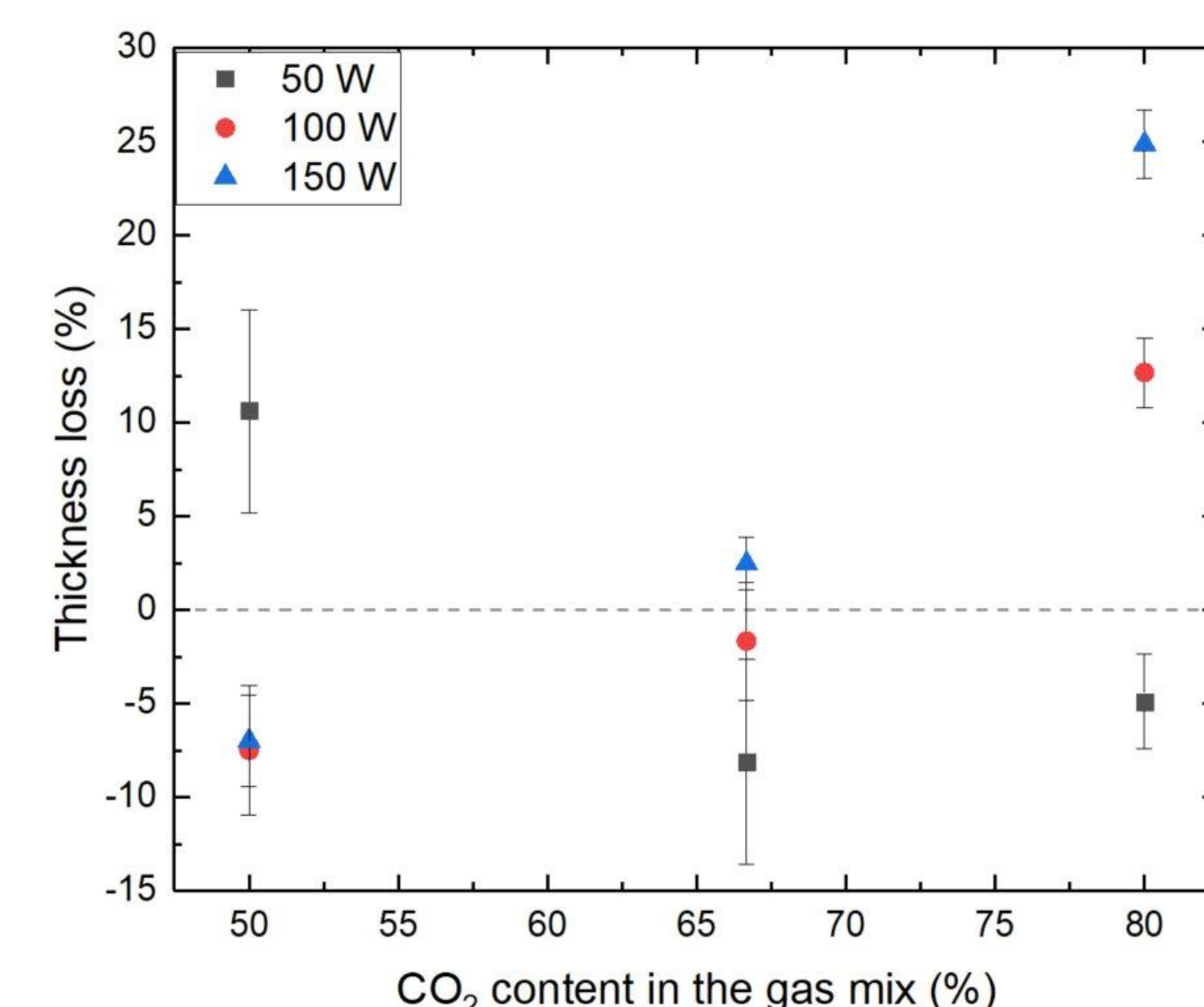


Figure 5 : Thickness loss of PPF after 24h of immersion in function of [CO₂] and P_{RF}

One of the critical parameters for the water resistance of PPF is the cross-linking density³, which could be assessed by ToF-SIMS analysis⁴.

- The total intensity of the secondary ions is inversely proportional to the **cross-linking density**⁴.

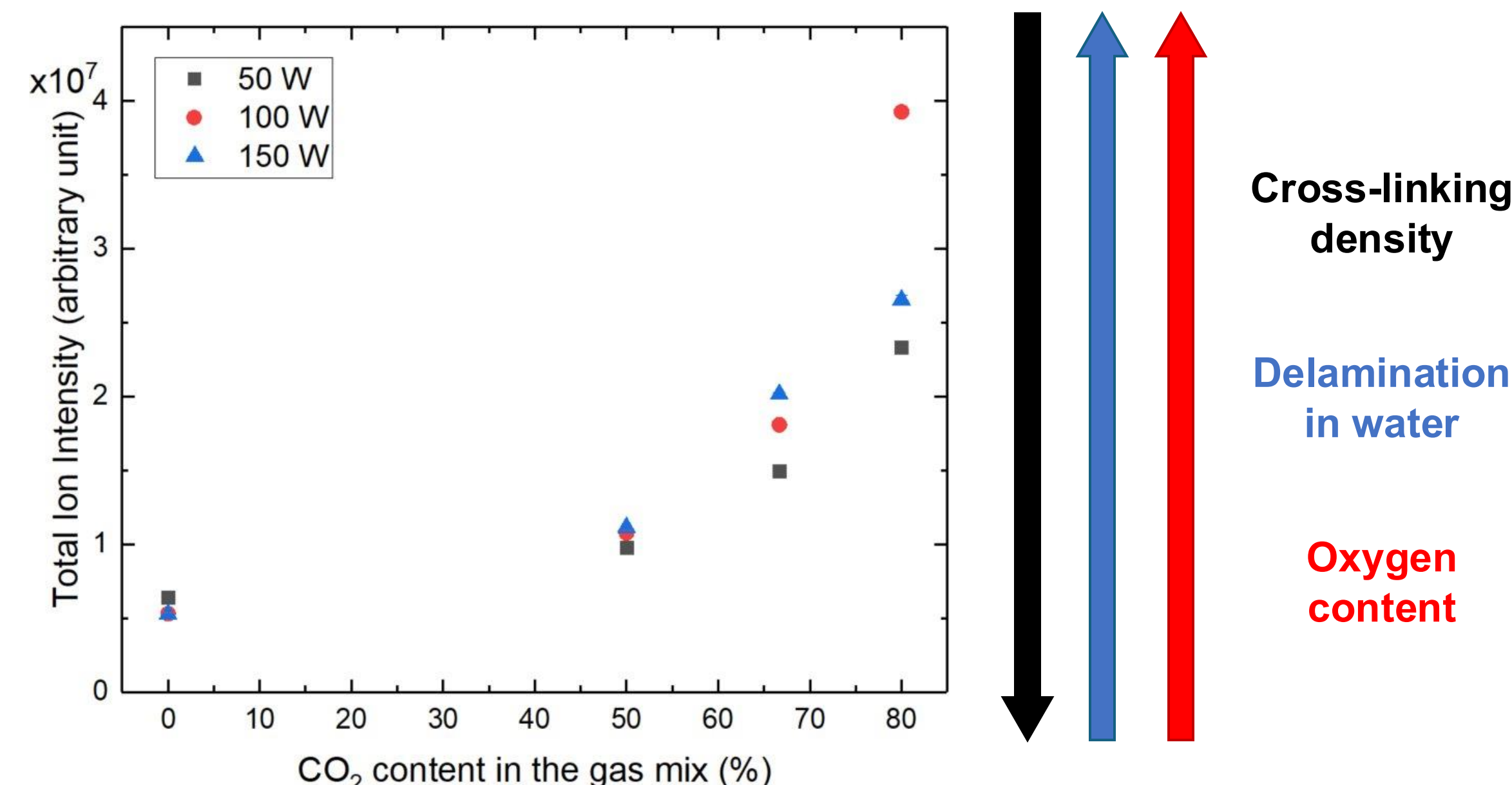


Figure 6 : Total ion intensity in the ToF-SIMS spectra of the PPF in function of [CO₂] and P_{RF}

- Oxygen reduces the cross-linking density** due to its low valence
→ The functionalization and the delamination in water follow the same trend

Conclusions

- Tunable content of -OH and -COOH functional groups for enhanced metal grafting
→ Suitable for metal (i.e., Al) grafting
- High resistance to immersion in water**
→ Requires tuning of the properties to increase the delamination process

Perspectives

- Increasing the deposition pressure to reduce the resistance to immersion in water
- Mass spectrometry of the plasma to identify the species involved in the growth mechanism
- Evaluation of glass transition temperature of the PPF
- Assessing other delamination stimuli than immersion in water

Method advantages

Plasma Polymer Films with high content of carboxylic acid and alcohol functions have been synthesized through **PECVD** using C₂H₄ and CO₂ as precursor gases.

- Cheap
- Solvent-free, one-step process
- Easy industrial upscaling
- Tunable properties

References

- Hegemann, D. and al. Plasma Process. Polym. 2009, 6, 246-254.
- Friedrich, J. F. and al. Surface & Coatings Technology 2005, 200, 565-568
- Vandenbossche, M. and al. Polymer Degradation and Stability 2018, 156, 259-268.
- Thiry, D. and al. Langmuir 2018, 34, 26, 7655-7662.