

Bologna, July 18<sup>th</sup>, 2015

Dear Prof. Favia,

thank you for giving us the opportunity to improve our Manuscript and resubmit it after minor revisions. The answers to the Editor's and Reviewers' comments are reported below in this document

In addition, the Authors would ask the Editor to accept a change in the order of the Authors, due to the most relevant role assumed by Dr. Matteo Gherardi in the field of plasma and materials inside the Group for Industrial Applications of Plasmas at Alma Mater Studiorum – Università di Bologna and his leading role in the research activities reported in this Manuscript and in its revision phase. As a consequence, in the revised paper Dr. Matteo Gherardi appears as last and corresponding Author.

Best regards,

Prof. Vittorio Colombo

Dear Prof. Favia,

we would like to thank you and the Reviewers for your comments and suggestions, that stimulated us to better highlight the novelty of our work and improve the overall quality of our Manuscript.

As reported below, we took into account and addressed the Editor's and the Reviewers' comments, and their criticisms and suggestions, and based on these comments we have changed corresponding points of the Manuscript.

In particular, we better highlighted the intended scope of our research, namely the chemical characterization of a pPAA layer deposited by means of an atmospheric pressure plasma source with the aim of showing the potential of nanosecond high voltage signals to deposit polymeric coatings with a high retention of functional groups; to the best of our knowledge, the only two papers also reporting on this subject are focused on the deposition of a different polymer.

Taking this into account, we believe a detailed study of the stability and morphology of the coating to be beyond the scope of our Manuscript and the results presented on these subjects (characterization after short time water dipping and 3D optical microscopy) were intended as preliminary information to support the discussion and indicate the way of our ongoing research activities. Therefore, following the Editor's request for minor revisions, we explicated further the preliminary nature of these results throughout the text and added a perspective section at the end of the Conclusions to describe the future steps we envision for complementing the chemical characterization of the coating with stability and morphological analysis, also in view of potential biomedical applications.

With best regards,

Dr. Matteo Gherardi

04-Jul-2015

Dear Prof. Colombo,

Manuscript ppap.201500080 entitled "Deposition of plasma-polymerized polyacrylic acid coatings by a non-equilibrium atmospheric pressure nanopulsed plasma jet" which you submitted to *Plasma Processes and Polymers* has been reviewed. The comments of the referee(s) are included at the bottom of this letter.

I'd like to personally add the following comments:

- since this is a novelty, highlight better the advantage of using a nanosecond pulsed generator in this context

**WE AGREE WITH THE EDITOR'S COMMENT AND CONSEQUENTLY WE INSERTED A PARAGRAPH IN THE INTRODUCTION IN WHICH THE NOVELTY AND ADVANTAGES OF USING A NANOPULSED GENERATOR FOR PLASMA POLYMERIZATION WERE EXPLAINED IN MORE DETAIL.**

INTRO

- explain clearly how ppAA coatings are used for non fouling coatings in cited ref [3], the text as it is may be misleading. Maybe in that ref the ppAA layer is used as functionalized layer to covalently bind non fouling chains?

**THE EDITOR IS RIGHT. WE SUBSTITUTED THE REFERENCE WITH A MORE PERTINENT ONE AND MODIFIED THE TEXT IN ORDER TO BETTER EXPRESS THE POSSIBLE APPLICATIONS OF PPAA.**

- it should be reported somewhere that HIGH (how much ?) density of -COOH groups is not necessary for cell-adhesive surfaces and immobilization of biomolecules. In effect the stability in water is very important for applications (such as biomedical) in water media.

**WE AGREE WITH THE EDITOR'S COMMENT AND THUS WE DELETED ALL THE REFERENCES TO THE "HIGH AMOUNT" OF COOH GROUPS; TO BETTER SPECIFY THE RELEVANCE OF COOH GROUPS, WE INTRODUCED AND DISCUSSED IN THE INTRODUCTION A PAPER [REF 5] WHERE THEIR ROLE IN FAVORING CELLS ADHESION OR FOR BIOMOLECULE IMMOBILIZATION IS HIGHLIGHTED; AND WHERE IT IS STATED THAT THE REQUIRED AMOUNT OF CARBOXYL GROUPS FOR CELLS ADHESION OR BIOMOLECULE IMMOBILIZATION DEPENDS ON THE CELL LINE OR THE BIOMOLECULE WHICH INTERACTS WITH THE SUBSTRATE.**

- a very recent paper by Fanelli on PPP should be cited, on the jet deposition of stable coatings by AA/ethylene at atm pressure.

**THE PAPER IS VERY PERTINENT; THEREFORE WE CITED IT, REPORTING AND COMMENTING ITS RESULTS IN THE RESULTS & DISCUSSION SECTION OF OUR WORK. FURTHERMORE, RELYING ON THE PROCEDURES THERE PRESENTED, WE BETTER EXPLAINED OUR FUTURE STEPS TOWARDS A MORE COMPREHENSIVE EVALUATION OF COATING STABILITY AND CHEMICAL COMPOSITION AFTER WATER IMMERSION.**

- the text "vacuum devices" should change in "vacuum pumps". In effect. Also at atm P pumps are required to keep constant the composition of the atmosphere around the substrate.

**OK, WE AGREE WITH THE EDITOR'S COMMENT AND WE MODIFIED THE TEXT.**

- beside cited ref 13, and before, in Palumbo et al (Plasmas Polym 4, 133, 1999) it is reported, probably for the first time, the OES vs XPS correlation “more AA fragmentation, less –COOH in the coating”.

**WE THANK THE EDITOR FOR THE COMMENT. WE CITED THE WORK IN THE INTRODUCTION AND ADDED A SENTENCE ABOUT THE OES VS XPS CORRELATION.**

- Please explain well the advantages of using nanosecond square-pulse AP-DBD to maximize the retention of the monomer in the coating, as this is the true novelty of the paper.

**THANK YOU FOR THE COMMENT, WE ADDED A PARAGRAPH IN THE INTRODUCTION PROVIDING THE SUGGESTED EXPLANATION, TAKING ALSO INTO ACCOUNT THE CONSIDERATIONS REPORTED BY CHOQUET AND COWORKERS IN THEIR RECENT WORKS.**

- at page 3, second half, again it is reported that “high amount of functional groups ...” are requested for biomedical applications. But can we quantify this for the various applications ? probably not.

**ACCORDING TO THE EDITOR'S COMMENT, ALL OCCURRENCES OF THE EXPRESSION “HIGH AMOUNT” WERE REMOVED FROM THE TEXT.**

- Stability in water and high (probably < 10% in any case) density of COOH/R groups can be obtained, at low P, by increasing the power, or/and by adding an unsaturated hydrocarbon; France et al did probably first (J Mat Chem 8, 37, 1998) with 1-7 octadiene, Pistillo et al (Surf Coat Tech 205, S534, 2011) with ethylene. Fanelli (see above, on PPP) added ethylene at Atm P. If nanosecond pulses can give similar results without adding ethylene this should be highlighted.

**WE THANK THE EDITOR FOR HIGHLIGHTING THIS VERY IMPORTANT POINT. SINCE IN OUR CASE THE STABILITY OF THE COATING WAS EVALUATED AFTER 30 SEC OF WATER DIPPING, OUR RESULTS CANNOT BE COMPARED WITH THE ONES REPORTED IN THE MENTIONED PAPERS. NONETHELESS, COMPARING THE DIPPING PROCEDURE WE ADOPTED WITH THE ONES IN THE MENTIONED PAPERS, WE THINK THAT THE EXPRESSION “WATER STABLE COATINGS” IS MEASLEDING IN OUR CASE; THEREFORE, WE SUBSTITUTED IT WITH “COATINGS STABLE UPON WATER CONTACT” THROUGHOUT THE TEXT. MOREOVER, WE ADDED THE INFORMATION REGARDING THE DIPPING TIME IN THE TEXT AND CAPTIONS. THE SUGGESTED PAPERS WILL BE DEFINETELY TAKEN INTO ACCOUNT IN OUR FUTURE ACTIVITIES, WHERE THE COATING CHARACTERISTICS (MORPHOLOGY AND STABILITY) WILL BE FURTHER INVESTIGATED, ALSO IN THE PERSPECTIVE OF POSSIBLE APPLICATIONS.**

#### EXPERIMENTAL

- SOURCE A scheme would help much in understanding how the jet is arranged, beside references and texts. I don't understand here how a 12-hole diffuser is defined. Also, a detailed scheme would help to understand how the primary and the secondary gas are injected.

**FOLLOWING THE EDITOR'S REQUEST, WE INTRODUCED A DETAILED SCHEME IN FIGURE 1 AND WE PROVIDED A DESCRIPTION OF THE DIFFUSER.**

- slew rate ? is the generator a pulsed DC or AC ?

**THE GENERATOR IS A PULSED DC, WE INTRODUCED MORE INFORMATION ABOUT IT. THE SLEW RATE EXPRESSES THE MAXIMUM RATE OF CHANGE OF**

THE OUTPUT VOLTAGE PER UNIT OF TIME (I.E. KV/NS) AND IS THE KEY FEATURE OF PULSE GENERATORS, ESPECIALLY NANOPULSED ONES. SINCE THIS VALUE IS INDEPENDENT OF THE MAXIMUM PEAK VOLTAGE REACHED BY THE PULSE, IT IS MORE SIGNIFICANT THAN THE RISE TIME, WHICH IS DEPENDENT ON THE SPECIFIC OPERATING CONDITIONS SELECTED FOR THE EXPERIMENT.

#### FEED

- what is, exactly, the AA content in the primary gas, i.e., when 3 slpm are bubbled in 35 ml AA per 3-20 min.

THE EDITOR IS RIGHT, WE APOLOGIZE FOR THIS MISSING INFORMATION. THE AA MASS FLOW RATE WAS 0.05 ML/MIN. WE INTRODUCED THIS INFORMATION IN THE EXPERIMENTAL PART.

#### PLASMA PROCESSED AREA

- what is the area of the pre-treated and of the plasma-coated zone of the substrates ? larger than the WCA analysis spot ?

THE AREA OF THE COATING AS WELL AS THE AREA INTERESTED BY THE PLASMA ACTIVATION WAS FOUND TO BE AROUND 1CM<sup>2</sup>. WE ADDED THIS INFORMATION IN THE TEXT. THIS AREA IS SIGNIFICANTLY LARGER THAN THE SPOT OF WCA ANALYSIS AND ALSO THAN THAT OF THE PLASMA SOURCE OUTLET, SIMILARLY TO WHAT SHOWN IN REF. 35.

#### XPS-FT-IR

the text "surface sensitivity" should be deleted, you mean "sampling depth".

THE TEXT WAS CHANGED ACCORDING TO THE COMMENT

#### RESULTS

- in Fig 5 the widescan spectra could be deleted

OK, THE WIDESCAN SPECTRA WAS DELETED AND TEXT AND CAPTION WERE MODIFIED ACCORDINGLY.

- the FT-IR spectra are too overlapped, please try to make the Figures more readable. Add labels to the relevant bands, for clarity.

THANK YOU FOR THE SUGGESTION. WE TRIED TO MAKE ATR-FTIR FIGURES MORE READABLE BY DELETING THE HORIZONTAL LINES IN THE GRAPHS AND ADDING LABELS TO THE MOST RELEVANT PEAKS AND BANDS. FURTHERMORE, WE MODIFIED THE Y AXIS OF THE GRAPH, SUBSTITUTING THE COMMA WITH THE POINT, AS SUGGESTED BY THE FIRST REFEREE. WE HOPE THIS MODIFICATIONS WILL INCREASE THE FIGURES READABILITY

- -COOH groups are retained, but -COOR are formed. To distinguish them derivatization techniques should be used.

THANKS FOR THE SUGGESTION. IT WILL BE SURELY TAKEN IN ACCOUNT FOR FURTHER ANALYSIS MORE FOCUSED ON THE INVESTIGATION OF ALL THE FUNCTIONAL GROUPS PRESENT IN THE DEPOSITED COATING. IN THIS WORK, WE UNDERLINED IN THE TEXT THAT MECHANISMS OF CROSSLINKING ARE STILL UNCLEAR AND SO, DERIVATIZATION TECHNIQUE WILL BE

IMPLEMENTED IN THE FUTURE TO GET MORE INSIGHTS ABOUT THE CROSSLINKING OF THE COATING. WE ALSO PREFERRED NOT PERFORMING THE CHEMICAL DERIVATIZATION IN THIS WORK SINCE, TO THE BEST OF OUR KNOWLEDGE, A UNIVOCALLY ACCEPTED METHOD FOR THE QUANTIFICATION OF -COOH GROUPS DOES NOT SEEM TO EXIST YET.

Reviewer: 1

Comments to the Author

Dear authors,

i enclose some comments to help improving the paper.

- Fig. 2, could maybe be put as additional information, it is not critical for the comprehension of the paper.

OK, FIG. 2 WAS REMOVED AND MOVED TO THE SUPPORTING INFORMATION SECTION.

- Please, explain why PE and PVC were selected.

WE ADDED A PART (AND TWO REFERENCES) IN THE INTRODUCTION IN ORDER TO EXPLAIN THE CHOICE OF USING PE AND PVC AS SUBSTRATES FOR THE PROCESS. BRIEFLY, PE AND PVC WERE SELECTED AS SUBSTRATE DUE TO THEIR WIDE USE IN THE INDUSTRIAL AND BIOMEDICAL FIELD, MAINLY AS A CONSEQUENCE OF THEIR INTERESTING MECHANICAL AND THERMOPLASTIC PROPERTIES. HOWEVER, FOR SOME SPECIFIC APPLICATIONS THEIR SURFACE CHEMICAL PROPERTIES REQUIRE TO BE MODIFIED, I.E. TO INCREASE THE HYDROPHILICITY OF THE MATERIAL.

- Page 13. XPS. Authors state that there are 4 peaks in the decomposition of the C peak, and an additional peak: "Furthermore, in the peak fitting of the C1s envelope of the 20 min deposited pPAA film..." However, this 5th peak is also present in the 3 min sample.

Please rewrite more clearly, as stating that there is only 4 peaks when 5 are clearly visible may lead to confusion.

THE REFEREE IS RIGHT AND WE ARE GRATEFUL FOR THE COMMENT. THE PEAK FITTINGS HAVE BEEN RECALCULATED FOR THE C1S ENVELOPES REPORTED IN FIGURES 4 AND 8 IN ORDER TO MAKE THEM CLEARER AND THE TEXT WAS ALSO CORRECTED.

- Table with the general quantification of XPS and O/C ratios should be added and the effects of the treatment on each sample should be discussed.

WE ADDED A COLUMN IN TABLE 1 REPORTING THE O/C RATIO FOR EACH SAMPLE. FURTHERMORE, WE ALSO INTEGRATED THE TEXT WITH INFORMATION AND DISCUSSION ABOUT THE O/C VALUE FOR EACH SAMPLE.

- Discuss the relevance of the functional groups created on the polymers for the applications intended and relationship with previous literature.

THANKS FOR THE COMMENT, WHICH PROMPTED US TO BETTER CLARIFY THE AIM OF THE PRESENTED PROCESS. WE INTRODUCED AND MODIFIED SOME SENTENCES IN THE INTRODUCTION TO MAKE BETTER EXPLAIN THE ROLE OF THE FUNCTIONAL GROUPS FOR CELL ADHESION AND BIOMOLECULES IMMOBILIZATION.

- p. 14. 2nd paragraph. Correct: "With the aim of gathering..."

**OK, THE EXPRESSION WAS CORRECTED.**

- How do authors explain this different thickness obtained in the coating between the two different polymers? Please discuss.

**THANK YOU FOR THE COMMENT. SINCE THE MEASUREMENTS OF THE COATING THICKNESS SHOULD BE CONSIDERED AS PRELIMINARY RESULTS (AS WE HAVE NOW BETTER SPECIFIED IN THE TEXT), WE DO NOT FEEL LIKE SPECULATING ABOUT THE EFFECT OF THE UNDERLYING SUBSTRATE ON THE COATING THICKNESS. MOREOVER, SINCE THE STANDARD DEVIATIONS OF THE MEASUREMENTS ARE QUITE HIGH DUE TO THE ROUGHNESS OF THE COATINGS, WE CANNOT REALLY SAY THAT THE TWO COATINGS ARE CHARACTERIZED BY TWO DIFFERENT VALUES OF THICKNESS. AS A NEXT STEP, WE WILL EVALUATE THE COATING THICKNESS FOR ALL THE EMPLOYED OPERATING CONDITIONS BY MEANS OF OTHER CHARACTERIZATION TECHNIQUES, JOINTLY TO THE ALREADY ADOPTED 3D MICROSCOPE, IN ORDER TO BETTER UNDERSTAND THE ROLE, IF ANY, OF THE SUBSTRATE ON THE COATING CHARACTERISTICS.**

- Fig. 6, figure legend: It would be more clear if instead of "pristine" authors used the term "masked area" or equivalent.

**OK, THE LEGEND WAS MODIFIED ACCORDINGLY.**

- Attention to the format of the ATR-FTIR images, which should not be in excel (or at least formatted similarly as the other images, avoiding the horizontal lines in the figures).

**THANK YOU FOR THE SUGGESTION. WE MODIFIED THE FIGURES DELETING THE HORIZONTAL AXIS AND, IN ORDER TO MAKE THEM MORE READABLE, LABELS TO THE MOST RELEVANT PEAKS AND BANDS WERE ADDED.**

- Attention also in ATR-FTIR images: In english, numbers with points, not commas.

**THANK YOU, FIGURES WERE MODIFIED ACCORDINGLY.**

- How long was dipping in water? Please specify (in the order of seconds, minutes...?)

**WE APOLOGIZE FOR THE MISSING INFORMATION. THE WATER DIPPING WAS PERFORMED FOR 30 S, WE ADDED THIS INFORMATION IN THE TEXT.**

- XPS of PVC in strong treatment conditions is lacking but authors present the results of FTIR....it would be interesting to have it in order to compare the two materials in this treatment conditions.

**WE THANK THE REFEREE FOR THE COMMENT. WE DECIDED NOT TO INTRODUCE THIS ADDITIONAL FIGURE SINCE WE BELIEVE IT DID NOT PROVIDE ADDITIONAL INFORMATION THAT COULD NOT BE ALREADY INFERRED BY THE OTHER PRESENTED RESULTS. WE TRY HERE TO EXPLAIN OUR REASONS AND WE HOPE THE REFEREE WILL AGREE.**

**COMPARING THE ATR-FTIR SPECTRA REPORTED IN OUR PAPER, NO SIGNIFICANT DIFFERENCES CAN BE OBSERVED BETWEEN THE SPECTRA OF THE COATINGS DEPOSITED ONTO PE AND PVC SUBSTRATES IN MILD CONDITIONS WITH THOSE DEPOSITED IN STRONG CONDITIONS. ON THE OTHER HAND, XPS RESULTS SHOWS THAT THE CHEMICAL COMPOSITION OF COATINGS**

DEPOSITED ONTO PE AND PVC IN MILD CONDITION IS EXTREMELY SIMILAR. THEREFORE, WE BELIEVE THE READER CAN INFER THAT THE CHEMICAL COMPOSITIONS OF COATINGS DEPOSITED ONTO PE AND PVC IN STRONG CONDITION ARE ALSO VERY SIMILAR; THUS WE WOULD PREFER TO OMIT AN ADDITIONAL XPS GRAPH THAT COULD DECREASE THE FLUENCY OF THE TEXT.

- Fig. 10 footlegend specifies 10 min Ar activation...was it the same in the other treatments prior to the polymerisation? in such a case, please ensure uniformity in the footlegends throughout the paper for clarity.

FIG. 10 IS THE ONLY FIGURE WHERE THE SPECTRA OF PPAA COATING ONTO PRETREATED SUBSTRATES ARE REPORTED. IN THE OTHER CASES, THE SUBSTRATE WAS NOT PLASMA ACTIVATED BEFORE THE POLYMERIZATION. WE TRIED TO BETTER SPECIFY THE PRESENCE OR ABSENCE OF THE PRETREATMENT THROUGHOUT THE TEXT.

- p. 21. The whole last paragraph of the results section is unclear, please rewrite.

WE REWROTE THE LAST PARAGRAPH, ALSO ADDING A COMPARISON BETWEEN OUR WORK AND A VERY RECENT WORK WRITTEN BY BOSSO ET AL. AND SOME CONSIDERATIONS ABOUT THE FUTURE DEVELOPMENTS OF OUR WORKS.

- What happens if the samples are left longer in water? To show that there is indeed crosslinking and suitable binding to the substrate, it is suggested that authors compare between different soaking times in water.

WE THANK THE REFEREE FOR THE COMMENT, WHICH IS INDEED VERY PERTINENT. IN THIS PAPER WE PERFORMED ONLY A PRELIMINARY ANALYSIS OF THE COATING STABILITY, DIPPING THE SAMPLES FOR 30 SEC. AS A CONSEQUENCE, WE DECIDED TO MODIFY THE EXPRESSION "WATER STABLE COATING" IN "COATING STABLE UPON WATER CONTACT" TO BETTER DESCRIBE THE OBSERVED RESULTS.

NONETHELESS, WE COMPLETELY AGREE THAT FOR APPLICATION PURPOSES THE STABILITY OF THE COATING SHOULD BE EVALUATED AFTER LONG (DAYS) SOAKING TIMES. THEREFORE, OUR FUTURE ACTIVITIES WILL BE AIMED TO CHARACTERIZE THE COATING STABILITY, INVESTIGATING ITS CHEMICAL AND MORPHOLOGICAL CHARACTERISTICS AFTER LONGER WATER IMMERSION BY MEANS OF FTIR, XPS, AFM AND SEM. A SENTENCE WAS ADDED IN THE CONCLUSION PARAGRAPH TO DESCRIBE THE PATH WE ARE UNDERTAKING.

- I suggest to improve the discussion in the direction of the biomedical applications mentioned in the introduction, which are not detailed afterwards in the results and discussion section.

OK, THANK YOU. A SENTENCE WAS ADDED IN THE DISCUSSION.

Reviewer: 2

Comments to the Author

The present paper by Liguori et al. reports on the deposition of plasma-polymerized polyacrylic acid coatings by an atmospheric pressure cold plasma jet. The novelty of the papers mainly resides in the utilization of a nanopulsed plasma jet for the deposition of thin films; however, considering the results obtained on thin film deposition from acrylic acid, I personally believe that the novelty of this work is very limited and that the characterization of the deposited coatings is inaccurate and incomplete. I believe that the scientific quality of the manuscript needs to be seriously improved before being considered for publication in this Journal. I have the

*following comments and suggestion for major improvement of the manuscript:*

1) *In the introduction as well as in the list of references, the authors completely skipped the literature on thin film deposition from acrylic acid using atmospheric pressure plasmas and, very often, plasma jets. Some references that should be reported and discussed in the introduction are listed below:*

- G. Chen et al., *Plasma Process. Polym.* 2011, 8, 701.
- Donegan et al., *Surf. Coat. Technol.* 2013, 234, 53.
- Bosso et al., *Plasma Process. Polym.* 2015, DOI: 10.1002/ppap.201500005.
- Cools et al., *Plasma Process. Polym.* 2015, DOI: 10.1002/ppap.201500007
- Carton et al. *Plasma Process. Polym.* 2012, 9, 984.
- Salem et al., *Plasma Process. Polym.* 2014, 11, 269.
- Morent et al., *Appl. Surf. Sci.* 2010, 257, 372.
- Ward et al., *Chem. Mater.* 2003, 15, 1466.
- Beck et al., *Surf. Coat. Technol.* 2008, 203, 822.

**WE THANK THE REVIEWER FOR HIS COMMENT; WE WOULD JUST UNDERLINE THAT THE TWO PAPERS PUBLISHED IN 2015 WERE NOT TAKEN INTO ACCOUNT BECAUSE THEY WERE PUBLISHED AFTER THE SUBMISSION OF OUR WORK. EVEN THOUGH OUR PAPER WAS NOT MEANT TO BE AN INTRODUCTORY REVIEW TO ATMOSPHERIC PRESSURE DEPOSITION OF ACRYLIC ACID, NONETHELESS SOME OF THE SUGGESTED REFERENCES SHOULD HAVE BEEN CONSIDERED. WE HAVE NOW CONSIDERED ALL OF THEM, DISCUSSING THEIR CONTENT IN VARIOUS PARTS OF THE PAPER.**

2) *I suggest the authors to improve the figures containing ATR-FTIR spectra, moreover spectra should be background corrected and normalized.*

**OK, THANKS FOR THE SUGGESTION. FIGURES HAVE BEEN IMPROVED BY DELETING THE HORIZONTAL AXIS AND ADDING LABELS TO THE MOST RELEVANT BANDS AND PEAKS. CONCERNING SPECTRA, THEY WERE ALREADY BACKGROUND CORRECTED AND NORMALIZED.**

3) *I suggest the authors to deposit the thin films on glass or silicon substrates to give a better indication of the coating thickness. I know that the coating thickness could be "substrate dependent", however I believe that an estimation using glass or silicon substrates should be provided.*

**WE THANK THE REVIEWER FOR HIS SUGGESTION. INDEED, WE ARE AWARE THAT THE DEPOSITION ON GLASS OR SILICON WOULD BE BETTER FOR THE COATING CHARACTERIZATION, BUT, AS THE REVIEWER MENTIONED, DEPOSITION COULD BE SUBSTRATE DEPENDENT AND THUS MEASURING THE THICKNESS OF THE COATING DEPOSITED ON SILICON/GLASS COULD HAVE LED TO RESULTS UNREPRESENTATIVE OF THE COATING DEPOSITED ON PE/PVC. THIS IS ESPECIALLY TRUE SINCE THE SOURCE EMPLOYED FOR THE DEPOSITION IS A SINGLE ELECTRODE PLASMA JET; AS A CONSEQUENCE, THE TREATED MATERIAL BEHAVES AS A PART OF THE ELECTRICAL CIRCUIT (IN THE CASE OF SILICON, ACTUALLY ACTING AS A FLOATING COUNTER ELECTRODE) AND THUS DIRECTLY INFLUENCES THE CHARACTERISTICS OF THE PLASMA DISCHARGE. FOR THESE TWO REASONS WE DECIDED NOT TO DEPOSIT AND EVALUATE COATINGS ON GLASS OR SILICON.**

**ON THE OTHER HAND, AS OUR FUTURE ACTIVITIES WILL BE DEDICATED TO CHARACTERIZE MORE DEEPLY THE COATING MORPHOLOGY, WE WILL TAKE INTO ACCOUNT THE REFEREE'S SUGGESTION AND COMPARE RESULTS FOR LAYER DEPOSITED ON PE, PVC AND SILICON/GLASS IN ORDER TO EVALUATE THE SUBSTRATE DEPENDANCY OF THE PROCESS.**



4) XPS results:

*-The authors should carefully revise the curve fitting of high resolution XPS C1s spectra. Considering for instance the fact that a non-monochromatic X-ray source was been utilized, I suggest to remove the C1s component due to C-COOH groups and to use for curve fitting the components reported in reff. 2, 6, 13.*

**WE APOLOGIZE, BUT IN THIS CASE WE DO NOT AGREE WITH THE REFEREE'S COMMENT.**

**WE CARRIED OUT THE CURVE FITTING ELABORATION LINKING C-COOH AND COOH PEAK AREAS IN ORDER THAT THEY MAINTAINED A CONSTANT 1:1 RATIO. IN THIS WAY THE CURVE FITTING WAS "GUIDED" USING CHEMICAL KNOWLEDGE, RATHER THAN ALLOWING THE PRODUCTION, THAT MAY BE A GOOD MATHEMATICAL FIT, BUT MAY LACK OF PHYSICAL MEANING.**

**MOREOVER, CONSIDERING THE FACT THAT A NON-MONOCHROMATIC X-RAY SOURCE WAS USED, WE THINK THAT THIS SET UP, ALTHOUGH DETERMINING WIDER FWHM (WHILE SATELLITE PEAKS FALL OUTSIDE THE STUDIED RANGE), JUSTIFIES THE USE OF THE C-COOH COMPONENT DURING THE FITTING.**

**ANYWAY, WE COMPARED OUR SPECTRA WITH THE ONES REPORTED IN THE SUGGESTED REFERENCES AND CONCLUDED THAT THE C<sub>1s</sub> COMPONENTS REPORTED THERE ARE PRESENT IN OUR STUDY. FOR THIS REASONS WE PREFER TO AVOID REMOVING C-COOH COMPONENT.**

*-In the text at p.13 and in Table 1 the binding energies reported for the different C1s components are quite reasonable, however in Figures 5 and 9 something is not clear: for instance it's not clear why there is a component centred at a binding energy lower than 284 eV.*

**THANK YOU FOR THE COMMENT, THE REFEREE IS RIGHT. THE PEAK FITTINGS HAVE BEEN RECALCULATED FOR THE C1S ENVELOPES REPORTED IN THE FIGURES IN ORDER TO MAKE THEM CLEARER.**

*-I suggest to remove survey spectra in Figure 1.*

**OK, THE WIDESCAN SPECTRA WAS DELETED AND THE CAPTION WAS ACCORDIGLY MODIFIED.**

*5) How large is the treated area using the nanopulsed plasma jet used in this work? This information should be provided. Considering the dimensions of the jet I could expect a treated area of a few mm<sup>2</sup>; then considering for instance WCA measurements I was wondering if WCA results obtained with a 2 microliter drop can be acceptable. Is the dimension of the drop, when placed on the substrate, sufficiently smaller that the treated area? Moreover, I suggest the authors to carefully consider WCA results; due to the poor water stability of the coatings WCA measurements can provide only indicative WCA values.*

**THE AREA OF THE COATING WAS MEASURED TO BE AROUND 1CM<sup>2</sup>. WE ADDED THE INFORMATION IN THE TEXT. THIS AREA IS HIGHER THAN THE ONE OF THE PLASMA SOURCE OUTLET (4 MM DIAMETER), IN ACCORDANCE TO WHAT RECENTLY REPORTED IN (I. Onyschchenko, A. Y. Nikiforov, N. De Geyter, R. Morent, Plasma Process. Polym., 2015, 12, 466., CITED IN THE TEXT), AND IS ALSO HIGHER THAN THE SPOT FOR WCA ANALYSIS.**

**AS THE STABILITY OF THE COATINGS WAS VERIFIED UPON WATER CONTACT (30 SEC DIPPING), WE SPECIFIED IN THE TEXT THAT WCA MEASUREMENTS CAN PROVIDE ONLY INDICATIVE, BUT STILL SIGNIFICANT, RESULTS.**

6) *Water stability of the coatings: authors reports results after water dipping. How long were the substrates dipped in water. 10 s? 1 hour? 24 hours? If substrates were soaked in water for a few minutes or a few hours, I personally believe that the improvement of coatings water stability cannot be claimed. Moreover since deposited coatings seems to be very thick, the authors should report thickness loss after water immersion for all the investigated conditions.*

AS THE STABILITY ANALYSIS WAS PERFORMED DIPPING SAMPLES IN WATER FOR ONLY 30 SEC, WE MODIFIED THE EXPRESSION "WATER STABLE COATING" IN "COATING STABLE UPON WATER CONTACT".

ON THE SIDE OF EVALUATING THE THICKNESS LOSS AFTER WATER IMMERSION, WE BELIEVE THAT IT WOULD NOT PROVIDE A VERY SIGNIFICANT ADDITION BECAUSE OF THE PRELIMINAR NATURE OF THE STABILITY TESTS PERFORMED IN OUR WORK. ON THE OTHER HAND, THIS MEASUREMENT WOULD BE CRITICAL IN SUPPORTING A MORE DETAILED DISCUSSION OF THE STABILITY OF THE COATING AND ITS MORPHOLOGY BEFORE AND AFTER SOAKING IN WATER; NONETHELESS, THIS WAS BEYOND THE SCOPE OF THE PAPER, WHICH WAS PARTICULARLY FOCUSED ON THE CHEMICAL CHARACTERIZATION OF THE DEPOSITED LAYER. INDEED, BESIDE THE THICKNESS MEASUREMENT PERFORMED BY MEANS OF 3D OPTICAL MICROSCOPE, ALL CONSIDERATIONS ON THE MORPHOLOGY OF THE DEPOSITED LAYERS WERE INFERRED FROM THE SAMPLING DEPTH OF ATR-FTIR ANALYSIS AND AS A CONSEQUENCE SHOULD BE REGARDED AS PRELIMINAR.

WE ADDED CONSIDERATIONS ON THESE POINTS IN THE RESULTS & DISCUSSION SECTION OF THE WORK. MOREOVER, IN THE CONCLUSIONS WE INDICATED THE FUTURE STEPS WE ENVISION FOR DEEPENING THE CHARACTERIZATION OF THE COATING, INVESTIGATING ITS CHEMICAL AND MORPHOLOGICAL CHARACTERISTICS AFTER LONGER WATER IMMERSION BY MEANS OF FTIR, XPS, AFM AND SEM.

7) *There is no information about coatings morphology before and after water dipping. The morphological characterization should be carried out by either scanning electron microscopy or atomic force microscopy.*

WE THANK THE REVIEWER FOR HIS COMMENT, BUT WE DO NOT COMPLETELY AGREE. INDEED, THE AIM OF THIS PAPER WAS INVESTIGATING THE CHEMICAL CHARACTERISTICS OF THE COATING BY MEANS OF ATR-FTIR AND XPS, IN ORDER TO DEMONSTRATE AND DISCUSS THE POTENTIAL OF PLASMAS DRIVEN BY NANOSECOND HIGH VOLTAGE PULSES FOR THE DEPOSITION OF POLYMERIC LAYERS WITH A HIGH RETENTION OF FUNCTIONAL GROUPS. IN THIS FRAME, THE 3D OPTICAL MICROSCOPY MEASUREMENT OF THE COATING THICKNESS WAS INTENDED ONLY AS A PRELIMINAR RESULT, TO BE COMPLEMENTED IN THE FUTURE WITH SEM AND AFM ANALYSIS.

AS NOW BETTER SPECIFIED IN THE TEXT, OUR FUTURE EFFORTS WILL BE DEVOTED TO THE CHARACTERIZATION OF COATING THICKNESS AND MORPHOLOGY BEFORE AND AFTER WATER IMMERSION AND SONICATION, RELYING ON SEM, AFM AND WEIGHT LOSS MEASUREMENTS TO ALSO EVALUATE THE COATING STABILITY. WE HOPE THAT THE REFEREE WOULD UNDERSTAND THAT THIS WAS BEYOND THE SCOPE OF THIS PAPER AND WE KINDLY ASK TO BE SPARED FROM ADDING SEM AND AFM RESULTS AT THIS MOMENT.

8) *In the Experimental Section the amount of acrylic acid injected in the discharge should be provided (e.g., mg/min).*

**WE APOLOGIZE FOR THE MISSING INFORMATION. THE AA MASS FLOW RATE WAS 0.05 ML/MIN. WE INTRODUCED THIS INFORMATION IN THE EXPERIMENTAL PART.**