THE 3^{r d} PLASMA NANOTECHNOLOGIES AND BIOAPPLICATIONS WORKSHOP



SCIENTIFIC PROGRAM & BOOK OF ABSTRACTS

> Hotel Rustikal Hustopeče Czech Republic

M A S A R Y K O V A U N I V E R Z I T A

OCTOBER 9-12, 2023

THE 3rd PLASMA NANOTECHNOLOGIES AND BIOAPPLICATIONS WORKSHOP

SCIENTIFIC PROGRAM & BOOK OF ABSTRACTS

Hotel RUSTIKAL, Hustopeče, October 9-12, 2023

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PREFACE

Dear participants,

I am pleased that we are meeting again after two years for the 3rd workshop, which is dedicated to *Plasma Nanotechnologies and Bioapplications*. The initially small workshop of the Plasma Nanotechnologies and Bioapplications research group at the Department of Plasma Physics and Technology and the CEPLANT research centre, both located at the Faculty of Science, Masaryk University in Brno, is gradually becoming a workshop registered and perceived by the scientific community abroad. We are pleased that in addition to the regular participants from the Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava from Slovakia, participants from HAWK University of Applied Sciences and Arts in Göttingen and the University of Stuttgart from Germany, the University in Ljubljana from Slovenia as well as the University of Natural Resources and Life Sciences (BOKU) in Vienna from Austria will also participate in this year's workshop. Our effort is to preserve the original purpose of the workshop, which is the sharing and exchange of knowledge, experience and results achieved in the field of basic and applied research in Plasma Physics, Physics of Electrical Discharges, Plasma Chemistry and Plasma Bioapplications. That is also the reason why we stick to the format of a workshop with a three-day scientific program, while trying to give the participants enough time for personal meetings and informal discussions outside the lectures. I believe that social events such as a welcome party, a social event or a workshop trip will contribute to the pleasant atmosphere of the workshop and a stimulating environment for establishing new contacts and cooperation.

During the workshop, interesting lectures will be given from the above-mentioned scientific fields related to plasma, which are included in following topics: *New developments and diagnostics of DBD, Plasma and glass processing, Plasma in contact with liquids & Plasma water purification, Plasma and bioapplications, Plasma reduced graphene oxide, and Plasma surface processes.* In addition, the workshop program also provides space for the presentation of research by participants from German universities. I am convinced that some of them, even if they have not used "plasma" in their research so far, will leave the

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workshop with more ideas on incorporating this "tool" into future research and perhaps even with concrete proposals for cooperation.

In conclusion, I would like to express my wish that the 3rd workshop will be at least as successful as the previous ones held in Broumov (2021) and Telč (2019), that we manage to create a pleasant and stimulating atmosphere so that everyone will find a lecture or a whole section in the program that is close to their field of research and thus expand their knowledge! I believe that we will also succeed thanks to the pleasant environment and picturesque surroundings of the town of Hustopeče, considered the heart of vineyards and almond orchards, where the workshop takes place, and thanks to the Hotel Rustikal and its facilities.

Dušan Kováčik

VENUE



Hustopeče is a town situated in the picturesque countryside near the Pálava and Novomlýnské reservoirs. It is usually referred to as the heart of vineyards and almond trees. The town center is dominated by two buildings: a neo-Renaissance town hall from 1906 and the modern church of St. Wenceslaus and Agnes of Bohemia from 1994. There is also a fountain from 1595 in Dukelské Square, a Baroque plague column and, most importantly, the Renaissance house U Synků from 1579.

Hotel *** RUSTIKAL



Hotel * Rustikal** is a great place for organizing a workshop. The whole complex includes a hotel, restaurant, pizzeria, bowling, winery with wine cellar, conference hall with a capacity for up to 200 persons and two training rooms for up to 20 persons (for more details, visit the website https://www.rustikal.cz/en).

The 3rd Plasma Nanotechnologies and Bioapplications Workshop

Organizing committee

Mgr. Dana Skácelová, Ph.D. Chair of the 3rd PNB workshop

doc. Mgr. Dušan Kováčik, PhD.

Head of Plasma Nanotechnologies and Bioapplications research group

Mgr. Petra Šrámková, PhD.

Mgr. Jakub Kelar, Ph.D.

MSc. Pedram Ghourchi Beigi

SCIENTIFIC PROGRAM

MONDAY, 9th October 2023

- 15:00 17:30 Arrival & Check-in and accommodation
- 17:30 18:30 Registration
- 18:30 23:00 Welcome party

TUESDAY, 10th October 2023

- 7:00 8:30 Breakfast
- 8:45 9:00 Opening words

SECTION 1: Presenting the research of the participants from Germany

Chairman: Dušan Kováčik

- 9:00 9:40 Georg Avramidis (HAWK) Overview of the plasma research at the HAWK Göttingen
- 9:40 10:00 Jens Take & Johannes Baur (UNI-STUTTGART) Composite manufacturing technologies at the Institute of Aircraft Design
- **10:00 10:20** Johannes Baur (UNI-STUTTGART) Optimization of sustainable natural fiber reinforced composites
- **10:20 10:40** Jens Take (UNI-STUTTGART) Energy efficiency UV curing for composite parts
- 10:40 11:10 COFFEE BREAK

SECTION 2: New developments and diagnostics of DBD - part 1

Chairman: Jakub Kelar

 11:10 – 11:30
 Sebastian Dahle (UNI-LJUBLJANA)

 Dielectric barrier discharge treatments of heterogeneous and structured substrates

- 11:30 11:50Michal Pazderka (MUNI)Cr-doped alumina ceramics and their properties
- 11:50 12:10 Michal Pazderka (MUNI)

Recent developments in electronics for DBD and measurements

12:30 – 14:00 Lunch

SECTION 3: New developments and diagnostics of DBD – part 2

Chairman: Mirko Černák

- 14:00 14:20Richard Krumpolec (MUNI)New low temperature atmospheric plasma source for remote
plasma surface modification of materials
- 14:20 14:40Jianyu Feng (MUNI)Atmospheric pressure plasma diagnostics by ion mobility
spectrometry and mass spectrometry
- 14:40 –15:00 Vlasta Štěpánová (MUNI) Measurement of ozone concentration produced by MSDBD
- 15:00 –16:00 COFFEE BREAK

SECTION 4: Plasma and glass processing

Chairman: Tomáš Homola

- 16:00 16:20Dušan Kováčik/Richard Krumpolec (MUNI)Atmospheric plasma technology for large area modification of float
glass and polymer interlayers for laminated glass
- 16:20 16:40 Jakub Kelar (MUNI) Surface treatment of glass and its influence on the reliability of adhesive bonding
- 16:40 17:00 Slavomír Sihelník (MUNI)
 Effects of ambient air plasma on flexible glass before deposition of PEDOT:PSS thin films: In-depth XPS analysis
- 17:00 18:30 Free time & Informal discussion
- 18:30 20:00 Dinner

WEDNESDAY, 11th October 2023

7:00 – 8:45	Breakfast	
SECTION 5: Plasma in contact with liquids & Plasma water purification		
	Chairman: Anna Zahoranová	
9:00 – 9:20	Zdenko Machala (FMPI CU) Plasma-liquid transport of reactive species underlies biomedical/agriculture applications	
9:20 – 9:40	Oleksandr Galmiz (FMPI CU) Quantifying the chemical compounds that emerge during the polymer processing by a SDBD utilizing liquid electrodes	
9:40 – 10:00	Jiří Fujera (MUNI) Comparative study of the efficacy of nitrogen fixation and fungal growth inhibition by various atmospheric-pressure plasma sources	
10:00 - 10:20	Tomáš Homola (MUNI) Low-cost biochar sorbents for eliminating pharmaceuticals and drugs from wastewaters	
10:20 - 10:40	František Zažímal (MUNI) Towards purification of water from antibiotics using photocatalytic and plasma processes	
10:40 - 11:10	COFFEE BREAK	
SECTION 6: Plasma and bioapplications		
	Chairman: Richard Krumpolec	
11:10 - 11:30	Leila Zahedi (MUNI) Preparing the electrospun nanofibers as a drug delivery substrate (system) assisted by atmospheric plasma	
11:30 - 11:50	Petra Šrámková (FMPI CU) Exploring the ageing behaviour of cold plasma treated pea seeds: physicochemical and physiological changes	
11:50 – 12:10	Zlata Kelar Tučeková (MUNI)	

Atmospheric pressure plasma-activated gaseous media and its implementation into decontamination process

12:30 – 13:30 Lunch

SECTION 7: Plasma reduced graphene oxide

Chairman: Dušan Kováčik

- 13:30 14:00 Richard Krumpolec (MUNI) Fast plasma-triggered reduction-exfoliation of graphene oxide and its applications
- 14:00 14:20František Zelenák (MUNI)Sorption and electrochemical properties of plasma reduced
graphene oxide paper
- 14:30 18:30 Trip or individual program
- 18:30 23:00 Dinner & Social event

THURSDAY, 12th October 2023

7:00 – 8:45 Breakfast

SECTION 8: Plasma surface processes

Chairman: Petra Šrámková

9:00 – 9:20	Dana Skácelová (MUNI) Plasma treatment of fabrics as a tool to increase mechanical parameters of FRP composites
9:20 – 9:40	Ali Jamaati Kenari (MUNI) Comparative study of different atmospheric-pressure plasma sources for surface treatment of BOPP foil
9:40 – 10:00	Sandra Ďurčányová (FMPI CU) Challenges in creating functional layers through atm. pressure plasma polymerization
10:00 - 10:20	Pedram Ghourchi Beigi (MUNI) Low-temperature atmospheric pressure plasma crosslinking of polysilazane coating
10:20 - 10:40	Martin Kuťka (FMPI CU) Graft polymerization of acrylic acid on PP membranes using plasma activation in argon or oxygen
10:40 - 11:10	COFFEE BREAK

9th - 12th October 2023, Hustopeče, Czech Republic

11:10 – 11:50 Dušan Kováčik, Mirko Černák

PNB research group & CEPLANT as open access LRI: current research activities and services; new and modernized equipment; further direction of research

- 11:50 12:30 Open discussion & Closing words
- 12:30 14:00 Lunch & Departure

The 3rd Plasma Nanotechnologies and Bioapplications Workshop

9th - 12th October 2023, Hustopeče, Czech Republic

List of participants

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MUNI SCI

9th - 12th October 2023, Hustopeče, Czech Republic

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ABSTRACTS

SECTION 2

New developments and diagnostics of DBD - part 1

DIELECTRIC BARRIER DISCHARGE TREATMENTS OF HETEROGENEOUS AND STRUCTURED SUBSTRATES

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Abstract

Among the non-thermal plasma technology, the dielectric barrier discharge (DBD) is a very common and versatile implementation, usable over a wide range of pressures and for applications on all types of materials. Most commonly, DBDs utilize ambient air at atmospheric pressure and exhibit a filamentary structure.



Fig. 1: A piece of hardwood being treated using a dielectric barrier discharge plasma. (Photo by Dr. Jure Žigon)

The filamentary nature of most DBD plasmas is not an issue by and in itself, but on materials with inhomogeneous properties or geometries, this can have a number of consequences (see fig.1). The treatment of heterogeneous or structured work pieces can lead to inhomogeneous or undesirable outcomes of the plasma treatment, and even to charring or other destructive effects.

In this contribution, we take a look at a number of specimens' features of heterogeneity and geometrical structuring, how these influence the plasma discharge formed in a DBD setup, their consequences for selected applications, and possible pathways to mitigate such effects,

Keywords: dielectric barrier discharge, wood, COMSOL

CR-DOPED ALUMINA CERAMICS AND THEIR PROPERTIES

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Abstract

Dielectric barrier discharges (DBDs) play an important role in many branches of industry as well as in plasma research. Due to the nature of the DBDs the dielectric barrier (e.g. ceramics) is in direct contact with plasma. Thus, changing properties of the dielectric barrier can affect properties of the discharge. The influence of the Cr doping on discharge properties was investigated because Cr forms a monophasic material with Al₂O₃, where Cr ions replace Al ions in alumina matrix. Properties of biphasic material (Al₂O₃ doped with MgAl₂O₄) were investigated in [1].

Cr-doped ceramics revealed an interesting property when used as a dielectric barrier for coplanar DBD. The sample doped with 1 vol% of Cr_2O_3 showed 11% decrease in ignition voltage compared to commonly used ELCERAM ceramics [2]. This decrease in ignition voltage was measured not only in well controlled pure nitrogen atmosphere but also in ambient air atmosphere.

Furthermore, curves of surface potential decay (SPD) [3] were measured for all considered ceramics. An interesting observation was made that samples doped with 10 vol% of Cr₂O₃ showed a significant change in charge trapping properties. The SPD for all samples but 10Cr dropped maximally to the 80% of initial value in 10 hours, however, SPD curve for 10Cr sample dropped below 10% of initial value

in 30 minutes. This suggests potential structural changes on grain boundaries that were not been observed yet.

Finally, Cr-doped ceramics were used as dielectric barrier also for atmospheric pressure Townsend discharge (APTD). Compared to commonly used alumina ceramics (e.g. ELCERAM ceramics), some ceramics showed significantly greater working domain of APTD in voltage amplitude as well as shift towards higher frequencies. This shows relevance of Cr-doped ceramics for plasma research and applications.



Fig. 1: Alumina ceramics doped with 3% Cr₂O₃ equipped with electrode system and placed on holder with connector for HV.

Acknowledgments: This research has been supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic. CzechNanoLab project LM2018110 funded by MEYS CR is gratefully acknowledged for the financial support of the measurements at CEITEC Nano Research Infrastructure.

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RECENT DEVELOPMENTS IN ELECTRONICS FOR DBD AND MEASUREMENTS

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Abstract

Dielectric barrier discharges (DBDs) become these days more and more important in various branches of industry as well as in research. Electrodes for DBD usually contain metallic electrodes connected to high voltage and dielectric barrier (e.g. ceramics, quartz glass, etc.) that prohibit discharge to promote into an arc. The main consequence dielectric barrier's presence is the limitation of the discharge lifetime. For example, full width at half maximum (FWHM) of current peaks for volume DBD in ambient air can be of the order of 1-10 ns [1]. However, the frequency of power supplies for DBD (for sinusoidal profiles) is usually of the order of 10 kHz. Thus, the active phase of the discharge is a relatively small ratio of the full period.

It could be beneficial to increase the ratio of the active phase of discharge for various applications, e.g., ozone production, CO₂ conversion, etc. It can be assumed that the FWHM does not change dramatically. Therefore, a possible way to increase the active phase of DBD could be to increase number of individual gas breakdowns in a period (increase power) or decrease the period (increase frequency). Therefore, it would be beneficial to increase the usable frequency given by power supplies.

A modification towards higher frequencies requires the modification of highvoltage (HV) transformers used for DBDs. To reach a level of MHz, it is necessary to reduce the leakage inductance of HV transformer as much as possible. This can

be done by using planar transformers [2]. We implemented the planar transformer technology for DBDs and it was possible to reach up to 2.8 MHz with small coplanar DBD. An interesting properties of coplanar DBDs appeared, e.g. light emission from the discharge is present during the full period of the discharge in an Ar + N_2 mixture or even in a pure N_2 atmosphere.

Such behavior is welcome for applications like atomizers.

Acknowledgments: This research has been supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic and GF23-05974K funded by Czech Science Foundation.

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SECTION 3

New developments and diagnostics of DBD - part 2

NEW LOW TEMPERATURE ATMOSPHERIC PLASMA SOURCE FOR REMOTE PLASMA SURFACE MODIFICATION OF MATERIALS

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Abstract

Plasma surface modifications play important role in modern surface processing technologies of materials. Low-cost, chemical free, fast-throughput and effective scalable plasma technologies working at atmospheric pressure are preferred by industry.

Atmospheric pressure plasma technology based on diffuse coplanar surface barrier discharge (DCSBD) with its unique properties proved the capability to meet the industry requirements for fast, effective, robust and scalable solution of surface modification of various materials. DCSBD technology has been widely used for surface activation of glass, polymer and textiles modification, as well as for treatment of e.g., seeds and plants.

High power density, plasma uniformity, robustness and virtually unlimited lifetime of the electrode system and capability to generate scalable atmospheric pressure plasma in all technically important gases make DCSBD very versatile technology for large area plasma surface modification of materials. DCSBD generates atmospheric plasma of high-power density of ~ 100 W.cm⁻³ because it is generated as a thin film of plasma of effective thickness ~ 0.3 mm. This makes DCSBD very effective source for surface plasma modification of flat sheets and flexible foils/textiles.

Considering the limited active distance of the plasma, the conventional DCSBD system is not suitable for the modification of materials with rough and structured surface. Therefore, other plasma sources generating remote afterglow plasma are more suitable for such applications. Commercially available atmospheric plasma systems, however, generate highly localized discharge (plasma jets) or generate highly nonuniform plasma not suitable for temperature sensitive materials (gliding arc).

Considering the application potential of treatment of various 3D surfaces, we designed a new plasma source based on DCSBD technology (Fig. 1) suitable for remote low temperature treatment of rough, curved and structured surfaces carried out at effective treatment distance 1-20 mm.

The operational parameters of the plasma system and generated plasma, as well as examples of results of plasma modification of selected materials will be presented. The comparison between the new plasma source and conventional surface DCSBD plasma as well as similar commercial plasma systems generating remote plasma will be shown.

This research has been supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic.



Fig. 1: Snapshots of the discharge generated by a new DCSBD-based plasma source designed for remote treatment of materials.

Keywords: DCSBD plasma, remote plasma, low temperature plasma, plasma source, surface modification, activation, adhesion

ATMOSPHERIC PRESSURE PLASMA DIAGNOSTICS BY ION MOBILITY SPECTROMETRY AND MASS SPECTROMETRY

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Abstract

As it is well known, low-temperature plasma has been widely used in modern society due to its numerous advantages. In recent years, Diffuse Coplanar Surface Barrier Discharge (DCSBD) has been proven to be an efficient plasma source, especially for large-area surface modification of materials [1]. With the deepening of research, plasma generators based on DCSBD technology have been designed to meet different requirements. Plasma generators with different DCSBD configurations may produce different effects on the same target surface. This fact makes us curious about the types of ions generated by plasma generators with different DCSBD configurations. To identify the ions generated by plasma sources, the Ion Mobility Spectrometry (IMS) and Mass Spectrometry (MS) are suitable tools. IMS and MS are high-speed, sensitive, technically simple, and good selectivity analytical methods [2,3].

In this work, atmospheric pressure plasma, generated by five different types of plasma generators, in particular standard DCSBD units, such as DCSBD with small and large stripes, a remote plasma source based on DCSBD technology, and the plasma curtain (ULD 60), have been analyzed by IMS and MS methods with different experimental conditions. The experiments were carried out using a

homemade IMS (Fig. 1) and MS device installed at the Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava. The results of IMS measurements show that the plasma generated in ambient air can generate more active ions like NO_2^- (H₂O), NO_3^- , $N_2O_3^-$, NO_3^- (HNO₃). However, the main negative ions of the N₂ plasma are $CO_3^-/N_2O_2^-$ and CO_4^-/O_2^- (these ions are reactant ions in IMS without plasma). As for the results of MS measurement, it can be found that new ions like NO_2^- (HNO₂) (93 Da), NO_3^- (HNO₃) (125 Da) are generated by air plasma. In the case of plasma generated in the N₂, the type of negative ions is the same as that of Reactant Ions. We believe that the results will not only contribute to a deeper understanding of the atmospheric plasma generated by DCSBD technology, but also help us to select the plasma sources for future applications with specific requirements.



Fig. 1: The sketch of the IMS device.

Keywords: low-temperature plasma, plasma diagnosis, DCSBD, plasma curtain, ion mobility spectrometry (IMS), mass spectrometry (MS)

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MEASUREMENT OF OZONE CONCENTRATION PRODUCED BY MSDBD

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Abstract

The Multi-hollow Surface Dielectric Barrier Discharge (MSDBD) generated in ambient air at atmospheric pressure is frequently used for different purpose [1,2]. The concentration of produced gaseous products such as ozone is an important parameter [3], especially for remote plasma applications when the plasma-activated gaseous media is used for decontamination. Ozone concentration was measured using an ozone photometer. The motivation was to evaluate the influence of input power and gas flow rate used for MSDBD plasma generation on the ozone concentration. Both mentioned parameters affect the temperature of the ceramics plate and, therefore, the ozone production as well. It is generally known that ozone production / decomposition is temperature-dependent. The plasma generation at input power in the range of 10-30 W and air flow rate in the range of 1-20 L/min was investigated. It was observed that ozone concentration was decreasing with increasing gas flow rate. While higher input power led to higher ozone production. The temperature of the ceramics plate was monitored continuously during ozone concentration measurement.

Keywords: ozone generation; MSDBD

This research has been supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

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SECTION 4

Plasma and glass processing

ATMOSPHERIC PLASMA TECHNOLOGY FOR LARGE AREA MODIFICATION OF FLOAT GLASS AND POLYMER INTERLAYERS FOR LAMINATED GLASS

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Abstract

Ambient air atmospheric plasma generated by diffuse coplanar surface barrier discharge (DCSBD) was studied for in-line surface treatment of float glass and polymer interlayers for improvement of mechanical properties of laminated glass. Extremely high DCSBD plasma power density and uniformity, even at a very short plasma exposure time 4 seconds (i.e., treatment speed 2 cm/s), resulted in effective surface cleaning and activation of a glass surface. The effect of plasma studied on both tin- and airside of float glass revealed effective cleaning of glass with significantly improved micro- and macro-uniformity of glass surface also in comparison with the standard "wet" chemical cleaning protocol. As shown, a clean and uniform surface after ambient plasma treatment plays an important role in glass bonding. The improved micro-uniformity, together with increased adhesion properties, may eliminate local weak points that can initiate delamination and the subsequent formation of cracks in laminated glasses and thus lead to performance improvement of e.g., laminated safety glass products.

Special structural interlayers with large stiffness, such as SentryGlas Ionoplast interlayer, are available on the market for high-demanding glass applications, such as stairs, overhead glazings, and railings to increase the safety of the laminated glass. Ionoplast interlayers, however, require special processing. For example, in the case of multiply laminations, a chemical treatment of glass by a primer is needed for proper adhesion to the air side of the glass sheet. Ambient air atmospheric DCSBD plasma was therefore studied also for large area surface activation of SentryGlas Ionoplast interlayers and also for adhesion improvement to the air side of the float glass.

This research was done within TAČR Trend project together with two industry partners. In collaboration with the company OGB s.r.o, the research team of CEPLANT manufactured a tremendous number of laminated glasses. The samples were subsequently examined by official laboratory measurements carried out by IKATES, s.r.o. company. Various mechanical, optical, and thermal properties were tested even on real large area (2 m²) laminated glass samples (Fig. 1). The results show huge application potential of the DCSBD plasma technology with unique scalability, safety, energy efficiency and possibility of easy integration into commercial flat glass processing lines.

This research has been supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic.



Fig. 1: An example of large area 2 m² laminated glass after the Pendulum test manufactured with DCSBD plasma technology.

Keywords: float glass, ionoplast interlayer, DCSBD, plasma activation, cleaning, laminated glass, adhesion improvement

SURFACE TREATMENT OF GLASS AND ITS INFLUENCE ON THE RELIABILITY OF ADHESIVE BONDING

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Abstract

Glass load-bearing structural elements are currently used more often, but due to the brittle fracture of glass, it is necessary to design these structures with sufficient reliability. Adhesive joints have a number of advantages over mechanical connectors commonly used in construction. Adhesives can provide more uniform stress distribution along the connection; it does not weaken the bonded material and eliminate thermal bridges.

The main goal of this work is to effectively study atmospheric pressure plasma surface activation for the purpose of adhesion improvements between the glass surface and specially selected transparent adhesives. This approach will eliminate the need for the so-called primer interlayer, where the primer is usually considered a heavy chemical with significant environmental impact.

The presented results will dive into the preliminary results of three year project that is in its first year. The main focus of this experiment was an investigation of free surface energy and adhesion improvement studied by peel test measurements on different heat-treated and tempered glass surfaces.


Fig. 1: Example of bond measuring set for bond strength measurement

Keywords: plasma treatment, tempered glass, dielectric barrier discharge

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EFFECTS OF AMBIENT AIR PLASMA ON FLEXIBLE GLASS BEFORE DEPOSITION OF PEDOT:PSS THIN FILMS: IN-DEPTH XPS ANALYSIS

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The present study deals with the effects of surface modification of flexible glass using plasma generated in ambient air. Ultra-thin flexible glass (UTFG) is used as a substrate and packaging material for fabrication of optoelectronic devices such as displays, sensors and solar cells [1]. Plasma treatment is an effective tool for cleaning and activating the surface of small size glasses under laboratory conditions [2]. The aim of our work is the selection of a suitable plasma source and its operating parameters for use in real industrial conditions [3]. Three various plasma sources based on dielectric barrier discharges—DCSBD, industrial corona and Panel Treater were compared in order to replace standard liquid-cleaning protocol. Plasma-treated UTFG was consequently tested as a substrate for an organic conductive layer consisting of PEDOT:PSS. The effects of plasma treatment of UTFG and the properties of deposited layers were studied using advanced scientific analyses with emphasis on deep understanding of plasmachemical processes and their impact on the quality of deposited PEDOT:PSS-based layers (Fig. 1). The proportional distribution of concurrent processes of surface material

removal and polar groups incorporation revealed the mechanisms behind the effects of plasma treatment and subsequent storage of UTFG in ambient air. The electrical conductivity of PEDOT:PSS-based coatings sprayed on plasma-treated UTFG was two times higher compared to the (410 ± 50) S/cm value evaluated on liquid-cleaned samples. The achieved results provided valuable information about potential use of ambient air plasma treatment instead of wet liquid-cleaning to condition the UTFG surface prior to deposition of organic thin films.



Fig. 1: SEM-SE images of UTFG surface with PEDOT:PSS-based coating sprayed on a) uncleaned UTFG and, b) UTFG treated by DCSBD in roll-to-roll arrangement for 1 s.

This research has been supported by the projects CEPLANT LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic and VEGA 1/0488/19 funded by the Slovak Grant Agency.

Keywords: ultra-thin flexible glass, ambient air plasma sources, PEDOT:PSS layers, cleaning, activation, ageing recovery

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SECTION 5

Plasma in contact with liquids & Plasma water purification

PLASMA-LIQUID TRANSPORT OF REACTIVE SPECIES UNDERLIES BIOMEDICAL/AGRICULTURE APPLICATIONS

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Abstract

Atmospheric air plasma produces a cocktail of reactive oxygen and nitrogen species (RONS) with multiple functions relevant to applications in biomedicine, agriculture, air and water cleaning, etc. In plasmas interacting with liquids, the transport of RONS into the liquid through plasma-liquid interface can be significantly enhanced by converting bulk water to aerosol microdroplets [1]. The plasma discharge regime, deposited power, and gas flow conditions determine the plasma properties. Understanding physical, transport and chemical processes of the cold plasma-liquid interactions is crucial for the control of the chemical composition and biomedical effects of water and water solutions activated by air plasma for emerging applications in biomedicine and agriculture [2].

Figure 1 shows the schematic diagram of elementary processes of ionization, excitation and dissociation in air plasma, the formation of radicals and other RONS, as well as their mutual reactions in the gas phase. Then it shows their transport into the liquid water based on their solvation, indicating the Henry's law coefficients. Finally, in the liquid, the plasma-formed, as well as the new ionic RONS, diffuse and undergo further reactions [2].

Examples of successful applications of such plasma activated liquids for water or surface bacterial disinfection, biofilm treatment, dentistry, urinary tract infection treatment, cancer cell viability reduction and apoptosis induction, as well as plant

growth promotion will be shown. Besides the dominant effects of RONS, the synergy of peroxynitrites with pulsed electric field will be demonstrated.



Fig. 1: Plasma-liquid chemical and transport processes [2].

Keywords: non-thermal plasma, plasma-activated liquid, reactive oxygen and nitrogen species, electrospray, microdroplets, antibacterial effects

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QUANTIFYING THE CHEMICAL COMPOUNDS THAT EMERGE DURING THE POLYMER PROCESSING BY A SURFACE DIELECTRIC BARRIER DISCHARGE UTILIZING LIQUID ELECTRODES

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Abstract

In spite of the rapid expansion of low-temperature plasma physics and technology applications, numerous plasma processes remain inadequately comprehended, particularly the physical and chemical interactions occurring between plasmas and solid or liquid substrates. Consequently, it becomes imperative to implement precise diagnostic methodologies to quantify the flow of chemically active species generated during these processes, identify the relevant reaction pathways, customize product formations to suit specific applications, and gain further insight into plasma-induced reactivity.

Prior research has documented the utilization of Surface Dielectric Barrier Discharge (SDBD) configurations, which generate gaseous plasma at the interface with conductive liquids serving as electrodes, for the treatment of hollow dielectric structures, such as polymer tubes [1-3]. Despite the extensive development and application of such discharges for diverse purposes, dedicated experiments under well-defined conditions are required for further insights into the potential possibilities for plasma processing applications, especially for developing material processing technology.

In the presented work, we undertook the measurement and quantification of reactive oxygen and nitrogen species (RONS) generated both in the gaseous and

liquid phases. We explored their correlations with the power supplied to the reactor, the reactor's configuration, and their temporal evolution. Furthermore, we conducted an examination and quantification of by-products present in the liquid phase, particularly those arising during the processing of specific polymers by the SDBD.

Keywords: surface dielectric barrier discharge, liquid electrodes, RONS

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COMPARATIVE STUDY OF THE EFFICACY OF NITROGEN FIXATION AND FUNGAL GROWTH INHIBITION BY VARIOUS ATMOSPHERIC-PRESSURE PLASMA SOURCES

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Abstract

The ongoing interest in the study of electrical discharges in or with water is fueled both by the many unsolved problems concerning the mechanism of such complex discharges and also by possible novel applications of plasma-activated water (PAW). The applications of plasma-activated water, which are related to water decontamination, environmentally friendly synthesis of fertilizers, or plasmaassisted agriculture, appear to be the subject of rapidly expanding research [1]. In this comparison study, the efficacy of nitrogen fixation in PAW and its potential in inhibition of fungal growth were studied for three atmospheric plasma sources with various positions of discharge channels with respect to the water surface: surface DBD (plasma without direct contact with water surface), volume DBD (discharge channels perpendicularly touching water surface [2] (discharge channels parallel to the water surface). The properties of the plasma were studied

using electrical measurements and plasma-induced emission (PIE), while Fouriertransform infrared spectroscopy and ion chromatography were utilized to determine the chemical composition of outlet gas and PAW respectively. The biological effects of PAW were studied for three species of fungi (Botrytis cinerea, Penicillium italicum, and Aspergillus carbonarius) often encountered in agriculture, especially in the cultivation of citrus fruit and grapevines, with the possible aim of employing created PAW in modern hydroponics or aquaponics as decontaminants and/or nitrogen-based fertilizers. All three setups were flowthrough with a flow rate of 10 ml/min thus allowing for the continuous and stable generation of PAW over longer periods of time, further improving its potential industrial applicability.

Keywords: SDBD, VDBD, PAW, nitrogen fixation, fungal growth inhibition

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LOW-COST BIOCHAR SORBENTS FOR ELIMINATING PHARMACEUTICALS AND DRUGS FROM WASTEWATERS

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Abstract

The presence of pharmaceuticals and drugs in wastewater is a growing environmental concern due to their potential impacts on ecosystems and human health. This study focuses on the development and evaluation of low-cost biochar sorbents for the efficient removal of pharmaceutical residues from real wastewater samples. The adsorption performance of these sorbents was assessed using comprehensive liquid chromatography-mass

spectrometry (LC-MS) analysis, allowing for the identification and quantification of over 150 compounds.

The investigation aimed to provide insights into the efficacy of biochar materials in addressing the complex challenge of pharmaceutical contamination in wastewater.



Fig. 1: SEM image of biochar surface tested as adsorbent against pollutants in wastewater.

TOWARDS PURIFICATION OF WATER FROM ANTIBIOTICS USING PHOTOCATALYTIC AND PLASMA PROCESSES

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Abstract

It has been estimated the usage of antibiotics is in the range of 100,000 – 200,000 tons annually and nearly 70 % of the total volume is discharged into raw wastewater [1]. However, the current conventional wastewater treatment plants are not capable of complete purification of water from some antibiotics consequently leaking in small concentrations (from ng/L to μ g/L) to the aquatic environment [2]. Although present at low concentrations, long exposure to antibiotics yields potential risks to human health and the marine environment [3]. This leads the scientific community to study new environmentally friendly technologies for quaternary water purification. Our work focused on the applications of photocatalytic and plasma technologies feasible for the purification of water containing the cephalexin antibiotic. Cephalexin is a representative example of the large group the cephalosporins antibiotics and belongs to the commonly prescribed drug for the treatment of urinary or respiratory infections. The cephalosporins are detected in the aquatic environment and, similarly, as for other intensively used antibiotics, the main concern is related to the enhancement of antibiotic-resistant bacteria [4]. We study promising and relatively new (firstly

synthesized in the year 2014 [5]) biocompatible material showing photocatalytic activity against degradation of cephalexin or other antibiotics. It is graphitic carbon nitride (g-C3N4), which is an organic semiconductor with a band gap of around 2.8 eV allowing absorption in visible light spectra. However, current challenges need to be addressed, including suppressing the electron-hole recombination rate and tuning the optoelectronic and structural properties. To tackle these problems, we use low-temperature atmospheric pressure plasma generated in Diffuse Coplanar Surface Barrier Discharge (DCSBD) for the treatment of the g-C3N4 and study the properties of the plasma-modified material. The aim of our work is to use g-C3N4 of the desired photocatalytic properties in the laboratory-scale water treatment reactor, currently under development at our workplace. The design of the presented reactor utilizes a combination of various technologies: photocatalysts, UV/ VIS source of radiation and plasma units.

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SECTION 6

Plasma and bioapplications

COLD ATMOSPHERIC PRESSURE PLASMA TREATMENT OF SOYBEANS: CORRELATION BETWEEN GERMINATION, DNA DAMAGE AND PLASMA COMPOSITION

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Abstract

The use of cold atmospheric pressure (CAP) plasma in agriculture is a promising technology, which has been confirmed by many scientific studies [1]. The advantage of CAP plasma is its low-temperature approach, suitable also for heat-sensitive biomaterials, minimization of harmful chemicals, it works at atmospheric pressure, without the need for vacuum chambers and pumps, or rare gases. Over the past two decades, a lot of scientific knowledge has been obtained confirming the positive effect of CAP plasma on various types of seeds, but also on dry fruits, spices and nuts. It has been found that plasma treatment of seeds has both an effect on germination and growth parameters of seedlings as well as a decontamination effect on commonly occurring undesirable pathogens on the surface of seeds, which are currently mainly solved by coating the seeds with fungicides [2,3]. For a wider application of the technology, it is important to know the mechanism of interaction of CAP plasma as well as the safety of this technology from the point of view of possible DNA damage.

This study is focused on the correlation between the effect of plasma treatment on soybean seeds (Glycine max L.) and the main plasma parameters. A Diffuse coplanar surface barrier discharge (DCSBD) operating in nitrogen, ambient air and oxygen at atmospheric pressure was used as the CAP plasma source. Results of germination and the level of DNA damage of soybean seeds treated in different working gases $(O_2, N_2 \text{ and air})$ showed that the plasma treatment using ambient air is the most advantageous. Water contact angle (WCA) of samples treated in plasma showed a significant reduction of WCA values compared to the reference sample. Using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), we did not observe significant changes between the spectra of individual samples, which indicates that there is no damage on the surface of the samples during the treatment, only the binding of polar groups. The method of optical emission spectroscopy and Fourier transform infrared spectroscopy were used to study the plasma parameters. The most radiant system observed in ambient air and nitrogen plasma was the second positive system of nitrogen $N_2(C^3\Pi_u \rightarrow B^3\Pi_a)$. FTIR measurements showed the presence of reactive oxygen and nitrogen species O₃, NO₂, N₂O, NO, HNO₂ depending on the working gas.

In summary, it can be assumed that the positive effect of CAP plasma on the seed is caused not only by the individual components of the plasma, but also by their synergistic effect, while the treatment time and the ratio of individual active particles (plasma composition) are important for a specific type of seed.

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Keywords: atmospheric pressure plasma, soybean seeds, germination, DNA damage, plasma diagnostics

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PREPARING THE ELECTROSPUN NANOFIBERS AS A DRUG DELIVERY SUBSTRATE (SYSTEM) ASSISTED BY ATMOSPHERIC PLASMA

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Abstract

Electrospinning (ES) is a versatile method employed to fabricate an artificial extracellular matrix (ECM) with precise control over parameters such as voltage, distance, and flow rate, which is essential for mimicking the natural ECM [1]. Developing efficient drug carrier systems necessitates formulating a composite structure comprising a matrix (polymer) and a filler (drug carrier, with or without the drug). While various polymers possess distinct properties, the paramount requirement for a drug delivery system is biodegradability, given its intended implantation within the body [2].

This study explores the application of three distinct polymers, namely Polyhydroxybutyrate (PHB), Polylactic acid (PLA), and Polycaprolactone (PCL), each tailored for specific drug delivery objectives. The key objective is to produce nanofibers with minimal diameter, as smaller fiber diameters facilitate quicker dissolution and enhance the release kinetics of pharmaceutical components [3]. To achieve this, we employ diffuse coplanar surface barrier discharge (DCSBD) technology, which allows the fabrication of even finer nanofibers while maintaining parameters consistent with conventional ES devices.

In parallel, an innovative approach is pursued wherein the surface of biocompatible reduced graphene sheets [4] undergoes treatment with air and nitrogen plasmas to enhance surface stability, rendering them suitable for pharmaceutical applications. This research endeavors to enhance both the efficiency and biocompatibility of drug delivery systems employing graphene-based materials. The study aims to push the boundaries of drug delivery systems by improving the characteristics of graphene-based materials. These efforts are anticipated to lead to pharmaceutical applications that are not only more effective but also safer and more compatible with the human body.

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Keywords: Electrospinning, PHB, PLA, PCL, rGO, DCSBD.

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EXPLORING THE AGEING BEHAVIOUR OF COLD PLASMA TREATED PEA SEEDS: PHYSICOCHEMICAL AND PHYSIOLOGICAL CHANGES

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Abstract

The application of non-thermal plasmas in agriculture is nowadays an emerging and exciting topic in the interdisciplinary community involving plant physiologists, genetists, plasma physicists and plasma chemists. Plasma treatment of sensitive biological material such as seeds is preferably done with non-thermal plasma generated at atmospheric pressure, which is a straightforward method to achieve the desired changes in a few seconds. Plasma treatment of seeds has already been shown to promote seedling germination and vigour [1] and to have a decontaminating effect on microorganisms on the seeds/dry fruits surface [2]. Plasma treatment can, therefore, be considered an environmentally friendly process, as it minimizes or completely eliminates the need for fungicides or pesticides [3], which is also economically advantageous.

However, measurements of physicochemical and physiological changes after plasma treatment are usually carried out immediately after seed exposure to the plasma. There is little information on the durability of the plasma-induced changes, but considering the so-called ageing effect on the seed surface is essential,

as the seeds must be stored and distributed in different places, which takes time. The ageing effect is well known for plasma-treated substrates of different compositions (glass, metal, plastic). Depending on the conditions of the plasma treatment and the nature of the substrate, the plasma-induced changes are not permanent, and the surface properties may reach the initial stage in time.

Our research aims to fill this knowledge gap on the ageing effect of seed properties induced by plasma. As a reference seed, we chose the pea (Saxon variety) treated with a non-thermal plasma generated by a diffuse coplanar surface barrier discharge (DCSBD) under different plasma treatment conditions. The physicochemical surface properties such as wettability, morphology and chemical changes of the plasma-treated seeds were determined by water contact angle (WCA) measurements, X-ray photoelectron spectroscopy (XPS), Fouriertransformed infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The physiological and genotoxicological characteristics of the plasmatreated pea seeds, such as germination, growth parameters (length of roots and aboveground part, their fresh and dry weights, germination vitality indices) and DNA damage (comet assay), were carried out on the seeds every week after plasma treatment over a period of five weeks.

The time course of the water contact angle measurements showed that the improved wettability achieved was still maintained five weeks after the plasma treatment. Similarly, in the tests on germination and seedling growth, the physiological properties induced by the plasma treatment were also maintained over a period of five weeks.

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ATMOSPHERIC PRESSURE PLASMA-ACTIVATED GASEOUS MEDIA AND ITS IMPLEMENTATION INTO DECONTAMINATION PROCESS

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Abstract

The plasma-activated gaseous media can decontaminate surfaces of different materials at remote distances. For this purpose, the multi-hollow surface dielectric barrier discharge was used for plasma activation of gaseous media to produce an atmosphere with a high ratio of hydrogen peroxide and/or ozone. These active species were generated in pure water vapour [1] and oxygen with an admixture of water vapour with an aim to determine parameters for efficient decontamination and/or sterilisation of thermally sensitive materials at atmospheric pressure.

The thermal and electrical properties of the used plasma source were measured. Optical emission spectroscopy was used to analyse the characteristics of the generated plasma. The reactive species in plasma-activated gas and condensed activated vapour were detected and compared for different plasma parameters, such as water vapour concentration, gas flow and source power input.

The generated media was then applied to microorganisms in the form of planktonic bacteria, bacterial biofilm, and bacterial spores, often used as biological indicators for standard sterilisers. The germicidal efficiency of short and long exposure to plasma-activated media was evaluated by standard microbiological

cultivation and fluorescence analysis using a fluorescence multi-well plate reader. The test was repeated at different distances from the plasma source.

The decontamination efficiency of plasma-activated water vapour increased with the exposure time and the plasma source power input. Similar results were obtained for the decontamination by plasma-activated oxygen and oxygen with the admixture of water vapour. The longer decontamination cycles (several hours) inactivated resistant bacterial spores and affirmed the possibility of achieving efficient microorganism inactivation. The main results of this study are a decontamination chamber prototype and verified technology for constructing scalable commercial plasma devices for utilisation in medicine and bioresearch.

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SECTION 7

Plasma reduced graphene oxide

FAST PLASMA-TRIGGERED REDUCTION-EXFOLIATION OF GRAPHENE OXIDE AND ITS APPLICATIONS

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A top-down approach by oxidation of graphite to graphene oxide (GO) and its reduction via various techniques gained popularity for a mass production of thin conductive graphene-like films. The most advantageous alternative to pure graphene is reduced graphene oxide (rGO) as it is almost alike graphene in terms of properties but can be easily manufactured in large scale using several reduction/exfoliation techniques. The known reduction/exfoliation techniques, however, have limitations such as high levels of toxicity, hazardousness, risk of explosions, and high time consumption. The complicated reduction/exfoliation of GO become a major bottleneck that restricts the large-scale production of rGO. The research team of CEPLANT have developed a simple, fast, low-cost and chemical-free fabrication method of 2D and 3D rGO structures using an electrical plasma-triggered reduction/exfoliation of 3D porous GO aerogel-like materials [2] and also 2D GO paper-like films [3] starting at temperatures not higher than 100 $^{\circ}$ C.

The exposition of the fabricated GO samples to low-temperature plasma, generated by atmospheric Diffuse Coplanar Surface Dielectric Barrier Discharge (DCSBD) in technical nitrogen or standard air, triggers the self-propagating reduction/exfoliation modification of GO into black rGO (Fig. 1, rGO paper sample), while the rGO structures retained its original shape without abrupt disintegration. The rapid modification of GO to rGO results in an approximately 10⁵-fold decrease of the rGO resistivity compared to the original GO. This novel plasma-triggered reduction/exfoliation method opens new opportunities for low-cost industrial-scale production of conductive rGO and rGO-based composites for various modern industrial applications. Methods of rGO impregnation to improve its mechanical properties will be presented. Moreover, we will show how fabricated rGO-based composites for electromagnetic shielding applications and b) rGO/GO composite membranes for water treatment applications.





Fig. 1: GO paper before and after the fast (<1s) plasma reduction; 3D aerogel-like GO and rGO samples (GO is left and rGO right).

This research has been supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

Keywords: graphene oxide, reduced graphene oxide, atmospheric plasma, DCSBD, reduction, exfoliation

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SORPTION AND ELECTROCHEMICAL PROPERTIES OF PLASMA REDUCED GRAPHENE OXIDE PAPER

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Abstract

Graphene based materials offer a plethora of possible applications across various research areas, ranging from material science, trough energy to bioapplications. Despite its potential, mass production is still of concern. Graphene oxide (GO) has the most promising potential for industrial scale production, as it can be easily processed to thin GO paper. However, GO needs to be further reduced to reduced graphene oxide (rGO) to restore electrical properties of the graphene structure. We developed scalable and fast methods for preparation and reduction-exfoliation of A4 format GO paper using vacuum spraying of GO suspension on to PTFE foil, followed by reduction utilizing Diffuse Coplanar Surface Barrier Discharge (DSCBD) [1]. During the rapid reduction, concurring exfoliation caused by released gaseous products expands the rGO paper from a few micrometers to tens of micrometers, making the material more fragile, yet still stiff enough for manipulation. (Fig 1a). Residual oxygen content in rGO after reduction by DCSBD plasma provides chemically active sites that are not present in pure defect-free graphene and combined with high porosity structure (>400 m^2/g), prepared rGO paper finds promising use in sorption and electrochemical applications. We will demonstrate the rGO paper potential in these fields in two specific applications: a) absorption of organic dyes and metallic ions from water solution and b) fabrication of simple flexible supercapacitors with rGO as active electrode material (Fig. 1b).



Fig. 1: a) rGO/GO paper cross section; b) Flexible supercapacitor.

This research has been supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

Keywords: graphene oxide paper, reduced graphene oxide paper, DCSBD, plasma reduction, dye absorption, supercapacitors

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SECTION 8

SECTION 8: Plasma surface processes

PLASMA TREATMENT OF FABRICS AS A TOOL TO INCREASE MECHANICAL PARAMETERS OF FRP COMPOSITES

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Abstract

Laminated fiber-reinforced polymer (FRP) composites are important materials with a wide range of applications due to their excellent specific stiffness and strength. Laminated FRP composites typically consist of synthetic and/or natural fabrics combined with thermoset or thermoplastic resin.

The final mechanical characteristics of FRP composites depend on different factors, such as fiber type, resin, and the construction of textile reinforcements, however, the fiber-resin interfacial adhesion is a crucial factor. Synthetic and natural fibers are the most used fibers in FRP composites, but their poor hydrophilic properties negatively affect interfacial adhesion, and subsequent surface pre-treatment is required [1,2].

Our research is focused on the fundamental research of plasma-enhanced fibermatrix interfacial bonding leading to improved properties of aramid, glass, and flax reinforcing fabrics. We have two main research targets (a) a study of the effect of plasma treatment on surface properties of aramid, glass, and flax fabrics used as reinforcing materials and (b) an investigation of the influence of plasma-treated reinforcing fabrics on the final mechanical properties of FRP composites.

Plasma treatment of aramid, glass, and flax fabrics significantly increased the wettability, improved the surface chemical activity, and slightly increased the

surface roughness. Our pilot tests lead to an improvement of mechanical properties of FRP composites.

Plasma treatment was realized by the various plasma sources, namely diffuse coplanar surface barrier discharge (DCSBD), commercial volume dielectric barrier discharge (VDBD), and curved DCSBD. The surface activation and wettability of fabrics were determined by the Washburn measurements, water contact measurements and strike-through test. The mechanical properties were studied by tensile tests. The morphology of modified fabric was investigated by SEM.

The obtained data will later be used to optimize the behavior and parameters of the laminated composites under specific loading regimes such as blast and ballistic loading.

Keywords: DCSBD, VDBD, FRP composites, glass fabrics, aramid fabrics, flax fabrics, wettability, surface activation

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COMPARATIVE STUDY OF DIFFERENT ATMOSPHERIC-PRESSURE PLASMA SOURCES FOR SURFACE TREATMENT OF BOPP FOIL

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Abstract

Polymers stand out for their low density, flexibility, ease of production, and costeffectiveness characteristics. One of the most frequently employed polymers is polypropylene. Biaxially oriented polypropylene (BOPP) foils are crafted by stretching molten polypropylene in both machine and transverse directions, yielding thin, transparent, and durable sheets. Through this process, BOPP foil acquires a range of valuable properties, including chemical resistance, exceptional optical qualities, high strength, lightweight attributes, and a great ability to protect against moisture. Consequently, BOPP foils find widespread utility in the electrical industry, as well as in gift wrapping and food packaging. Nonetheless, due to the inherent hydrophobicity of polypropylene and its low surface energy, certain limitations emerge in industries involving composite materials, printing, dveing, and coatings. To deal with these challenges, various surface modification techniques, such as physical, chemical, UV, and plasma treatments [1], are employed to enhance the wettability of BOPP films. Among these techniques, one of the most prevalent methods for polymer surface modification is cold plasma treatment, primarily generated through dielectric barrier discharges (DBDs) at atmospheric pressure. This approach boasts several advantages, including rapid treatment, absence of toxic waste and solvents, ease of control, a dry process, and the ability to induce anisotropic effects. Depending on the configuration of the plasma source and the choice of working gas, various chemical functional groups
and free radicals can be generated, leading to significant alterations in the polymer's surface properties. In this comparative study, we subjected thermally sensitive BOPP film to various atmospheric-pressure plasma sources, including a nitrogen multi-hollow surface dielectric barrier discharge (MSDBD) [2], an argon cylindrical plasma jet array [3], a diffuse coplanar surface barrier discharge (DCSBD) generated in ambient air and nitrogen gas [4], and a linear nitrogen DCSBD-based plasma system. The samples underwent plasma treatment for exposure times of 1 s, 5 s, and 10 s. To assess the wettability, morphology, and surface chemical composition of the plasma-treated BOPP film, we utilized water contact angle (WCA) measurements, scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) analyses. Additionally, adhesion properties were evaluated through peel force measurements. The surface wettability of the BOPP film treated with all plasma sources was examined by measuring the water contact angle (WCA) immediately after treatment, as well as after 1, 3, 7, and 21 days, to analyze treatment stability and potential aging effects. The most notable reduction in WCA, down to 37.9° from the reference sample's value of 100.8°, was observed immediately after treatment with the linear nitrogen DCSBD-based plasma system at a 10 second exposure time. However, the most stable treatment was observed with air DCSBD at a 5 second exposure time. SEM and roughness measurements produced similar results, confirming that the plasma sources are suitable for treating thermally sensitive materials. Furthermore, adhesion increased approximately fourfold immediately after treatment with air DCSBD. Overall, our findings emphasize the effectiveness of different atmospheric pressure plasma sources in enhancing the wettability and adhesion properties of thermosensitive BOPP films even after just 1 second of plasma exposure without any damage.

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CHALLENGES IN CREATING FUNCTIONAL LAYERS THROUGH ATMOSPHERIC PRESSURE PLASMA POLYMERIZATION

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Abstract

Preparation of thin, functional coatings is an important process in various industries. One way to prepare such coatings is plasma polymerization (PP), which uses a plasma source to deposit polymer-like layers. This method is an environmentally friendly alternative to conventional chemical polymerization, as it does not require solvents or catalysts to assist the polymerization process [1].

Properties of the deposited layers are influenced by a multitude of working conditions, including exposure time, flow rate, temperature, substrate properties, input power, electrode system configuration, etc. This provides the opportunity for a more precise tailoring of layer properties compared to conventional polymerization. By adjusting relevant parameters, it is possible to create layers with a desired thickness, chemical composition and functionality (protective, hydrophobic/hydrophilic, anti-corrosion, anti-icing etc.) [2].

This, however, poses a disadvantage for the reproducibility of PP experiments, since very slight variations in parameters that are not carefully controlled might negatively affect the results of the PP process. Although many works have been conducted on the topic of PP, it is still not clear how exactly each of the working

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conditions affects the layer properties and which ones play the key role. Thus, detailed PP research remains an important matter.

Our work aims to study and optimize PP of hexamethyldisiloxane (HMDSO) using a Diffuse Coplanar Surface Barrier Discharge (DCSBD) operating at atmospheric pressure to create functional layers on aluminum and glass. We built on our previous promising research in this field [3, 4]. The prepared layers were studied with surface diagnostics such as WCA, SEM, ATR-FTIR, XPS, and their stability was examined with ageing tests. The layer preparation process has undergone various modifications with the goal of improving reproducibility as well as functionality of the layers. We encountered several challenges related to achieving layer homogeneity and hydrophobicity, as well as new parameters of the PP process that affect the resulting layer properties and need to be taken into consideration.

This work was financially supported by the Slovak Grant Agency for Science VEGA (No. 1/0811/21).

Keywords: plasma polymerization, atmospheric pressure plasma, functional coatings, DCSBD, HMDSO

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LOW-TEMPERATURE ATMOSPHERIC PRESSURE PLASMA CROSSLINKING OF POLYSILAZANES COATING

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Abstract

Polysilazanes (PSZs), with a Si-N-Si backbone, are coating materials applicable to a wide range of substrates such as glass, metals, and polymers, which can be coated using various coating techniques, e.g., spin-, spray-, and dip-coating. They serve multiple purposes, such as anti-graffiti, anti-adherent, anti-fouling, anti-scratch, and anti-icing coatings.[1] While these coatings naturally self-crosslink at ambient conditions within seven days, high-temperature crosslinking (>150°C) limits their use with thermosensitive materials. [2]

This study explores the crosslinking of PSZ coatings using low-temperature atmospheric plasma generated by Multi-Hollow Surface Dielectric Barrier Discharge (MSDBD). This innovative approach utilizes active chemical species created by passing a working gas through the holes of MSDBD for "remote" treatment of the samples. This research presents a promising method for controlled, low-temperature plasma curing of PSZ coatings, expanding their utility to thermosensitive materials. This work offers possibilities for advanced PSZ coatings with improved durability and functionality.

The cross-linking process, which can be explained by substituting a nitrogen atom with an oxygen atom in the Si-N-Si backbone of the PSZ [3], was investigated by detecting Si-O and Si-N bonds through the ATR mode of FTIR and XPS analysis. Furthermore, water contact angle (WCA) measurements and surface free energy (SFE) calculations evaluated the coatings' hydrophobicity and can predict its

behavior as an anti-fouling and anti-bacterial coating. [4] These attributes are crucial for applications involving resistance to graffiti, fouling, etc.

Acknowledgment: This research has been supported by the project LM2023039, funded by the Ministry of Education, Youth and Sports of the Czech Republic.

Keywords: Plasma Curing, Cross-linking, Polysilazane Coating, Si-based Coating, MSDBD

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GRAFT POLYMERIZATION OF ACRYLIC ACID ON POLYPROPYLENE MEMBRANES USING PLASMA ACTIVATION IN ARGON OR OXYGEN

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Abstract

This work is focused on the preparation of microporous membranes with specific properties enabling their application as inter-electrode separators in alkaline water electrolysis cells for hydrogen production. The desired properties are mainly high conductivity of current-carrying OH⁻ ions and low permeability of molecular hydrogen and oxygen to suppress mutual contamination of these gases. These properties can only be achieved with good wettability of the membrane by aqueous alkaline electrolyte (usually 30 wt.% KOH) [1].

Nowadays, microporous separators are made of a composite of polymer, which gives them toughness, and ceramic filler, which is evenly dispersed in the material and gives the membranes wettability. However, to achieve the necessary wettability, a high amount of the ceramic filler is required, which reduces the mechanical strength [2]. In this work, wettability of polypropylene microporous membranes was achieved by plasma-initiated graft polymerization of acrylic acid. Membranes were activated in a low-pressure capacitively-coupled radiofrequency discharge in argon or oxygen, to compare two grafting methods, the trapped radical method and the hydroperoxide method. In the trapped radical method, argon plasma was used to create radicals required for grafting. In the hydroperoxide method, oxygen plasma was used to create hydroperoxide functional groups, which create radical when heated [3].

The grafted membranes were characterized by gravimetric grafting degree, ATR-FTIR spectroscopy, and scanning electron microscopy. To compare the

long-term stability of grafted membranes activated by argon and oxygen plasmas, aging tests in 30 wt.% KOH aqueous electrolyte were conducted. In addition, the membranes were characterized as separators in alkaline water electrolysis cell in terms of electrical resistance and diffusion flux of hydrogen through membranes.

The results of aging tests indicate that membranes grafted after argon plasma activation exhibit better stability over time than membranes grafted after oxygen plasma activation. All grafted membranes retained some polyacrylic acid copolymer after approximately 5000 hours even at elevated temperature of 60 °C. Results of electrical resistance and diffusion flux of hydrogen through membranes show that with higher grafting degree the values for both parameters are lower.

This work was financially supported by the Slovak Grant Agency for Science VEGA (No. 1/0811/21) and by Comenius University Grants 2023 (No. UK/209/2023).

Keywords: plasma-initiated graft polymerization, acrylic acid, microporous membrane, water electrolysis

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SCHEDULE

MON (Oct 9)	TUE (Oct 10)	WED (Oct 11)	THU (Oct 12)
	Opening words		
	Avramidis	Machala	Skácelová
		Galmiz	Jamaati Kenari
	Take & Baur	Fujera	Ďurčányová
	Take	Homola	Ghourchi Beigi
	Baur	Zažímal	Kuťka
	Coffee break	Coffee break	Coffee break
	Dahle	Zahedi	Kaufžili, Čamáli
	Pazderka	Šrámková	Kovácik, Černák
	Pazderka	Kelar Tučeková	Open discussion &
			Closing words
		Lunch	
	Lunch	Lunch	Lunch & departure
		Krumpolec	
	Krumpolec	Zelenák	
	Feng		
	Štěpánová		
	Coffee break	_	
Arrival, check-in and	Kováčík/Krumpolec	Trip or individual	
accommodation	Sihelnik	program	
	Kelar		
	Free time & Informal		
Registration	discussion		
	Dinner		
		Dinner	
Welcome party		&	
		social event	
	MON (Oct 9)	MON (Oct 9)TUE (Oct 10)Opening wordsAvramidisTake & BaurTake & BaurTake & BaurBaurCoffee breakDahlePazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaPazderkaFengSitépánováSihelníkKetarFree time & Informat discussionMelcome partyVelcome party	MON (Oct 9)TUE (Oct 10)WED (Oct 11)Opening wordsAvramidisMachalaAvramidisMachalaGalmizTake & BaurFujeraTake & BaurFujeraTake & BaurZažímalBaurZažímalCoffee breakCoffee breakDahleZahediPazderkaŠrámkováPazderkaŠrámkováPazderkaKrumpolecKrumpolecKrumpolecFengStěpánováStěpánováSihelníkrprogramKetarRegistrationDinnerWelcome partyDinnerVelcome partyDinner

Section 1	Presenting the research of the participants from Germany
Section 2 + Section 3	New developments and diagnostics of DBD
Section 4	Plasma and glass processing
Section 5	Plasma in contact with liquids & Plasma water purification
Section 6	Plasma and bioapplications
Secton 7	Plasma reduced graphene oxide
Section 8	Plasma surface processes
	PNB research group & CEPLANT presentation

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