ACS APPLIED MATERIALS & INTERFACES

Letter

www.acsami.org

Atmospheric Pressure Plasma-Initiated Chemical Vapor Deposition (AP-PiCVD) of Poly(diethylallylphosphate) Coating: A Char-Forming Protective Coating for Cellulosic Textile

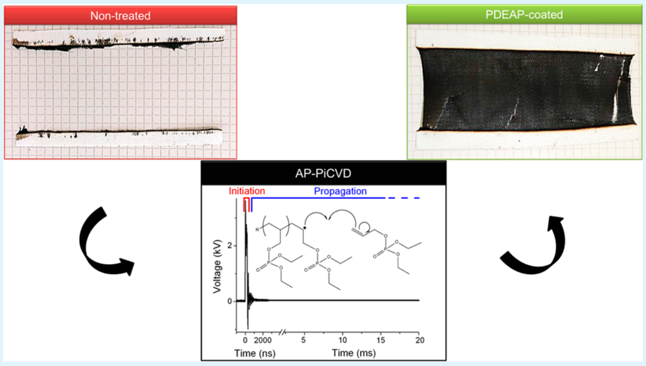
Florian Hilt,[†] Nicolas D. Boscher,*[,†] David Duday,[†] Nicolas Desbenoit,[†] Joëlle Levalois-Grützmacher,[‡] and Patrick Choquet[†]

[†]Science and Analysis of Materials Department , Centre de Recherche Public−Gabriel Lippmann, Belvaux L-4422, Luxembourg

[‡]Laboratory of Inorganic Chemistry, ETH Zürich, 8093 Zürich, Switzerland

Supporting Information

ABSTRACT: An innovative atmospheric pressure chemical vapor deposition method toward the deposition of polymeric layers has been developed. This latter involves the use of a nanopulsed plasma discharge to initiate the free-radical polymerization of an allyl monomer containing phosphorus (diethylallylphosphate, DEAP) at atmospheric pressure. The polymeric structure of the film is evidence by mass spectrometry. The method, highly suitable for the treatment of natural biopolymer substrate, has been carried out on cotton textile to perform the deposition of an efficient and conformal protective coating.



KEYWORDS: *atmospheric pressure plasma-initiated CVD, free-radical polymerization, char-forming coating, phosphorus-containing coatings, cotton fabrics*

The interest of textiles has been illustrated many times over and has flooded the market as they have been employed in a huge variety of applications. Among all the available textiles fibers, natural polymers are especially promoted because of their specific properties (biodegradable, excellent mechanical properties, etc.) and cotton textile is one of the most used for clothes or in household applications. However, it is also one of the most flammable materials, limiting oxygen index (LOI) = 18.5, and the durable fire resistance of this natural biopolymer made of cellulose fibers remains an unsolved issue.[1] Surface treatment is the only way to confer protective properties to biosourced polymers and it is of great interest to developed deposition methods to improve their fire resistance. Among all the known flame retardant materials, halogen-free phosphorus-based compounds are the most widely used on cotton textiles to prevent this latter from burning. Most of the methods to deposit phosphorus-containing thin films have been based on wet-chemistry.[2] However, wet methods present important drawbacks, such as the use of solvents and the impossibility to form conformal coatings, which are of great interest for complex shape substrates like polymer fibers.[3−5]

Chemical vapor deposition (CVD) processes have the capability to produce uniform and conformal organic thin films without involving the use of solvents, catalysts, or separation agents.[6] CVD methods are well-controlled processes and offer the possibility to easily tune the quantity of material by adjusting the thickness of the coating. In recent years, new CVD processes have been developed for the deposition of polymeric coatings,[3,7] which is interesting for improved monomer structure and properties retention. To perform the deposition of such coatings, initiating (iCVD) or oxidizing species (oCVD) can be introduced with the monomer to induce polymerization reactions.[8,9] However, the necessity to work at low-pressure remains a drawback for number of applications and the use of initiators or oxidizing species increases its environmental impact. Atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) is an attractive alternative as it works at atmospheric pressure under ambient temperature and does not require the use of monomer's auxiliary substances.[10−15] However, AP-PECVD generates a wide range of reactive species, which lead to undesirable side-reactions such as fragmentations and dissociations.[10,12,16,17] As a consequence, resulting coatings, called plasma-polymers, do not exhibit the repeating units structure of conventional polymers. The high degree of cross-linking and the integration of a lot of fragments into the structure[18] entail a loss of functionalities. It is known that organophosphorus compounds including ester phosphates derivatives such as DEAP interact with cellulose through acidic intermediates to

Received: July 24, 2014
Accepted: October 27, 2014
Published: October 27, 2014

dx.doi.org/10.1021/am504892q | *ACS Appl. Mater. Interfaces* 2014, 6, 18418−18422

reduce its flammability.[19] Therefore, the necessity to keep the phosphate pattern is a fundamental requirement.

To minimize the effect of the plasma on the monomer dissociation, PECVD can operate in the pulsed mode, where the plasma alternates on (t_{on}) and off periods (t_{off}).[10,12,16] It has been shown, from low-pressure works, that reducing the pulses duration from milli- to microseconds can improve the structural retention of monomers and preserve its functional groups.[20,21] Recently, studies have indicated that homogeneous dielectric barrier discharge (DBD) can easily be generated at atmospheric pressure using micro- or nanopulsed DC power supply.[22,23] Ultrashort square-pulsed DBD have been shown suitable for the treatment of various surfaces and have been investigated to promote hydrophobicity with organic−inorganic hybrid coatings[24] and to deposit dense inorganic silicon oxides thin films.[25,26] Nevertheless, in comparison to chopped AC AP-DBD, atmospheric pressure nanosecond square-pulsed DBD has never been investigated for the deposition of organic and polymer coatings. It is well-known that different mechanisms occur during t_{on} and t_{off} in chopped AC AP-DBD.[27] In particular, free-radical polymerization is known to propagate up to several tens of milliseconds during t_{off} provided that the t_{on} activates the monomer. This paper reports the possibility to deposit conventional poly(diethylallylphosphate) (PDEAP) homopolymer layers through a free-radical polymerization pathway initiated thanks to an ultrashort square-pulsed DBD. To reduce the impact of the plasma discharge, t_{on} duration was decreased to nanoseconds, whereas t_{off} was ranged from hundreds of microseconds to several tens of milliseconds in order to favor the free-radical polymerization reaction.[28] A series of thin films were grown from various duty cycles (i.e., various t_{off}) in a laboratory scale DBD reactor[29] fed with DEAP and argon. The coatings were further characterized and compared to bulk free-radical polymerized DEAP to highlight the potential of this novel process in providing conventional polymer while keeping the advantages related to plasma CVD (high adhesion, control of thickness, conformality).

Figure 1 shows the typical applied voltage waveform delivered by the AHTPB10F generator from Effitech (Gif-sur-Yvette, France) and investigated in this study. The voltage pulses, with a 2.5 kV amplitude, have a duration of 245 ns and a rising time of 45 ns. Two distinct current discharges, with durations of 40 and 70 ns, are produced at the rising and falling edges of each voltage pulse, respectively. The smooth curves of the current pulses indicate that two diffuse and homogeneous ultrashort discharges are produced for each period.[22,30,31] Such homogeneous discharges are particularly suitable for the treatment of fragile substrates such as polymer textiles. The voltage pulses, with a constant duration of 245 ns, were repeated with frequencies ranging from 50 Hz to 10 000 Hz (see Table S1 in the Supporting Information), allowing to investigate t_{off} from 0.1 to 20 ms and duty cycles (DC) from 0.001% to 0.2%. Regardless of the t_{off} duration, the voltage and current pulses were shown to be identical (see Figure S1 in the Supporting Information).

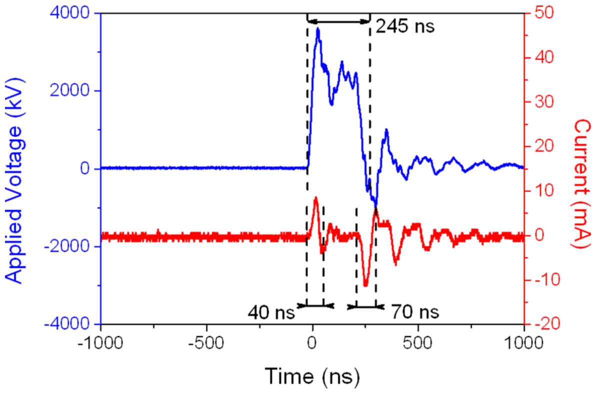


Figure 1. Traces of the voltage pulse and current discharges of an ultrashort square pulsed DBD.

Table S1 in the Supporting Information reports the relative atomic concentration of the different coatings obtained by XPS as a function of the duty cycle. The atomic concentrations of conventionally polymerized PDEAP and theoretical DEAP monomer are included as references. XPS compositions (Figure 2a) confirm the possibility to tune the chemistry of the coatings depending on the duty cycle used. High organic contents are present for low DC (i.e., 0.001 to 0.002%), whereas the amount of carbon clearly decreases when the duty cycle increases, indicating the higher fragmentation of the monomer. The loss of carbon is followed by a rise of oxygen quantity; meanwhile the concentration of phosphorus is almost constant. In comparison with the elemental concentration of the PDEAP used as reference, low DC are obviously needed to prevent the monomer from being significantly modified.

The FT-IR spectra of the PDEAP obtained by conventional free-radical polymerization and of the coatings obtained from nanosecond pulsed DBD for the conditions previously described are depicted in Figure 2b. Different chemistries can be outlined. The first ones (DC = 0.001% and 0.002%) lead to spectra with a fingerprint relatively close to the PDEAP pattern. The structure retention of the monomer is confirmed as the bands assigned to ν(P−O−C) and $\delta(CH_3)_{rocking}$ are conserved in accordance to the PDEAP reference spectrum. Only the difference in intensity of the bands has to be noticed, probably because of the difference of thickness. The second kind of coating's chemistry is observed for the highest duty cycles (DC = 0.02% and 0.2%) and differs from the reference. The disappearance of the vibration band associated with $\nu(CH_3)$ at 1105 cm^{-1} (DC = 0.02%) and the red-shift of the P−O group indicate a loss of the organic character of the coatings, which confirms the coating compositions obtained by XPS.

XPS and FT-IR have shown that the use of unipolar square nanosecond pulses with duty cycles as low as 0.001% is suitable for the deposition of coating with high monomer structure retention. In an attempt to go further in the analysis of the structure of the different coatings, high-resolution mass spectrometry (HR-MS) was performed. HR-MS may notably highlight the chemical structure disparities between the plasma deposited coatings and the PDEAP of reference (data not shown). After 2′,4′,6′-trihydroxyacetophenone monohydrate (THAP) matrix deposition on the coating, the mass spectrum was acquired in positive ion mode with the atmospheric pressure matrix assisted laser desorption/ionization mass spectrometry (AP-MALDI-MS). Molecular structures were identified and assigned thanks to the high mass accuracy provided by the Orbitrap analyzer (<2 ppm). The presented mass spectrum was obtained after subtraction of the matrix THAP signal. Figure 3a shows the molecular structure of PDEAP corresponding to the chemical formula: $[H-(C_7H_{15}PO_4)_nH + H]^+$ with "n" being the number of repeating units, the mass spectrum in mass range m/z = 100−1000 (Figure 3b), and the mass spectrum corresponding to the

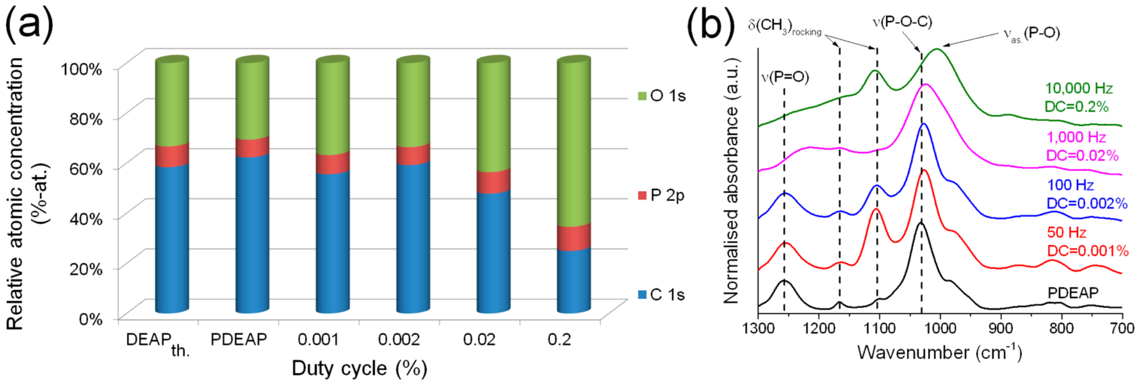


Figure 2. (a) Relative atomic concentration of the deposited films, PDEAP, and theoretical composition of DEAP. (b) FT-IR spectra of DEAP plasma polymers deposited using the conditions reported in Table S1 in the Supporting Information and of the PDEAP synthesized by conventional free-radical polymerization.

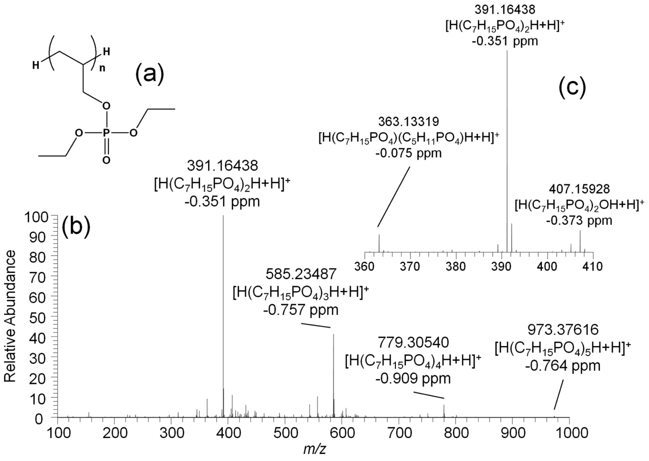


Figure 3. (a) Molecular structure of PDEAP and (b, c) AP-MALDI-Orbitrap mass spectra of the plasma-polymerized DEAP obtained at a duty cycle of 0.001% in mass range (b) m/z = 100−1000 and (c) m/z = 360−410.

enlargement in mass range m/z = 360−410 (Figure 3c). The mass spectrum was dominated by the PDEAP proton adduct with proton terminal groups $[H(C_7H_{15}PO_4)_nH + H]^+$. Moreover, oligomers were detected with a high mass accuracy (<1 ppm) and repeating units up to n = 9 (see Table S2 in the Supporting Information), which is the highest oligomer mass that can be detected because of the detection range limit of the Orbitrap mass analyzer (m/z = 2000). The enlargement shows two modifications of molecular structures corresponding to the C_2H_2 neutral loss at m/z = 363.13319 assigned to $[H(C_7H_{15}PO_4)(C_5H_{11}PO_4)H + H]^+$, and a hydroxyl terminal group at m/z = 407.15928 assigned to $[H(C_7H_{15}PO_4)_2OH + H]^+$, with a low mass deviation of −0.075 ppm and −0.373 ppm, respectively. These two modifications were also detected with oligomers composed of up to n = 9 repeating units.

AP-PiCVD have been reported to allow the synthesis of conventional poly(diethylallylphosphate) coatings by free-radical polymerization using low frequency unipolar and nanosecond square pulsed DBD. This high-potential proof-of-concept has been effectively up-scaled as an opening perspective for industrial production within the field of flame retardancy. The deposition was then carried out in a semi-industrial AP-DBD prototype, described elsewhere,[32] to treat larger substrates (typically of DIN-A4 size) and then to proceed to the fireproofed test on cotton fabrics. The up-scaling deposition experiment was performed using the condition corresponding to a duty cycle of 0.001%, which was previously shown to lead to plasma coatings similar to conventional polymers. It has to be mentioned that the structure of the coating deposited with this semi-industrial prototype was checked by HR-MS and confirms that a conventional PDEAP was deposited. Moreover, it was confirmed by SEM that the nanosecond pulsed plasma did not degrade the cotton fabrics, as it did not present any burn trace or any other alteration in its outward appearance at the micron scale (Figure 4g). Likewise, its tensile or tear strengths are not affected and the soft handle of the fabric has been preserved. The treated fabric reveals a weight gain of 3.3 mg, which would represents a relative polymer add-on on the fiber material of 0.3% (w/w) and a considerably low estimated P atom content (0.05% w/w). However, the measured weight gain and the values calculated from it are likely to be underestimated because of a highly plausible water loss of the cotton fabrics. Indeed, cotton is known to absorb a lot of water from air and exposure of the fibers to the plasma discharge could lead to a non-negligible loss of water resulting in an underestimated weight gain during the deposition process.

The generated homogeneous discharge is then proved to be suitable for the surface treatment of thermally sensitive biobased cellulosic substrates. The burning behavior of the PDEAP treated cellulosic sample has been investigated by means of LOI measurement, which is a straightforward and reliable analysis to compare the flammability of different polymers. The LOI value and the amount of residual char left after burning of the plasma-coated cellulosic fabric is indicated in Table S1 in the Supporting Information in comparison to untreated cotton. Flame retardant test exhibits a consistent LOI of 21.0 which is 2.5 units higher than the value of pure cotton fabric (18.5). However, this value is not sufficient to promote significant flame retardant properties. This is not surprising, as the amount generally required for this class of phosphorus-containing polymer to observe a relevant flame retardant effect (LOI > 27%)[4,33] is about 3% (w/w). Nevertheless, more than the LOI value is the high amount of remaining char of the PDEAP-treated cotton which is interesting (i.e., 18% of the initial mass remaining after combustion), whereas almost no char remains for the untreated cotton. These results clearly evidence the higher flammability of the untreated cotton fabric compared to the plasma treated one (Figure 4). SEM pictures provide a closer look on the treated fabrics before (Figure 4g)

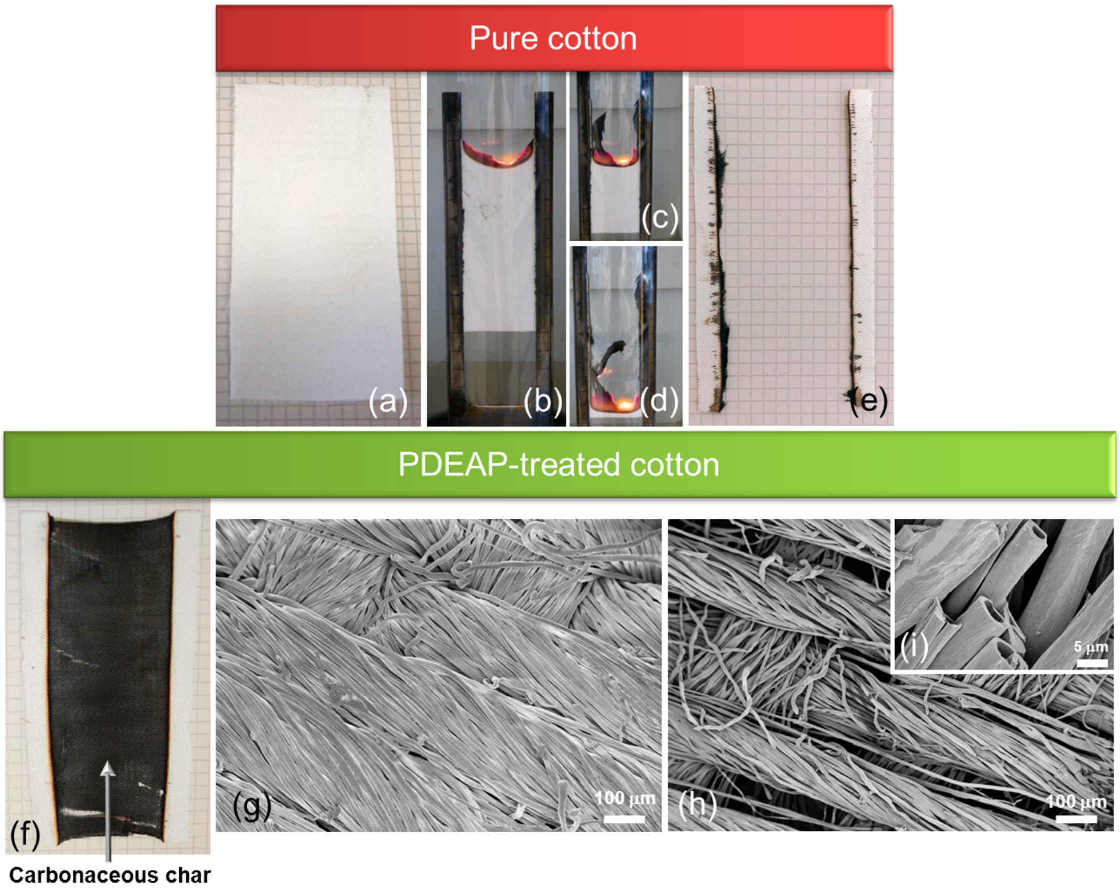


Figure 4. Photographs of (a) the pure cotton before the LOI test, (b) after 5 s of burning, (c) after 60 s of burning, (d) after 120 s of burning, (e) the pure cotton after the LOI test, and (f) the PDEAP-treated cotton after the LOI test and its char residue. SEM pictures of PDEAP-treated cotton (g) before and (h) after the LOI test. (i) Magnification of h.

and after the burning test (Figure 4h, i). The surface of the treated cellulosic fabric (Figure 4g) is smooth and uniform and does not exhibit any stacking of polymer in between and above the fibers. This suggests the formation of a thin homogeneous film gaining the surface of the fibers, allowing the breathability of the fabric. After burning, the structure of the fabric is perfectly retained as can be seen in Figure 4h. Interestingly, a deeper look (Figure 4i) indicates that the fibers are totally hollow. These observations confirm the presence of a homogeneous thin protective film on the surface of the fibers that, by reaction with the cellulose during the pyrolysis, promote the formation of char. This is consistent with an active condensed phase mechanism of the plasma PDEAP coating as usually observed for phosphorus-based flame retardants. As indicated by the hollow structure of the char, this effect is limited to the external layers of the cellulosic fibers. These results suggest that the deposited polymer via the AP-PiCVD process is conformal around all the fibers and maintain all its structural properties allowing the reduction of the fabric flammability, without affecting the properties of the cotton textile.

In conclusion, unipolar square nanopulses have been employed to polymerize diethylallylphosphate via free-radical polymerization through a novel method: Atmospheric Pressure Plasma-initiated Chemical Vapor Deposition (AP-PiCVD). Although ultrashort high voltage pulses create large quantities of energetic electrons, ions, radicals and metastables (in the gas phase containing the vaporized precursor), which can initiate the free-radical polymerization of the allyl monomer, the long t_{off} periods enable the propagation of the monomer free radicals to form PDEAP. It has been underlined that the duty cycle should be reduced (i.e., the t_{off} increased) to prevent the monomer from being fragmented and allow the reactive DEAP free radicals to propagate. This concept has been up-scaled to test its utility for functional coatings on a sensitive and complex biopolymer (cotton textile). The elaboration of a catalytic coating, which promotes the development of a char has been achieved and encouraging results (char yield = 18%) have been obtained, with a low content of phosphorus, as a perspective to future development of the concept.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further description of the experimental section and further details on the results and discussion section. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nboscher@lippmann.lu.

Author Contributions

All authors have given approval to the final version of the manuscript.

Funding

The present research work has been undertaken in the framework of the FRCOATINGS project, funded by the

"Fonds National de la Recherche" of Luxembourg (FNR), and of the self-funded PLASURF project.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Luxembourgish "Fonds National de la Recherche" (FNR) for financial support through the FRCOATINGS project. The authors thank S. Paquet and J.-P. Brasile from EFFITECH, and A. Robert and A. Moschetta from CRP-GL for their skilful help with the ultrashort square pulse source. Dr. G. Frache and J. Didierjean from CRP-GL and J.E. Low from ETH Zürich are gratefully acknowledged for their help with mass spectrometry, XPS measurements, and LOI tests.

■ REFERENCES

(1) Lewin, M. Unsolved Problems and Unanswered Questions in Flame Retardance of Polymers. *Polym. Degrad. Stab.* **2005**, *88*, 13−19.

(2) Guerrero, G.; Alauzun, J. G.; Granier, M.; Laurencin, D.; Mutin, P. H. Phosphonate Coupling Molecules for the Control of Surface/Interface Properties and the Synthesis of Nanomaterials. *Dalton Trans.* **2013**, *42*, 12569−12585.

(3) Alf, M. E.; Asatekin, A.; Barr, M. C.; Baxamusa, S. H.; Chelawat, H.; Ozaydin-Ince, G.; Petruczok, C. D.; Sreenivasan, R.; Tenhaeff, W. E.; Trujillo, N. J.; Vaddiraju, S.; Xu, J.; Gleason, K. K. Chemical Vapor Deposition of Conformal, Functional, and Responsive Polymer Films. *Adv. Mater.* **2010**, *22*, 1993−2027.

(4) Tsafack, M. J.; Levalois-Grützmacher, J. Flame Retardancy of Cotton Textiles by Plasma-Induced Graft-Polymerization (*PIGP*). *Surf. Coat. Technol.* **2006**, *201*, 2599−2610.

(5) Kamlangkla, K.; Hodak, S. K.; Levalois-Grützmacher, J. Multifunctional Silk Fabrics by means of the Plasma Induced Graft Polymerization (PIGP) process. *Surf. Coat. Technol.* **2011**, *205*, 3755−3762.

(6) Choy, K. L. Chemical Vapour Deposition of Coatings. *Prog. Mater. Sci.* **2003**, *48*, 57−170.

(7) Sreenivasan, R.; Gleason, K. K. Overview of Strategies for the CVD of Organic Films and Functional Polymer Layers. *Chem. Vap. Deposition* **2009**, *15*, 77−90.

(8) Coclite, A. M.; Gleason, K. K. Initiated PECVD of Organosilicon Coatings: A New Strategy to Enhance Monomer Structure Retention. *Plasma Process. Polym.* **2012**, *9*, 425−434.

(9) Tenhaeff, W. E.; Gleason, K. K. Initiated and Oxidative Chemical Vapor Deposition of Polymeric Thin Films: iCVD and oCVD. *Adv. Funct. Mater.* **2008**, *18*, 979−992.

(10) Massines, F.; Sarra-Bournet, C.; Fanelli, F.; Naudé, N.; Gherardi, N. Atmospheric Pressure Low Temperature Direct Plasma Technology: Status and Challenges for Thin Film Deposition. *Plasma Process. Polym.* **2012**, *9*, 1041−1073.

(11) Tendero, C.; Tixier, C.; Tristant, P.; Desmaison, J.; Leprince, P. Atmospheric Pressure Plasmas: A Review. *Spectrochim. Acta, Part B* **2006**, *61*, 2−30.

(12) Merche, D.; Vandencasteele, N.; Reniers, F. Atmospheric Plasmas for Thin Film Deposition: A Critical Review. *Thin Solid Films* **2012**, *520*, 4219−4236.

(13) Pappas, D. Status and Potential of Atmospheric Plasma Processing of Materials. *J. Vac. Sci. Technol. A* **2011**, *29*.

(14) Kogelschatz, U. Dielectric-Barrier Discharges: Their History, Discharge Physics, and Industrial Applications. *Plasma Chem. Plasma Process.* **2003**, *23*, 1−46.

(15) Fridman, A.; Chirokov, A.; Gutsol, A. Non-Thermal Atmospheric Pressure Discharges. *J. Phys. D* **2005**, *38*, R1−R24.

(16) Friedrich, J. Mechanisms of Plasma Polymerization − Reviewed from a Chemical Point of View. *Plasma Process. Polym.* **2011**, *8*, 783−802.

(17) Fouquet, T.; Petersen, J.; Ziarelli, F.; Bour, J.; Toniazzo, V.; Ruch, D.; Charles, L. Insights in the Architecture of Silicon-Based Plasma Polymers Using Partial Network Ethanolysis Combined with Electrospray Tandem Mass Spectrometry. *Plasma Process. Polym.* **2013**, *10*, 271−284.

(18) Bour, J.; Charles, L.; Petersen, J.; Michel, M.; Bardon, J.; Ruch, D. Insights in Molecular Structure of Organosilicon Plasma Polymer Produced by means of Atmospheric Pressure Dielectric Barrier Discharge Process. *Plasma Process. Polym.* **2010**, *7*, 687−694.

(19) Gaan, S.; Sun, G. Effect of Phosphorus and Nitrogen on Flame Retardant Cellulose: A Study of Phosphorus Compounds. *J. Anal. Appl. Pyrolysis* **2007**, *78*, 371−377.

(20) Tarducci, C.; Schofield, W. C. E.; Badyal, J. P. S.; Brewer, S. A.; Willis, C. Monomolecular Functionalization of Pulsed Plasma Deposited Poly(2-hydroxyethylmethacrylate) Surfaces. *Chem. Mater.* **2002**, *14*, 2541−2545.

(21) Han, L. M.; Timmons, R. B. Pulsed-Plasma Polymerization of 1-Vinyl-2-Pyrrolidone: Synthesis of a Linear Polymer. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 3121−3129.

(22) Fang, Z.; Shao, T.; Ji, S.; Pan, J.; Zhang, C. Generation of Homogeneous Atmospheric-Pressure Dielectric Barrier Discharge in a Large-Gap Argon Gas. *IEEE Trans. Plasma Sci.* **2012**, *40*, 1884−1890.

(23) Shao, T.; Yu, Y.; Zhang, C.; Zhang, D.; Niu, Z.; Wang, J.; Yan, P.; Zhou, Y. Excitation of Atmospheric Pressure Uniform Dielectric Barrier Discharge Using Repetitive Unipolar Nanosecond-Pulse Generator. *IEEE Trans. Dielectr. Electr. Insul.* **2010**, *17*, 1830−1837.

(24) Xu, J.; Zhang, C.; Shao, T.; Fang, Z.; Yan, P. Formation of Hydrophobic Coating on PMMA Surface Using Unipolar Nanosecond-Pulse DBD in Atmospheric Air. *J. Electrostat.* **2013**, *71*, 435−439.

(25) Opalinska, T.; Ulejczyk, B.; Schmidt-Szalowski, K. Applications of Pulsed Discharge to Thin-Film Deposition. *IEEE Trans. Plasma Sci.* **2009**, *37*, 934−940.

(26) Okazaki, K.; Nozaki, T. Ultrashort Pulsed Barrier Discharges and Applications. *Pure Appl. Chem.* **2002**, *74*, 447−452.

(27) Manakhov, A.; Moreno-Couranjou, M.; Boscher, N. D.; Rogé, V.; Choquet, P.; Pireaux, J. J. Atmospheric Pressure Pulsed Plasma Copolymerisation of Maleic Anhydride and Vinyltrimethoxysilane: Influence of Electrical Parameters on Chemistry, Morphology and Deposition Rate of the Coatings. *Plasma Process. Polym.* **2012**, *9*, 435−445.

(28) Boscher, N. D.; Choquet, P.; Duday, D.; Hilt, F. Method for Forming Regular Polymer Thin Films using Atmospheric Plasma Deposition, Luxembourg Patent Application LU92445.

(29) Hilt, F.; Duday, D.; Gherardi, N.; Frache, G.; Bardon, J.; Choquet, P. Plasma Deposition of an Organophosphorus Coating at Atmospheric Pressure. *Plasma Process. Polym.* **2013**, *10*, 556−563.

(30) Walsh, J. L.; Kong, M. G. 10 ns Pulsed Atmospheric Air Plasma for Uniform Treatment of Polymeric Surfaces. *Appl. Phys. Lett.* **2007**, *91*, 1−3.

(31) Yang, D. Z.; Yang, Y.; Li, S. Z.; Nie, D. X.; Zhang, S.; Wang, W. C. A Homogeneous Dielectric Barrier Discharge Plasma Excited by a Bipolar Nanosecond Pulse in Nitrogen and Air. *Plasma Sources Sci. Technol.* **2012**, *21*, 1−9.

(32) Boscher, N. D.; Choquet, P.; Duday, D.; Verdier, S. Advantages of a Pulsed Electrical Excitation Mode on the Corrosion Performance of Organosilicon Thin Films Deposited on Aluminium Foil by Atmospheric Pressure Dielectric Barrier Discharge. *Plasma Process. Polym.* **2010**, *7*, 163−171.

(33) Tsafack, M. J.; Levalois-Grützmacher, J. Plasma-Induced Graft-Polymerization of Flame Retardant Monomers onto PAN Fabrics. *Surf. Coat. Technol.* **2006**, *200*, 3503−3510.