ACS Sustainable Chemistry & Engineering

Letter

Cite This: ACS Sustainable Chem. Eng. 2018, 6, 104−109

pubs.acs.org/journal/ascecg

Paprika, Gallic Acid, and Visible Light: The Green Combination for the Synthesis of Biocide Coatings

Pauline Sautrot-Ba,[†] Jean-Pierre Malval,[‡] Mathilde Weiss-Maurin,[†,§] Jerôme Paul,[†] Agata Blacha-Grzechnik,[∥] Somia Tomane,[†] Pierre-Emmanuel Mazeran,[⊥] Jacques Lalevée,[‡] Valérie Langlois,[†] and Davy-Louis Versace*[,†]

[†]Université Paris-Est Créteil (UPEC), 61, Avenue Général de Gaulle, 94010 Créteil Cedex, Institut de Chimie et de Matériaux Paris-Est, Equipes Systèmes Polymères Complexes, UMR CNRS 7182, 2-8 rue Henri Dunant-94320, Thiais, France

[‡]Institut de Science des Matériaux de Mulhouse, IS2M-LRC 7228, 15 rue Starcky-68057, Mulhouse, France

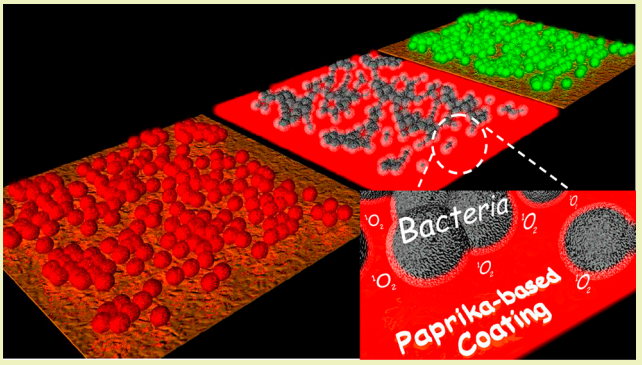
[§]Université de Paris-Est-Marne la Vallée (UPEM), Laboratoire de Modélisation et Simulation Multi-Echelles (MSME), 5 boulevard Descartes-77454, Marne-la-Vallée Cedex2, France

[∥]Faculty of Chemistry, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland

[⊥]Laboratoire Roberval, UMR CRNS-UTC 7337, Centre de Recherche de Royallieu, Université de Technologie de Compiègne, 60205 Compiègne Cedex, France

Supporting Information

ABSTRACT: A performing photoinitiating system based on paprika spice was developed (i) to efficiently initiate, according to a green photoinduced process, the cationic polymerization of a biosourced and renewable monomer, e.g., gallic acid, and (ii) to synthesize environmentally friendly antibacterial coatings in a reduced time. A decrease of 100% of the adhered bacteria was demonstrated upon visible light illumination without any remaining live bacteria.



KEYWORDS: *Photochemistry, Paprika, Gallic acid, Cationic photopolymerization, Green chemistry, Antibacterial coatings*

INTRODUCTION

As the need for synthetic polymer products increases each year—they are used in sectors as different as industry, households, and even coatings—, so does the public awareness of its consequences. Indeed, polymers are often synthesized using nonrenewable, oil-derived chemicals. This past decade, green chemistry has risen through the ranks, bringing an answer to the need for a more environmentally friendly chemistry. The green chemistry approach is based on 12 concepts,[1] among them the prevention of waste, the use of renewable chemicals in nonhazardous processes using as little solvent or CO_2 solvent[2−4] and other organic compounds as possible, and practicing an economy of reagents and of energy whenever it is possible. Similarly, the need for antibacterial coatings has steadily increased, along with the number of antibiotic-resistant infections developed each year by hospital patients (75 000 deaths in the U.S. alone in 2011). Indeed, stainless steel surfaces, which can be found in hospitals as well as households, do not exhibit any antibacterial properties. Thus, the search for antibacterial polymer coatings has garnered quite some attention.[5] Antibacterial polymer coatings are commonly divided in "active" and "passive" types, depending on their mechanism of action against bacteria: "passive" coatings[6] will prevent bacterial adhesion (antifouling mechanism), while "active" coatings will actually kill the bacteria[7] (either via biocide release in the environment or via direct contact with the bacteria).

Antibacterial coatings using greener chemistry have already been reported using many different pathways,[8−11] such as nature-mimicking coatings,[9,12] enzyme-grafted coatings,[6] and use of renewable biosourced chemicals as antibacterial agents[13−15] to cite but a few. Coatings mimicking gecko-skin, gecko-feet, lotus' leaves, or shark's skin have been also abundantly reported this past decade.[16,17] Using nature-derived polymers such as chitosan[18] or poly(ε-lysine)[19] has been a pivotal point in the field. Last but never least, the use of renewable and biosourced products, such as essential oils[20,21] especially, has garnered a lot of attention these past decades. The use of essential oils (i.e., clove, cinnamon, thyme, etc.) as antibacterial agents has

Received: October 14, 2017
Revised: November 20, 2017
Published: November 29, 2017

DOI: 10.1021/acssuschemeng.7b03723
ACS Sustainable Chem. Eng. 2018, 6, 104−109

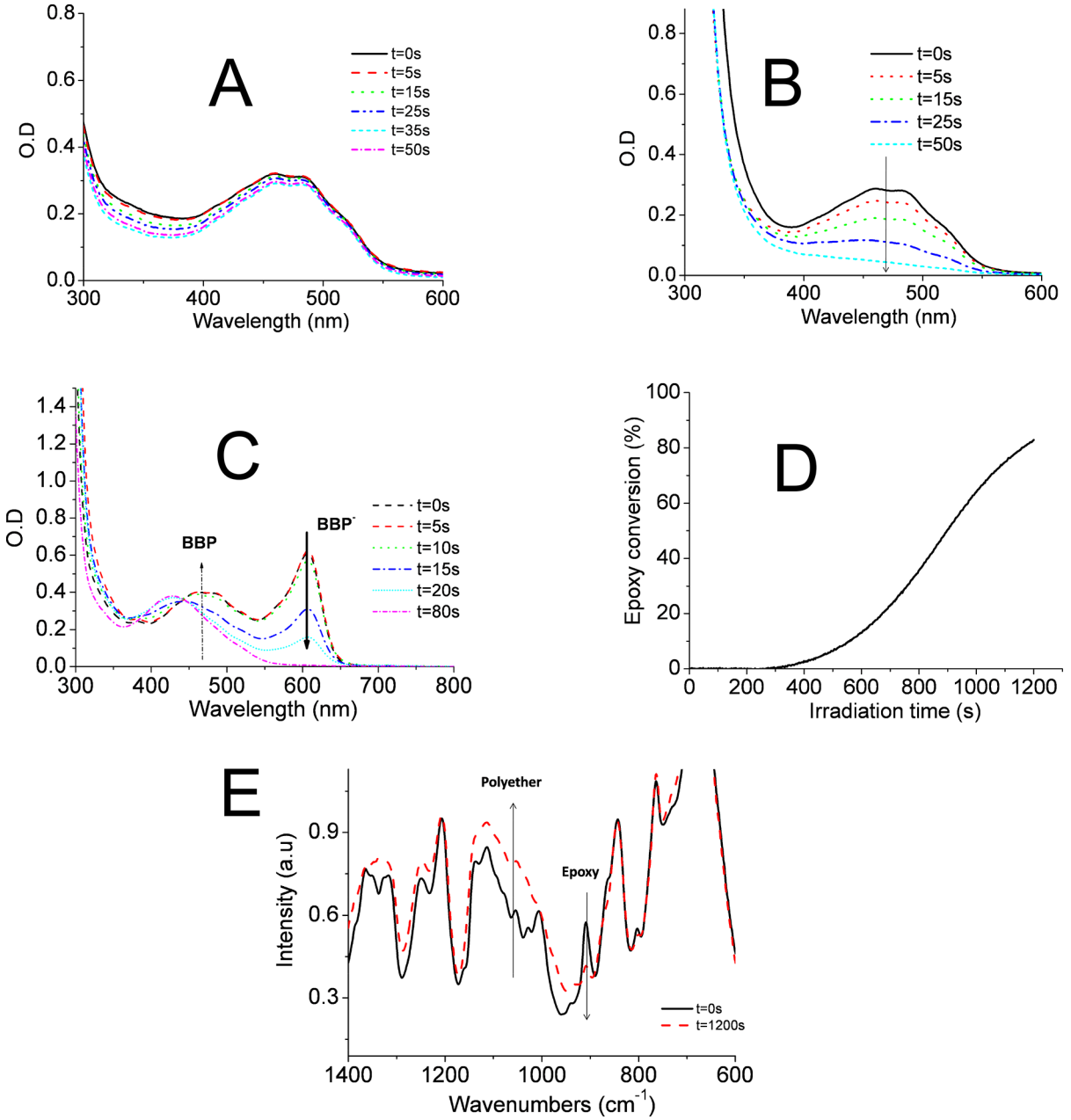


Figure 1. Photolysis of (A) paprika alone ([paprika] = 3.65×10^{-1} g/L) and (B) paprika/iodonium photoinitiating system after 50 s ([paprika] = 3.65×10^{-1} g/L and [Iod] = 6.7 g/L) in toluene after light illumination. (C) UV−visible spectra of the paprika/iodonium photoinitiating system in the presence of sodium salt of bromophenol upon light illumination (disappearance of the basic form of the sodium salt of bromophenol after 80 s of irradiation). (D) Kinetic of the epoxidized gallic acid monomer photopolymerization: disappearance of the epoxy groups as a function of light illumination by RT-FTIR. (E) FTIR spectra of epoxidized gallic acid monomer without irradiation (solid black line) and after 1200 s of irradiation in dot red line (Xe lamp. Film thickness = 100 μm).

blossomed as of late,[22] especially in the food packaging industry. Other kitchen-used ingredients have been investigated as potential biocides. Among the latter, spices have been proven a viable option.[23]

In this contribution, we report a simple and versatile strategy leaning on green chemistry for the synthesis of antibacterial polymer coatings for stainless steel substrates. Such a method answers several of the principles of green chemistry: this polymerization displays a high conversion rate, using biosourced renewable resources in a nonhazardous process. First, we describe, to the best of our knowledge and for the first time, the use of paprika—one of the oldest, most important, and commonly used carotenoid food dyes—as a photosensitizer for the cationic photopolymerization of epoxy gallic acid monomer, as well as an antibacterial agent for antibacterial coating applications. Gallic acid, the monomer that we selected, is biosourced and renewable. It can be found in a number of plants and can be extracted by different techniques, such as ultrasonic-assisted extraction or microwave-assisted extraction. Gallic acid has been grafted on a preformed polymer;[24−27] the grafting process of gallic acid on chitosan has been investigated by the teams of Spizzirri and Pasanphan in order to improve, respectively, the antioxidant properties and water solubility of the resulting polymers. However, its use as a monomer has only

DOI: 10.1021/acssuschemeng.7b03723
ACS Sustainable Chem. Eng. 2018, 6, 104−109

been investigated in thermal polymerization in the presence of amines as hardeners,[28] until now. Literature currently does not evidence any investigation concerning the use of gallic acid in a photopolymerization process. This lack of investigation prompted us to examine in details the cationic photopolymerization process of an epoxy gallic acid monomer, with the use of paprika/iodonium salt (Iod) as a photoinitiating system upon light illumination and at room temperature. Electron spin resonance experiments, fluorescence investigations, and steady-state photolysis have been used to elucidate the photochemical mechanism involved in the initiation process upon light irradiation. A particular effort was also made to characterize the synthesized coatings. For this purpose, the mechanical analysis and thermal resistance of the resulting coatings are evaluated as well by thermogravimetric analysis (TGA), nanoindentation, and scratch tests. In addition, the generation of singlet oxygen through the paprika-derived coatings under visible light irradiation was investigated. Afterward, the antibacterial property of the coatings has been tested against two bacteria strains, i.e., *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), and their viability is demonstrated via live/dead assays.

RESULTS AND DISCUSSION

To understand the photoinitiation of the polymerization, photolysis of either paprika alone or a mixture of paprika and iodonium salt were carried out in toluene under light illumination. Figure 1 displays the steady-state photolysis of the one- and two-component photoinitiating systems (Figure 1A and B) i.e., paprika and paprika/iodonium salt, and its efficiency in the light cationic photopolymerization of epoxidized gallic acid monomer. It is worth noticing that no photobleaching of the paprika dye alone is observed after 50 s under light illumination. When iodonium salt is added to paprika, a decrease in its UV absorption band (between 400 and 550 nm) is clearly demonstrated after the same time of irradiation, thus indicating a synergic effect between iodonium salt and paprika. The quenching of the paprika fluorescence by iodonium salt confirms that the photolysis occurs in the singlet state. The rate of the quenching constant was therefore evaluated at 78 M^{-1} s^{-1} (Figure S3). The efficiency of the photopolymerization process was first evidenced by (i) the formation of photoacids (Figure 1C) according to the sodium salt of bromophenol method[29] and (ii) the polymerization of the epoxidized gallic acid monomer which is followed by the disappearance of the epoxy groups as a function of light illumination by RT-FTIR (Figure 1D) leading to a decrease in the absorbance of the epoxy function at 910 cm^{-1} (Figure 1E) along with the increase in a new band at 1080 cm^{-1} which is attributed to the polyether chains (Figure 1E). The final conversion reaches 90% after 1200 s irradiation. The photoacids generation as well as the cationic polymerization are in accordance with literature data[30−34] (reactions r1−r7). According to other related photoinitiating systems,[30−34] we can therefore assume that the following mechanism is involved in the cationic photopolymerization of epoxy monomers. First, the excited singlet state of paprika is produced upon illumination. From this excited state, an electron transfer photosensitization reaction between the paprika excited state and the ground state of iodonium salt occurs, thus generating phenyl radicals, $Ph^{\bullet}$. Intermolecular hydrogen abstraction by $Ph^{\bullet}$ from the epoxy monomer also yields aliphatic α-ether radicals (epoxy$(-H)^{\bullet}$). The later are known in organic chemistry as reducing agents and iodonium salts as performing oxidizing molecules. In a further reaction, epoxy$(-H)^{\bullet}$ is oxidized by iodonium salts, thus forming epoxy$(-H)^{+}$. With water or in a moisture environment, epoxy$(-H)^{+}$ reacts with water and gives photoacids H^{+}. In a final reaction, H^{+} and epoxy$(-H)^{+}$ initiate the cationic photopolymerization of epoxy monomer.

$$\text{Paprika}^{*} + \text{Ph}_2\text{I}^{+} \rightarrow \text{Paprika}^{+\bullet} + \text{Ph}_2\text{I}^{\bullet} \quad \text{(r1)}$$

$$\text{Paprika}^{+\bullet} + \text{Ph}_2\text{I}^{\bullet} \rightarrow \text{Paprika}^{+\bullet} + \text{Ph}^{\bullet} + \text{PhI} \quad \text{(r2)}$$

$$\text{Ph}^{\bullet} + \text{epoxy} \rightarrow \text{Ph}{-}\text{H} + \text{epoxy}_{(-\text{H})}{}^{\bullet} \quad \text{(r3)}$$

$$\text{epoxy}_{(-\text{H})}{}^{\bullet} + \text{Ph}_2\text{I}^{+} \rightarrow \text{epoxy}_{(-\text{H})}{}^{+} + \text{Ph}_2\text{I}^{\bullet} \quad \text{(r4)}$$

$$\text{epoxy}_{(-\text{H})}{}^{+} + \text{H}_2\text{O} \rightarrow \text{epoxy}_{(-\text{H})}{-}\text{OH} + \text{H}^{+} \quad \text{(r5)}$$

$$\text{H}^{+} + \text{epoxy} \rightarrow \text{Polymer} \quad \text{(r6)}$$

$$\text{epoxy}_{(-\text{H})}{}^{+} + \text{epoxy} \rightarrow \text{Polymer} \quad \text{(r7)}$$

Nanoindentation and scratch resistance tests have been performed on the paprika-derivative coatings deposited on stainless steel substrates. The paprika coatings exhibit a typical visco-elastoplastic behavior with an important increase in the indentation depth during the first hold load plateau and an incomplete recovery during the unloading. The elastic modulus according to the Oliver and Pharr method[35] was evaluated at 5.45 ± 0.77 GPa (mean ± standard deviation) on the stainless steel substrate. Comparison of the height profiles before and after the scratch test reveals an incomplete recovery of the material confirming the elastoplastic behavior of the coating (Figure S4). No bulge on the height profile during and after the scratch test evidences the apparition of brittle fracture or delamination of the coating. Optical images of the sample after scratch tests confirm that neither brittle fracture nor delamination occur. The later confirms the high adherence of the coating to the stainless steel substrate and the good resistance of the coatings to fracture (Figure S5). It is interesting to observe that the paprika-derived films yield an excellent thermal stability up to 300 °C (Figure S6). The films reached 50% weight loss at 345 °C. The remaining and nonreacted paprika inside the coating was evidenced by epifluorescence experiments (Figure S7). It allows the opportunity to use such coatings as antibacterial substrates when a significant quantity of singlet oxygen could be generated, leading to the death of bacteria.

The generation of singlet oxygen from the illumination of paprika in solution was confirmed by EPR experiments (Figure 2A and B). Indeed, the singlet oxygen-forming molecules react with TEMP to form TEMPO, a well-known nitroxide radical which gives an isotropic triplet absorption line.[36,37] Before illuminating the paprika solution under air, no TEMPO signal was evidenced. However, when light is switched on, an intensive TEMPO signal appears (Figure 2A), and the more the paprika solution is irradiated (during 200 s) the more the concentration of TEMPO is increasing. According to the intensity of the TEMPO signals, the concentration of singlet oxygen was estimated and linearly increased with irradiation (Figure 2B). The singlet oxygen photogeneration at the surface of the paprika-derived coatings was monitored in situ applying DPBF as the specific singlet oxygen trap. The comparison of the DPBF spectra recorded in time for polymer coating with and without light illumination was made. Figure 2C presents a drop in the absorption of a singlet oxygen trap at 410 nm, while for the blank

DOI: 10.1021/acssuschemeng.7b03723
ACS Sustainable Chem. Eng. 2018, 6, 104−109

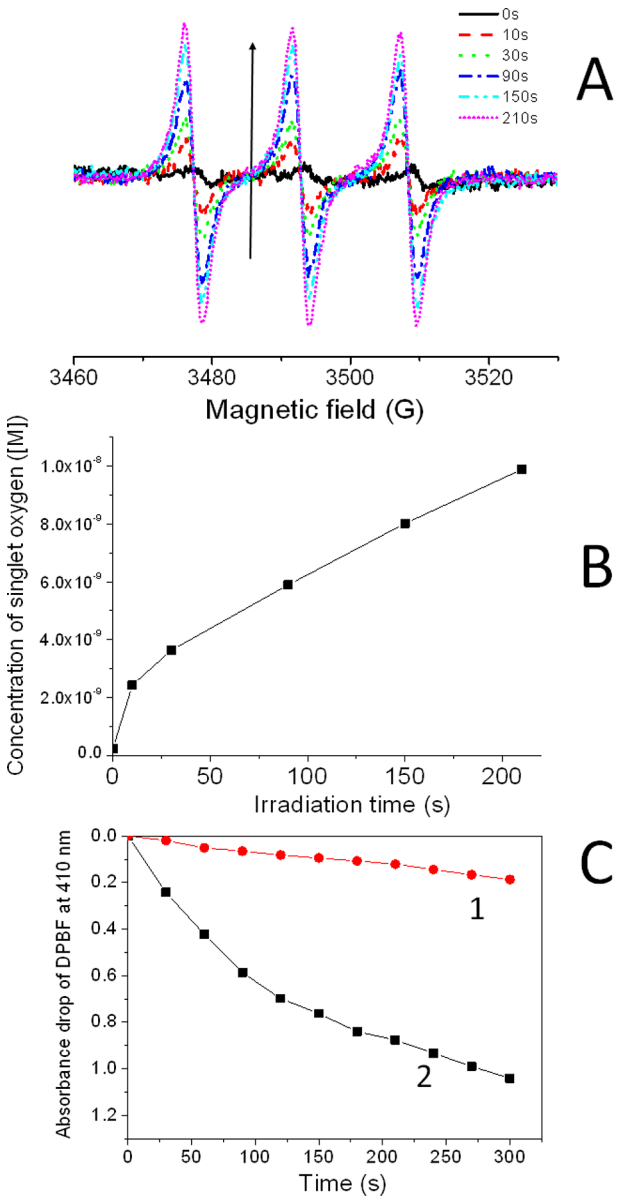


Figure 2. (A) ESR experiments demonstrated the generation of singlet oxygen from the illumination of paprika in *tert*-butylbenzene in the presence of PBN after 210 s. (B) Evolution of the concentration of singlet oxygen due to EPR experiments. (C) Evolution of singlet oxygen at the surface of the paprika-derived coatings according to the DPBF oxidation: (1) without light irradiation and (2) under a 445 nm laser irradiation after 300 s.

paprika coating without light the drop is close to 0.1 during 5 min (Figure 2C-1). For the paprika-derived coating upon light exposure, a decrease in the absorption close to 1.1 was observed (Figure 2C-2). This result highlights the generation of singlet oxygen close to the polymer surface under visible light illumination.

According to these results, it is likely that the paprika coatings could inhibit the bacteria growth on stainless steel substrates through $^1O_2$ generation. It is worth noticing that the diffusion of paprika was not observed outside the coatings as no visible absorption band from the paprika was evidenced after 6 h of incubation in water. This is likely due to the high final polymerization conversion of the polymer coatings after light illumination

Coatings are then introduced within a fixed concentration of bacteria and are incubated in bacteria solutions during 6 h. Half of the samples are stored in the dark at room temperature; the other ones are illuminated under visible light. The number of colony forming units (CFUs) was evaluated according to the well-known bacteria counting method in biological studies.[38,39] Figure 3 displays the number of CFUs after 2 and 6 h of

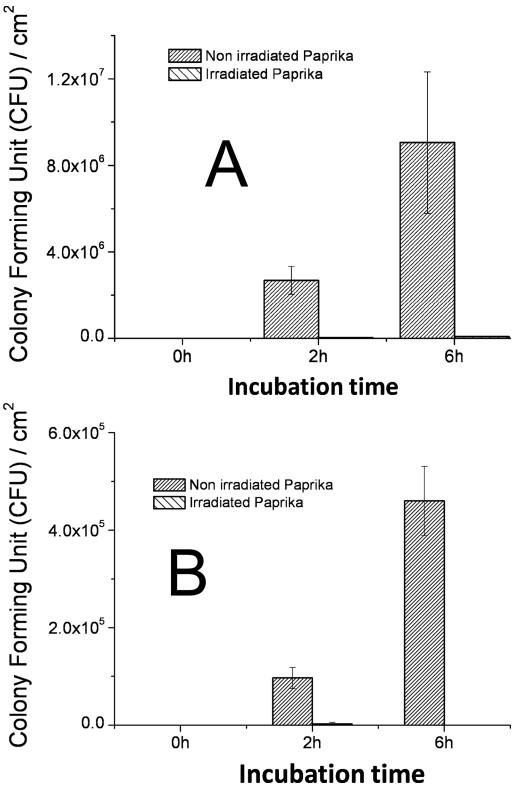


Figure 3. Antibacterial experiments against (A) *E. coli* and (B) *S. aureus* strains after 2 and 6 h of incubation.

incubation against two different bacteria strains both on irradiated and nonirradiated paprika-derived coatings. Whatever bacteria strains are used, we can observe a tremendous proliferation of bacteria on the paprika-derived coatings which have been stored in the dark. The CFUs number increases, respectively, from 3×10^6 to 9×10^6 and from 1×10^5 to 5×10^5 for *E. coli* and *S. aureus* after 6 h of incubation. On the contrary, no evidence of bacteria was observed on the surface of the illuminated paprika-derived coatings either with *E. coli* or *S. aureus* after 6 h of incubation. The proliferation of Gram-positive and Gram-negative bacteria was thus entirely inhibited. Indeed, singlet oxygen, generated under light illumination, can diffuse through the cell membrane to oxidize all the fatty acids necessary for bacterial growth, thus leading to the death of the cell.[40] The live/dead assays confirm the previous results and demonstrate that the illuminated coatings containing paprika are responsible for the bacterial death as red fluorescence of bacteria is observed whatever the strains used (Figure 4B and D). Opposite this, the gallic acid-derived coatings do not present any biocide effect (Figure 4A and C); this last result is in agreement with literature data as paprika alone did not show any inhibitory activity against pathogenic bacteria.[41]

DOI: 10.1021/acssuschemeng.7b03723
ACS Sustainable Chem. Eng. 2018, 6, 104−109

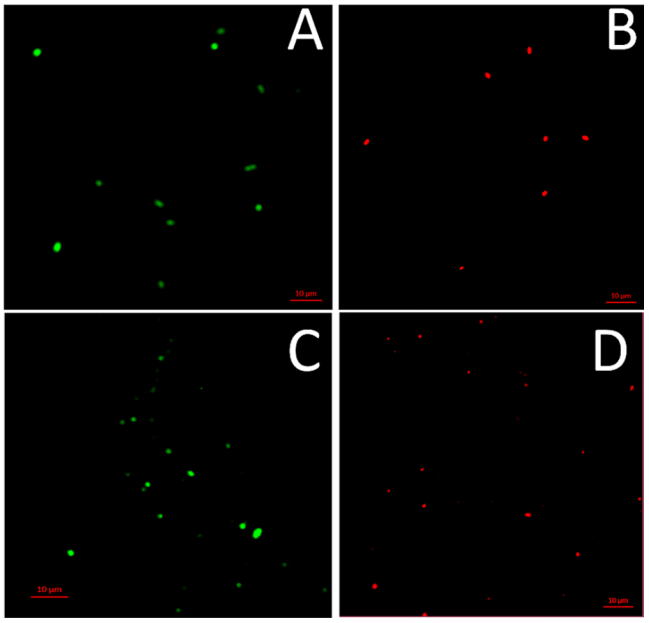


Figure 4. Live/dead assays after 6 h of incubation. Fluorescence images of the bacteria strains which are present on the surface of the paprika-derived coatings as a function of illumination: (A) *E. coli* without illumination, (B) *E. coli* after illumination, (C) *S. aureus* without illumination, and (D) *S. aureus* after illumination.

CONCLUSIONS

This study looked into the use of a natural spice, paprika, in the formation of environmentally friendly stainless steel coatings in a reduced time, and its use as photosensitizer was thus demonstrated for the first time. To this end, we demonstrated that a dye-sensitized reaction occurs between paprika and Iod upon light illumination. Polymerization was carried out at room temperature under air and light irradiation, using renewable biosourced gallic acid as the monomer. The resulting coatings showed good adherence to the stainless steel substrate, with thermal stability up to 300 °C. Moreover, we proved that even at a relatively low concentration of paprika, singlet oxygen can be generated, and the antiadhesion property of the resulting coatings was shown to be efficient; an average decrease of 100% of the adhered *E. coli* and *S. aureus* on the gallic acid/paprika-derived coatings was demonstrated after 2 and 6 h upon visible light illumination. The resulting irradiated paprika-containing coatings do not show any live bacteria after 6 h in the presence of either *E. coli* or *S. aureus*. These new coatings could be therefore applied on medical devices to eradicate the bacterial proliferation in hospitals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b03723.

^{1}H NMR spectra of the synthesized derived gallic acid monomers used in this study (Figure S1). Emission spectrum of the lamps used during the different incubation times (Figure S2). Quenching of paprika emission upon addition of iodonium salt (Figure S3). Height profile before, during, and after scratch on paprika coating (Figure S4). Optical image of the paprika-derived coating after scratch (Figure S5). TGA thermogram of the photo-induced paprika-derived coating under oxygen atmosphere (Figure S6). Epifluorescence of paprika located into the polymer coating after 1200 s of irradiation (Figure S7). Structure of the monomer and photoinitiating systems used in this work (Table S1). (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: versace@icmpe.cnrs.fr.

ORCID

Jacques Lalevée: 0000-0001-9297-0335
Valérie Langlois: 0000-0002-4465-7827
Davy-Louis Versace: 0000-0002-4272-5021

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank CNRS, UPEC, and French National Research Agency (project sPECTRAL) for financial support.

REFERENCES

(1) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998.
(2) Xu, W. Z.; Yang, L.; Charpentier, P. A. Preparation of Antibacterial Softwood via Chemical Attachment of Quaternary Ammonium Compounds Using Supercritical CO2. *ACS Sustainable Chem. Eng.* **2016**, *4*, 1551−1561.
(3) Chen, Y.; Yu, P.; Ren, G.; et al. Interpenetration of Polyethylene Terephthalate with Biocidal Quaternary Ammonium/N-Chloramine Polysiloxane in Supercritical CO2. *Ind. Eng. Chem. Res.* **2017**, *56*, 9560−9568.
(4) Chen, Y.; Zhang, Q.; Han, Q.; et al. Synthesis of polysiloxane with 5,5-dimethylhydantoin-based N-halamine pendants for biocidal functionalization of polyethylene by supercritical impregnation. *J. Appl. Polym. Sci.* **2017**, *134*, 44721−44729.
(5) Siedenbiedel, F.; Tiller, J. C. Antimicrobial Polymers in Solution and on Surfaces: Overview and Functional Principles. *Polymers* **2012**, *4*, 46−71.
(6) Banerjee, I.; Pangule, R. C.; Kane, R. S.; et al. Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms. *Adv. Mater.* **2011**, *23*, 690−718.
(7) Jain, A.; Duvvuri, L. S.; Farah, S.; et al. Antimicrobial Polymers. *Adv. Healthcare Mater.* **2014**, *3*, 1969−1985.
(8) Cloutier, M.; Mantovani, D.; Rosei, F. Antibacterial Coatings: Challenges, Perspectives, and Opportunities. *Trends Biotechnol.* **2015**, *33*, 637−652.
(9) Glinel, K.; Thebault, P.; Humblot, V.; et al. Antibacterial surfaces developed from bio-inspired approaches. *Acta Biomater.* **2012**, *8*, 1670−1684.
(10) Faure, E.; Falentin-Daudré, C.; Jérôme, C.; et al. Catechols as versatile platforms in polymer chemistry. *Prog. Polym. Sci.* **2013**, *38*, 236−270.
(11) Manecka, G. M.; Labrash, J.; Rouxel, O.; et al. Green Photoinduced Modification of Natural Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) Surface for Antibacterial Applications. *ACS Sustainable Chem. Eng.* **2014**, *2*, 996−1006.
(12) Liu, X.; Liang, Y.; Zhou, F.; et al. Extreme wettability and tunable adhesion: biomimicking beyond nature? *Soft Matter* **2012**, *8*, 2070−2086.
(13) Modjinou, T.; Versace, D.-L.; Abbad Andaloussi, S.; et al. Antibacterial and antioxidant bio-based networks derived from eugenol

DOI: 10.1021/acssuschemeng.7b03723
ACS Sustainable Chem. Eng. 2018, 6, 104−109

using photo-activated thiol-ene reaction. *React. Funct. Polym.* **2016**, *101*, 47−53.
(14) Hebbalalu, D.; Lalley, J.; Nadagouda, M. N.; et al. Greener Techniques for the Synthesis of Silver Nanoparticles Using Plant Extracts, Enzymes, Bacteria, Biodegradable Polymers, and Microwaves. *ACS Sustainable Chem. Eng.* **2013**, *1*, 703−712.
(15) Glaive, A. S.; Modjinou, T.; Versace, D.-L.; et al. Design of Antibacterial and Sustainable Antioxidant Networks Based on Plant Phenolic Derivatives Used As Delivery System of Carvacrol or Tannic Acid. *ACS Sustainable Chem. Eng.* **2017**, *5*, 2320−2329.
(16) Hasan, J.; Crawford, R. J.; Ivanova, E. P. Antibacterial surfaces: the quest for a new generation of biomaterials. *Trends Biotechnol.* **2013**, *31*, 295−304.
(17) Xu, Q.; Zhang, W.; Dong, C.; et al. Biomimetic self-cleaning surfaces: synthesis, mechanism and applications. *J. R. Soc., Interface* **2016**, *13*, 20160300.
(18) Elsabee, M. Z.; Abdou, E. S. Chitosan based edible films and coatings: A review. *Mater. Sci. Eng., C* **2013**, *33*, 1819−1841.
(19) El-Sersy, N. A.; Abdelwahab, A. E.; Abouelkhiir, S. S.; et al. Antibacterial and Anticancer activity of ε -poly-L-lysine (ε -PL) produced by a marine Bacillus subtilis sp. *J. Basic Microbiol.* **2012**, *52*, 513−522.
(20) Burt, S. Essential oils: their antibacterial properties and potential applications in foods—a review. *Int. J. Food Microbiol.* **2004**, *94*, 223−253.
(21) Campana, R.; Casettari, L.; Fagioli, L.; et al. Activity of essential oil-based microemulsions against Staphylococcus aureus biofilms developed on stainless steel surface in different culture media and growth conditions. *Int. J. Food Microbiol.* **2017**, *241*, 132−140.
(22) Hosseini, M. H.; Razavi, S. H.; Mousavi, M. A. Antimicrobial, physical and mechanical properties of Chitosan-based films incorporated with thyme,clove and cinnamon essential oils. *J. Food Process. Preserv.* **2009**, *33*, 727−743.
(23) Huhtanen, C. N. Inhibition of Clostridium botulinum by Spice Extracts and Aliphatic Alcohols. *J. Food Prot.* **1980**, *43*, 195−196.
(24) Spizzirri, U. G.; Iemma, F.; Puoci, F.; et al. Synthesis of Antioxidant Polymers by Grafting of Gallic Acid and Catechin on Gelatin. *Biomacromolecules* **2009**, *10*, 1923−1930.
(25) Pasanphan, W.; Chirachanchai, S. Conjugation of gallic acid onto chitosan: An approach for green and water-based antioxidant. *Carbohydr. Polym.* **2008**, *72*, 169−177.
(26) Cho, Y.-S.; Kim, S.-K.; Ahn, C.-B.; et al. Preparation, characterization, and antioxidant properties of gallic acid-grafted-chitosans. *Carbohydr. Polym.* **2011**, *83*, 1617−1622.
(27) Sun, X.; Wang, Z.; Kadouh, H.; et al. The antimicrobial, mechanical, physical and structural properties of chitosan−gallic acid films. *LWT - Food Sci. Technol.* **2014**, *57*, 83−89.
(28) Aouf, C.; Nouailhas, H.; Fache, M.; et al. Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin. *Eur. Polym. J.* **2013**, *49*, 1185−1195.
(29) Podemska, K.; Podsiadly, R.; Szymczak, A. M.; et al. Diazobenzo-[a]fluorene derivatives as visible photosensitizers for cationic polymerization. *Dyes Pigm.* **2012**, *95*, 74−78.
(30) Fouassier, J.-P.; Lalevee, J. *Photoinitiators for Polymer Synthesis: Scope, Reactivity, and Efficiency*; Wiley-VCH: Weinheim, 2012.
(31) Lalevee, J.; Mokbel, H.; Fouassier, J.-P. Recent Developments of Versatile Photoinitiating Systems for Cationic Ring Opening Polymerization Operating at Any Wavelengths and under Low Light Intensity Sources. *Molecules* **2015**, *20*, 7201−7221.
(32) Sundell, P.-E.; Josson, S.; Hult, A. Photo-redox induced cationic polymerization of divinyl ethers. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1525−1533.
(33) Timpe, H. J.; Kronfeld, K. P.; Lammel, U.; et al. Excited states of ketones as electron donors—ketone—iodonium salt systems as photoinitiators for radical polymerization. *J. Photochem. Photobiol., A* **1990**, *52*, 111−122.
(34) Al Mousawi, A.; Kermagoret, A.; Versace, D.-L.; et al. Copper photoredox catalysts for polymerization upon near UV or visible light: structure/reactivity/efficiency relationships and use in LED projector 3D printing resins. *Polym. Chem.* **2017**, *8*, 568−580.
(35) Oliver, W. C.; Pharr, G. M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* **1992**, *7*, 1564−1583.
(36) Zang, L.-Y.; van Kuijk, F. J. G. M.; Misra, B. R.; et al. The specificity and product of quenching singlet oxygen by 2,2,6,6-tetramethylpiperidine. *Biochem. Mol. Biol. Int.* **1995**, *37*, 283−293.
(37) Vogler, T.; Studer, A. Applications of TEMPO in Synthesis. *Synthesis* **2008**, *2008* (13), 1979−1993.
(38) Balazs, D. J.; Triandafillu, K.; Wood, P.; et al. Inhibition of bacterial adhesion on PVC endotracheal tubes by RF-oxygen glow discharge, sodium hydroxide and silver nitrate treatments. *Biomaterials* **2004**, *25*, 2139−2151.
(39) El Habnouni, S.; Darcos, V.; Garric, X.; et al. Mild Methodology for the Versatile Chemical Modification of Polylactide Surfaces: Original Combination of Anionic and Click Chemistry for Biomedical Applications. *Adv. Funct. Mater.* **2011**, *21*, 3321−3330.
(40) Dahl, T. A.; Midden, W. R.; Hartman, P. E. Pure singlet oxygen cytotoxicity for bacteria. *Photochem. Photobiol.* **1987**, *46*, 345−352.
(41) Witkowska, A. M.; Hickey, D. K.; Alonso-Gomez, M.; et al. Evaluation of antimicrobial activities of commercial herb and spice extracts against selected food-borne bacteria. *J. Food Res.* **2013**, *2*, 37−54.

DOI: 10.1021/acssuschemeng.7b03723
ACS Sustainable Chem. Eng. 2018, 6, 104−109