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Preface on Hot Topics in Surface Science: Organic Coatings (HTSS-OC)

The call of this Special Issue on “Hot Topics in Surface Science: Organic Coatings” was set to cover the most current developments of functional coatings in the nanometer to sub-micron range. Contributions from all researchers working on the surface modifications using molecules were welcomed.

Organic coatings are crucial for enabling improved function in many applications, from consumer goods to electronics and energy applications, from biomaterials and sensors to water treatment and remediation. Functional organic materials formed into a thin organic coating can establish, or even fine-tune, interactions with the environment to control function and performance. Examples include the control of antifouling, protective, anti-fogging, bioactive, ion-exchange, and liquid-crystal properties.

Many methodologies for depositing thin polymer films exist. While some of these techniques, such as spray or blade coating, are well-established, their combination with self-assembling materials leads to interesting nano-scale structures as well as novel functionalities. Reactive deposition techniques, from various chemical vapor deposition (CVD) approaches to interfacial reactions, expand the ability for forming ultra-thin films, form complex patterns, and control layer properties. Grafting-from approaches lead to polymer brushes with tuneable properties, whereas innovations in layer-by-layer deposition techniques broaden the applicability of this approach as well as chemical and morphological properties accessible by this method.

With eight open access, peer-reviewed contributions, this Special Issue covers work on organic coatings comprising novel polymeric materials [1–6] (of which three on polyelectrolytes [4–6] and three on bio/bio-inspired polymers [3,4,6]) as well as studies that involve the use of plant extracts to deposit a coating [7–8]. Next to this material-oriented classification, these studies can also be categorized by focusing on their application: four studies deal with corrosion inhibition [2,3,7,8], and two studies employ polyelectrolytes within the context of separation processes [5,6].

To start with the non-charged polymer work, the review by Li *et al.* [1] consolidates recent advancements in water-based or waterborne polyurethane (WPU) matting resins, focusing on physical and chemical matting types. WPU resins have found extensive application in surface coatings to diminish gloss, offering a pleasant tactile experience and a matte aesthetic. The review maps innovative matting agents, analyses and discusses the synthesis and characterisation of chemical matting resins, and focuses on matting mechanisms. The focus is on five distinct chemical self-matting WPU resins: epoxy-modified, silicone-modified, acrylic-modified, multicomponent-modified, and bio-based modified WPU resins.

Painting on a decade of research, it addresses current trends, challenges, and future design directions.

Epoxies form also the core in the work of Trentin *et al.*, who applied five independent pre-treatments – mechanical polishing, alkaline and acid etching, sol-gel primer, and anodizing – on mild steel and two types of aluminum) substrates before the deposition of epoxy coatings [2]. The latter was established by dip-coating the surfaces in a solution containing a commercial two-component epoxy coating composed of bisphenol A diglycidyl ether (DGEBA) and triethylenetetramine (TETA) as a curing agent in acetone, followed by a curing step an elevated temperatures to ensure solvent evaporation and complete polymerization of the coatings. Through systematic surface, mechanical, and electrochemical tests, the role of different pre-treatments in the adhesion and barrier properties of epoxy coatings was demonstrated by correlating them with mechanisms: i) mechanical etching, inducing physical interactions and mechanical interlocking, ii) chemical etching, enhancing the surface reactivity by depleting hydroxyls density, iii) anodization, to control the dimensions of porosity, again impairing mechanical interlocking, and iv) application of a sol-gel primer to increase mechanical strength and adhesion of the coatings.

As an alternative to the widely employed petroleum-based PU, [1]. Khan *et al.* explored the use of a bio-based monomer, cardanol (Col), to prepared a Col-based PU via an *in-situ*, one-pot, two-step preparation to yield Co(II)- and Ni(II)-coordinated Col nanocomposites [3]. The resulting materials, prepared as coating and also free-standing films (120-140 μm in thickness and water contact angles as high as 143° and 158°), exhibit improved thermal stability, flame retardancy, and antibacterial properties. The nanocomposites were studied in great detail, incl. elemental analysis, various spectroscopy studies, thermal studies, electron microscopy, X-ray diffraction, gas adsorption, and electrochemical impedance spectroscopy. The work includes data on their anti-corrosive and antibacterial performance. The main novelty of the proposed work is the development of PU nanocomposite by adopting an *in-situ* cleaner approach.

Within the context of biomedical applications, also Criveanu *et al.* worked on a hybrid material made from a metal and a bio-based polymer [3]. In contrast to the work of Khan *et al.* [4], the focus here is on (iron oxide, magnetic) core – (chitosan) shell materials. First, iron oxide nanoparticles (NPs) were synthesized by laser pyrolysis, followed by their chitosan-stabilized aqueous suspensions. Tuning of the ratio of gases O_2 and Ar at a constant flow of $Fe(CO)_5$ precursor vapor and C_2H_4 sensitizer molecules, allowed the researchers to influence, a.o., the particle size and magnetic properties. After chitosan loading, the resulting aqueous suspensions were found to be stable, which is a significant advantage for combing iron oxide NPs with cytostatic agents or drug delivery for other biomedical applications.

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Kaner *et al.* also reports on coatings that create functional nanostructures, with applications that span drug delivery, water treatment, and other separations [5]. Their report focuses on the formation of nanoscale, self-assembled structures upon the casting of amphiphilic copolymers with hydrophobic backbones and short, zwitterionic side-chains by various methodologies, from spin coating to phase inversion on porous and non-porous substrates. The resultant films exhibit a range of interesting morphologies, including porous structures with potential use in membrane filtration. They also note hysteretic morphological changes upon exposure to water and saline solutions, creating additional features that can be used for sensing.

Within this context, also Sahin *et al.* prepared films from charged polymers, albeit in a different way [6]. In this work, the polyelectrolytes were chemically modified with receptors (here, crown ethers) before applying them to a layer-by-layer scheme to yield functionalized polyelectrolyte multilayers (PEMs).The build-up of the PEMs onto gold surfaces, as well as their interactions with various cations, was monitored with quartz crystal microbalance with dissipation monitoring (QCM-D). Various polycations and polyanions from fossil origin were used as well as pectin, a bio-based polyanion. The differences in (dry and wet) thickness of the PEMs were rationalized and the QCM-D responses to the exposure of different salt solutions were mapped. It was found that the cation-exchange behavior of PEMs can be increased by the introduction of covalently attached crown ethers, and for the investigated crown ether, the order of preference was found to be $K^+ > Na^+ >> Li^+/Cs^+/Rb^+/Mg^{2+}$. Given the large toolbox of available polyelectrolytes and ionophores, functionalized PEMs are expected to facilitate the further development of ion separation applications.

The exploration of using bio-based materials as alternatives to materials derived from fossil fuels is advancing significantly in various fields, and this is also evidenced in this Special Issue, particularly for biomedical, [4] ion separation/sensing, [6] and corrosion inhibition [3] applications. Instead of using monomers [3] or biopolymers [4,6] that are well-defined to due extensive purification schemes, plant extractions also have found to be useful in inhibiting corrosion.

Within this context, two studies on the use of natural extracts as corrosion inhibitors have been included in this Special Issue. The first one [7] investigates the anticorrosive properties of Eucalyptus leaf extract (ELE) on aluminum alloy using multiple characterization methods, and also attempts to decipher mechanisms of its action. They report that adding ELE to acidic solutions reduces the corrosion rate by up to ~90-95% under optimal conditions. They also report that the corrosion inhibition arises from components of ELE adsorbing on the metal surface, creating a protective coating without additional processing.

The second study focuses on the use of the extract from another plant, *Aspilia Africana (A. Africana)*, as a corrosion inhibitor that also forms an adsorbed layer on the metal surface from the solution, which they document by spectroscopic analysis [8]. The main aim of this study, however, is to compare the predictive capabilities of response surface methodology (RSM) and adaptive neuro-fuzzy inference systems (ANFIS) for modeling aluminum and mild steel corrosion inhibition using this extract under various conditions (*e.g.* acid concentration, extract concentration, temperature, time). While both models exhibited similar predictive power for the corrosion of mild steel, ANFIS was significantly better in modelling aluminum corrosion.

In summary, this special issue highlights the wide range of applications that engineered, novel organic coatings can influence, from corrosion prevention on metal surfaces to biomaterials, as well as separations, sensing, and drug delivery. It spans the formation of coatings from a broad range of organic materials, with interdisciplinary research that bridges chemistry, physics, engineering, and materials science.

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