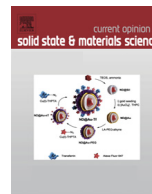




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Recent approaches to reduce aging phenomena in oxygen- and nitrogen-containing plasma polymer films: An overview

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ABSTRACT

Plasma polymer films (PPFs) are well-known for their enhanced stability compared to conventional polymer coatings. However, PPFs tend to undergo aging in air or in aqueous environments due to oxidation, hydrophobic recovery, hydrolysis and dissolution of oligomeric fragments. Such aging mechanisms cause modifications of the PPFs that entail a change in surface properties. For example, PPF surfaces which are probed for protein adsorption or cell adhesion might therefore be substantially different from the initial PPF. It becomes thus necessary to understand the chemical reactions involved in the chemical modification (and/or degradation) of PPFs. Here, a summary of the most important aging mechanisms occurring in PPFs is given. More precisely, chemical reactions that can potentially occur in oxygen- and nitrogen-containing plasma polymer films when stored in air and in water were highlighted. On the basis of this understanding, recent strategies to reduce or delay aging mechanisms and/or to provide time-controlled degradable PPFs are discussed: the enhancement of the degree of cross-linking, the formation of a gradient structure in the PPF during plasma deposition, and the chemical post-plasma treatment to reduce the number of reactive sites. Finally, potential applications of such coatings will be considered.

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1. Introduction

The “plasma” phase was described for the first time in 1920 by Irving Langmuir [1]. Since his discovery, numerous studies were carried out to determine the plasma composition, to describe its physical and chemical characteristics and to identify “plasma polymers”, which are characterized by extensive branching and cross-linking, made from such glow-discharges [1–3]. Once the scientific community agreed that the considered low temperature plasma is composed of energy-carrying electrons, ions, neutral species and photons in the gas phase yielding non-equilibrium conditions, another question was raised related to its value for applications. Several possibilities were tested over time, showing the excellent potential of plasma processing to modify the material superficial structure (e.g. etching and implantation), to functionalize surfaces, or to deposit organic (polymer-like) or inorganic (glass- or diamond-like, ceramic or metallic) coatings onto various substrates and for diverse applications in electrical, optical, biomedical, environmental or corrosion sciences as well as packaging, wear and tribology. Such “plasma polymer” deposits are the result of an organic gas or vapor (also named “precursor” or “monomer”,

where all kind of saturated and unsaturated molecules might be used) that has been activated and fragmented by passing through the plasma zone yielding film-forming species. Cross-linking and etching during the plasma polymerization process determine the organic/inorganic character of the deposit by partial or full removal of the organic phases. Due to the gradually proceeding film growth (layer-by-layer), a thickness range starting from ~1 nm up to several μm can be covered, whereby also gradual changes in chemical composition might be introduced. Using the energetic, non-equilibrium environment of the plasma, good adhesion of plasma polymer films (PPFs) can be achieved on many different substrate materials. Over the years, inorganic “plasma polymer” films found much more applications than their more organic, functional correspondents as depicted in Fig. 1. Deposition of inorganic films can be controlled by the energy delivered to the growing film (surface processes) yielding densification and thus stable, market-ready PPFs [4]. Incorporation of terminal (functional) groups in a more organic network, on the other side, creates a trade-off with functional group density and cross-linked degree resulting in stability issues [5].

Nevertheless, nowadays it is well-known that plasma processing provides polymer-like coatings being more stable than organic coatings prepared by conventional chemical methods [3,6]. Indeed, due to their higher degree of cross-linking (Fig. 2), PPFs are more

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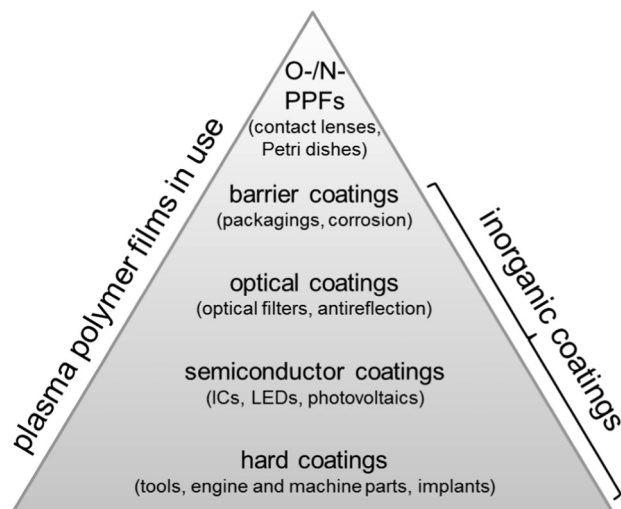


Fig. 1. Schematic representation of application examples for plasma polymer films.

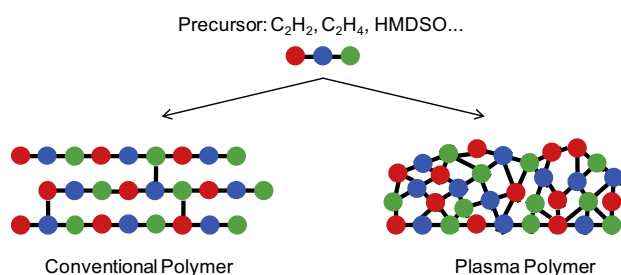


Fig. 2. Comparison of a conventional polymer (left) consisting of repeating units with a plasma polymer (right) showing a branched, cross-linked network, here derived from equivalent precursors (monomers).

stable and undergo less morphological changes than common thin polymer films made by self-molecular assembly, layer-by-layer or spin coating, for example [7,8]. This higher degree of cross-linking is in fact due to the plasma deposition process. Indeed, as explained initially by Yasuda in 1985, PPF deposition is a competitive process between formation by deposition of film-forming species and ablation of the polymer film [2]. Molecules in the gas phase undergo fragmentations due to collision with energetic particles in the plasma depending on their bond energies. Residual fragments can then randomly recombine, rearrange, and be fragmented again [9]. Neutral (as well as ionized) film-forming species produced by the plasma can diffuse in the gas phase and finally adsorb onto a substrate surface depending on their sticking probabilities [10]. Hence, some selectivity can be achieved. Moreover, during plasma treatment, a constant bombardment of energetic particles (ions and fast neutrals) as well as a constant ultraviolet (UV) irradiation allows the restructuring of the growing plasma polymer film (more details regarding plasma deposition mechanisms have already been described in several excellent review articles [9–13]). On the one hand, UV irradiation is well-known to enhance radical polymerization in the PPF by penetrating some tens of nm [14], while ion bombardment processes, on the other hand, promote bond scission and etching by depositing its energy close to the surface, thus permitting new chemical bonds in the PPF that enhance cross-linking, and consequently, the stability of the PPF itself. Subsequent layers are thus affected during PPF growth (mixing and interphase formation) [15].

Despite of their cross-linked network, PPFs can still undergo aging over long time storage in air and/or in water. As already

mentioned by Siow et al. [16]: “Aging is a widespread phenomenon that often has not been recognized, particularly in some of the earlier studies on the use of plasma-fabricated surfaces for bio-interfacial applications. It can prevent covalent interfacial reactions, masked by physisorption of proteins. Moreover, as the surface chemistry varies upon aging, it is essential to assess aging effects, and if they are present, one must characterize the surface chemistry at the time biological tests are performed in order to be able to correlate chemical surface composition with biological responses. Aging effects can be more important than the initial chemistries of the plasma surfaces.” Moreover, it has been recognized that functional plasma coatings showing the greatest stability also revealed the highest biocompatibility [17,18]. Thus, in many cases, surface properties are affected by the potential aging of PPFs, especially considering highly functional PPFs. As a consequence, a freshly prepared PPF exhibits different properties than the same film, e.g., during protein adsorption experiments. Indeed, the PPF starts to oxidize in air and then undergoes aging in aqueous environments before protein adsorption can occur. Therefore, pre-immersion is frequently used to equilibrate the PPF surface in the used environment – without knowledge of the actual (aged) surface conditions. On the one hand, it may be possible to analyze the PPF after aging studies in similar conditions, as suggested by Siow et al. [16]. The control of the plasma deposition conditions, on the other hand, could help to reduce aging phenomena or to anticipate the aging of a time-controlled degrading PPF. Regarding the inevitable trade-off with functionality and cross-linking, Oehrlein stated in the recent 2017 Plasma Roadmap [19]: “The challenges to control surface functionalities of the processed films therefore lie in the control of plasmas to achieve the optimal balance among the incident ion and radical species fluxes, and ion energies.” Furthermore, it becomes necessary to understand the aging mechanism itself to anticipate or to reduce aging effects.

The stability of a plasma polymer film can be related to thermal stability, mechanical stability or chemical stability, for example. This overview focuses on the chemical stability of oxygen- and nitrogen-containing hydrocarbon films – the most widely studied functional PPFs. We note, however, that sulfur- [20,21], phosphorus- [22], fluorine- [23], and chlorine-containing [24] functional PPFs are also attracting increasing interest which show similar characteristics with respect to aging and stability. At first, aging processes in air and in water will be discussed, followed by the introduction of potential methods to substantially reduce aging phenomena in functional PPFs. Note that it is not possible to fully avoid the aging process. Nonetheless, the methods presented here were found to considerably reduce or slowdown the aging effect. Finally, potential applications of O- and N-containing plasma polymer films will be presented.

2. Aging processes

Artificially modified surfaces undergo aging processes to recover an equilibrium state. Plasma activation of polymers using non-polymerizing gases, for example, is well known for increasing the wettability of polymers – a beneficial effect, e.g., for adhesion promotion [25]. The induced hydrophilicity, however, diminishes with storage time mainly due to reorientation of polar groups and migration processes – the so-called “hydrophobic recovery” [26]. The deposition of oxygen- and nitrogen-containing PPFs helps to reduce the aging processes by fixing the functional groups within the branched, cross-linked plasma polymer network (Fig. 3) as, e.g., observed by less increase in water contact angle (WCA) over the storage time. Nonetheless, after PPF deposition some aging mechanisms occur and cannot be fully avoided. As it was demonstrated by Siow et al., aging is affected by a balance

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