Degradable plasma polymerized poly (ethylene glycol)-like coatings as a matrix for controlled-release of components in food related applications

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Abstract: Here we employed an atmospheric pressure aerosol-assisted plasma deposition method to develop a biodegradable PEG-like coating for controlled-release applications. Different plasma operating parameters were optimized, including; power, monomer flow rate, and the gap between the plasma and substrate. The findings revealed that moderate power density (3 and 3.5 W/ (L /min)) and low distances should be applied to obtain smooth conformal coatings with reasonable water stability, along with retaining the structure of PEG polymer.

Keywords: Plasma polymerization, Atmospheric-pressure plasma, Controlled-release, Food packaging, Biodegradable polymer, PEG-like coating

1.Introduction

Nowadays, there is considerable interest in seeking an environmentally friendly technique for producing biodegradable polymers for the food packaging industry [1]. Among recent approaches, atmospheric pressure plasma polymerization is regarded as a low-cost and environmentfriendly alternative to chemical methods and low-pressure plasmas for obtaining degradable coating [2]. However, despite evident progress in the polymer science of plasma deposition, the applications in food packaging still need to be developed and thus remain a highly innovative research topic.

Among several biodegradable polymers, Polyethylene glycol (PEG) is a promising material, particularly for food packaging applications owing to its excellent properties. PEG is non-toxic, biodegradable, and highly biocompatible and Food and Drug Administration (FDA) approved the application of this polymer for human use. From this perspective, PEG polymer can safely be used as food contact material. However, developing a coating of PEG polymer with conventional approaches is exceedingly challenging since it forms a viscous liquid or wax at ambient temperature. In addition, to extend the applications of PEG polymer in food technology, advanced surface engineering is required, for instance, through the deposition of the thin layer with specific, well-defined properties [3]. In this regard, the aerosol-assisted atmospheric pressure plasma deposition technique is a promising environmentally friendly approach for producing PEG-like coating for food applications.

The present study utilized an atmospheric pressure aerosolassisted plasma deposition approach to engineering a PEGlike coating on polyethylene polymer. Different plasma operating parameters, including; power, monomer flow rate, application of nozzle, and distance to the substrate, were investigated as operational parameters to obtain a biodegradable PEG-like coating as a potential matrix for food packaging applications. Furthermore, the chemistry and morphology of obtained coatings were extensively investigated. In addition, the hydrolysis of films in the aqueous environment was analyzed, giving critical importance to future applications.

2. Materials and Methods

2.1. Plasma deposition

The PlasmaSpot® 500 (Molecular Plasma Group (MPG), Luxembourg), a dielectric barrier discharge (DBD) plasma system, was used for deposition. In this system, nitrogen is used as feeding plasma gas at 80 slm flow and a carrier gas for precursor injection. The injection system introduces the precursor (Tri (ethylene glycol) divinyl ether (DVE-3)) into the plasma afterglow in the form of aerosol droplets. Optimizing the precursor flow rate was conducted based on the stability of the deposition in contact with water. For this purpose, the silicon wafer was used as a substrate since the deposit is visible, and the disappearance of the plasma polymerized PEG-like coating in contact with water was visually monitored. Based on the obtained stability results, the flow rate of 0.6 slm was used for deposition. Ultra-high molecular weight polyethylene (UHMWPE)

Ultra-high molecular weight polyethylene (UHMWPE) was used as substrate in this study.

2.1. Atomic force microscopy (AFM)

To compare the surface morphology and roughness of the bare and plasma-coated UHMWPE, an XE-70 atomic force microscope (Park Systems) in the non-contact mode with a silicon cantilever (NanosensorsTM PPP-NCHR) was utilized. The XEI software was used to calculate the average roughness (Ra) and root mean square roughness (Rq).

2.2. Scanning electron microscopy (SEM)

Surface and cross-section SEM images were obtained to analyze the morphology and thickness of the coatings. A JSM-6010PLUS (JEOL, Japan) instrument was employed at an accelerating voltage of 7 kV. Before measurements, samples were coated with Au-sputtering using the JFC-130 auto fine sputter coater (JEOL, Japan).

2.3. X-ray photoelectron spectroscopy (XPS)

For the determination of coatings surface chemistry, the XPS analysis was performed. The PHI 5000 Versaprobe II spectrometer operating at a power of 24 W was employed. Survey scans were recorded at a pass energy of 187.85 eV (eV step = 0.8 eV) to inspect the different surface elements. In addition, for defining the specific types and relative amounts of the surface chemical bonds, high-resolution spectra (C1s, N1s, O1s) were recorded with a pass energy of 23.50 eV (eV step = 0.1 eV).

2.4. Fourier-Transform infrared spectroscopy (FT-IR)

FTIR analysis was conducted by a Bruker Tensor 27 spectrometer supplemented with a single reflection ATR accessory (MIRacle, Pike technology). A mercury cadmium telluride (MCT) detector was applied to record the spectra. The OPUS 6 software was used for analyzing the spectra.

3. Results and discussions

3.1. Effect of distance on the physicochemical properties of PEG-like coatings

During the first step of evaluation, plasma polymerization was conducted at various distances (2, 10, and 20 mm) from the tip of the electrode to the substrate at a constant power of 175 W.

Plasma polymerization of the DVE-3 precursor at the distance of 2 mm results in forming a conformal coating with a considerable degree of smoothness (Rq= 61.3 ± 3.2 , Ra= 50.6 ± 2.7 nm) and homogeneity. However, as a result of increasing the distance, non-conformal coatings with less uniformity were deposited in a manner that broadly represents the morphology of the substrate, particularly at a distance of 20 mm (Rq= 169.4 ± 3.1 , Ra= 142.3 ± 1.2 nm), as shown in Fig 1. These findings could be ascribed to the dilution of the chemically active species due to expanding the gap between the plasma source and

substrate. Accordingly, active species dilution can lead to a reduction in the plasma activation area [4]. The surface roughness increased with increasing the distance from the sample. The observed effect could be interpreted by gasphase nucleation. When the distance is short, the polymerization mainly occurs on the surface of the substrate, which contributes to the formation of a smooth conformal coating. On the other hand, increasing the distance makes the gas-phase nucleation dominant, leading to the clustering of polymerized precursors in the gas phase rather than on the substrate. Therefore, a non-conformal coating will be formed with enlarged surface roughness.



Figure 1: AFM and SEM images from surface of plasma polymerized coatings as a function of plasma-to-substrate distance.

Fig 2 depicts the high-resolution C1s and O1s spectra for the uncoated UHMWPE and the coatings deposited at different distances. As evidenced in the C1s spectrum of coating deposited at 2 mm, the dominant peak is related to C-OH groups. On the other hand, the relative concentrations of carbonyl (C=O) and carboxyl (O-C=O) groups are considerably higher than the coatings deposited at higher distances from the plasma. The obtained C1s spectrum in this study is in good accordance with the reported XPS curves of plasma-deposited PEG-like coating in other research papers [5], which proves the preservation of PEG polymer structure within our plasma polymerization process. However, by increasing the distance from the plasma source, the relative contribution of the four peaks changed noticeably in such a manner that more resembled the molecular structure of the untreated UHMWPE polymer, with the primary peak corresponding to the C-C/C-H bonds. As anticipated, increasing the distance from the plasma source will provide enough time for precursor molecules to dissociate, leading to the loss of functional groups.



Figure 2: High-resolution XPS spectra for UHMWPE polymer and plasma polymerized coatings as a function of plasma-to-substrate distance.

3.2. Effect of power on the physicochemical properties of PEG-like coatings

According to the obtained findings of the distance impact on the characteristics of PP PEG-like coating, a plasmasubstrate distance of 2 mm was selected in the following investigations. Therefore, the coatings were prepared at varied powers (175, 200, 250, 300, and 350 W) at a fixed plasma-substrate distance of 2 mm to explore the plasma power influence.

By changing the power, considerable variations in morphology and thickness were detected. It is revealed that the thickness of the coatings decreased with increasing power. At a lower applied power of 175 W, the thick coating was achieved with an average thickness of $2.21 \pm 0.18 \mu$ m. By implementing the highest power of 350 W, a substantial thickness reduction to $0.4 \pm 0.13 \mu$ m was observed, as indicated in Fig 3. The input power per molecule has a crucial impact on the extent of the precursor fragmentation in conjunction with the cross-linking degree of the coating, which can affect the coatings' thickness.



Figure 3: SEM images of A) the surface, and B) the crosssection of plasma polymerized coatings as a function of power.

The XPS analysis was conducted to determine the impact of the applied power on the chemical structure of the PEGlike coating. Table 1 indicates the surface elemental composition of the different coatings. The prepared coating at a power of 175 W primarily comprises carbon, oxygen, and a marginal amount of nitrogen. Conversely, the oxygen concentration decreased by increasing power from 36.8 \pm 0.6 to 29.3 \pm 1.7%. In comparison, the nitrogen concentration grew dramatically from 2 ± 0.7 to 19.6 ± 3 %, and subsequently, the carbon percentage decreased in retaliation to the nitrogen increase. The reduction in oxygen content at higher powers can be attributed to the loss of oxygen-containing functional groups of the original PEG structure presented in the precursor. On the other hand, the dissociation of nitrogen molecules to atomic nitrogen is intensified with increasing power, which may lead to an increase in atomic nitrogen density in the gas phase and subsequently results in the high incorporation of nitrogen functional groups on the surface, as confirmed by XPS results.

Table 1: Surface elemental compositions of plasma polymerized coatings as a function of power based on XPS results.

Sample	C (at. %)	O (at. %)	N (at. %)
175 W	$61.2^{a} \pm 1$	$36.8^{a}\pm0.6$	$2^{d} \pm 0.7$
200 W	$61.7^{a}\pm1.3$	$35.2^{ab} \pm 1.1$	$3.1^d \pm 0.3$
250 W	$61.1^{a}\pm1.2$	$32.9^{\circ} \pm 0.7$	$5.9^{\circ}\pm0.8$
300 W	$55.9^b\pm0.8$	$34^{bc}\pm0.6$	$10.1^b\pm0.9$
350 W	$51.1^{\rm c}\pm1.7$	$29.3^{\rm d}\pm1.7$	$19.6^{a} \pm 3$

3.3. The water stability of the coatings

Throughout the initial screening, the prepared samples demonstrated diverse characteristics in terms of degradability in water. In the case of the obtained coatings at low power (175 and 200 W), the coatings thoroughly vanished within one hour of contact with water. On the other hand, by raising the power, the stability of films was improved. Based on the preliminary findings, a power of 300 W was elected to investigate the performance of the PEG-like coating in contact with water in more detail. In this respect, the deposited coatings at a power of 300 W were immersed in distilled water and kept at room temperature. Samples were taken from the water at specific intervals (0, 24, 48, and 72 h). After drying in a vacuum oven, their morphology and chemical characterizations were thoroughly evaluated using FT-IR and AFM techniques.

The FT-IR spectra of PEG-like coating before and after contact with water are illustrated in Fig 4. As is evident; the spectra are nearly identical and dominated by three major peaks (excluding the substrate peak). However, the intensity of peaks linearly decreased with time duration. The samples showed broad, highly shouldered bands at 1000-1200 cm-1 that characterized the C-O stretching vibrations. The absorption band at 1633 cm-1 is assigned to a C=C stretch band of DVE-3, and the peak at 1724 cm-1 corresponds to the carbonyl group (C=O). The peak intensity reduction can be explained by the fact that the degradation of the coating starts from the surface resulting in the gradual release of the coating. The surface morphology and roughness of the coating was analyzed to probe this further. The assessed roughness values of the surface decreased from Rq = 112.6 ± 2.4 and Ra = 96 ± 0.1 to 79.7 ± 3.6 and 65.2 ± 3.9 nm, respectively, after 24h of contact with water. This proves that the coating surface becomes smoother with fewer cavities due to top-layer deletion. Typically, the top layer part of the coating is mechanically weak and can be readily abraded [6]. When the time duration was further increased to 48 h, the roughness values raised to $Rq = 113.7 \pm 4.0$ and Ra = 94.5 \pm 0.9 nm and finally reached 152.1 \pm 6.8 and 125.0 \pm 4.3 nm, respectively, after 72 h of exposure to the water. The drastically increased roughness indicates that the coating gradually becomes thinner and follows the morphology of the uncoated substrate UHMWPE. However, it is worth mentioning that the roughness of the coating after 72 h of contact with water is considerably less than UHMWPE, further proving the actuality of PEG-like coating, which aligns with the gained results from FTIR analysis.



Figure 3: FT-IR spectra of plasma polymerized coating at a power of 300 W, as a function of contact time with water.

4. Conclusion

The present study introduces an aerosol-assisted atmospheric pressure plasma deposition technique to produce plasma polymerized PEG-like coatings with tunable degradability suitable for food packaging applications. The feature of the coatings can be adjusted by carefully modifying the crucial plasma polymerization parameters; power, monomer flow rate, and distance to the substrate. The results revealed that the lowest distance to the substrate of 2 mm is critical for achieving a smooth conformal PEG-like coating with a chemical composition similar to typical PEG polymers. Moreover, highly stable coatings with a specific water penetration level can be achievable by employing a moderate power (300 W) which can guarantee the monomer functionality preservation. The present work revealed that the aerosol-assisted nonthermal plasma technique constitutes a promising green approach to developing a degradable PEG-like coating for controlled-release applications in the food packaging field.

5. References

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