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Polyethylene Glycol and Poly(vinyl alcohol) Hydrogels Treated with Photo-Initiated Chemical Vapor Deposition

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Abstract: This study was designed to determine if surface modification via Photo-initiated Chemical Vapor Deposition (PICVD) affects the physicochemical properties of polyethylene glycol (PEG) and poly(vinyl alcohol) (PVA) differently, given their different chemical structures and properties. Contact angle measurements showed that both polymers increase in surface hydrophobicity after PICVD treatment. Further, the improved hydrophobicity facilitated dispersion into non-polar solvents. Chemical changes were concentrated near the surface, evidenced by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements, indicating namely that partial oxidation occurs during treatment. These findings were discussed in the context of the difference of the molecular structures of PEG and PVA, which, in turn, control their surface functionalization and hydrophobicity.

Key words**:** contact angle; DLS; FTIR; PICVD; polymer; surface treatment.

Introduction

Hydrogels are hydrophilic water-swollen polymeric networks that do not dissolve in water.[1–5] This ability to swell, namely under biological conditions, makes them an ideal class of materials for biomedical applications, such as drug delivery and tissue engineering.[6–9]

Such networks can be classified into three major types, based on the polymers from which they are composed: natural, synthetic and hybrid (synthetic/natural) hydrogels.[10] These can be further classified as physical or chemical hydrogels, based on their cross-linking mechanism.[6,11] Entangled chains, hydrogen bonding, hydrophobic interaction and crystallite formation form physical crosslinks (permanent or not), whereas junctions formed by covalent bonds make permanent chemical crosslinks. Both kinds of crosslinking can be found in a hydrogel network. Network

properties, such as swelling, elastic modulus and transport of molecules, depend on the type and degree of crosslinking.[12] The ionic charge (neutral, cationic, anionic and ampholytic), structure (amorphous, semi-crystalline and hydrogen-bonded) and preparation methods (homopolymer, copolymer, multipolymer and interpenetrating polymer network) are important parameters for further classification of hydrogels.[11,12] Their design and characterization depends on a control of the hydrogel network structure, impacting the degradation of hydrogel scaffolds, diffusion of bioactive molecules and migration of cells through the network.[11,12]

Polyethylene glycol (PEG) and Poly(vinyl alcohol) (PVA) are biocompatible and biodegradable polymers widely used for the preparation of functional hydrogels in pharmaceutical industry.[13–15] PEG-based hydrogels can be prepared by ring-opening polymerization of ethylene oxide cyclic monomers, radiation crosslinking of PEG or free radical polymerization of PEG macromers, whereas PVA hydrogels can be prepared by the common freezing/thawing cycle without chemical crosslinking.[14,16,17]

The functionalization of PEG and PVA hydrogels has been explored via a plethora of methods such as the Passerini three-component reaction, polyelectrolyte multilayer microencapsulation and microwave-assisted functionalization.[18–20] The heterogeneous network structures containing dense crosslinking regions are produced by chain polymerization of hydrogels.[21] On the other hand, a crosslinker or co-monomer that can react with the terminal functional groups of the PEG macromers is required in step-growth polymerization. Greater network structure homogeneity can thus be obtained.[21]

In this study, we demonstrate a simpler and more rapid functionalization of PEG and PVA hydrogels via Photo-Initiated Chemical Vapor Deposition (PICVD). The technology presented here is applicable to various samples, such as polymers, nanomaterials, composites, etc. and has

the ability to modify their surface without additional steps for sample preparation. We have successfully modified metal substrates and nanomaterials using this technique.[22–24] We investigate herein the physicochemical properties of these polymers before and after their surface treatment. Surface modification of these natively hydrophilic hydrogels to render them hydrophobic may allow for greater control over drug delivery, for example, by limiting the diffusion rate of the drug housed in the hydrogel out to the patient[25]. Similarly, hydrophobic hydrogels could find applications in corneal lenses, to decrease the risk of bacterial infections[26]. To our knowledge, no study has been carried out on the surface treatment of PEG and PVA via PICVD.

Experimental

Chemicals

PEG 8000 and PVA 165000 were purchased from Fisher Scientific and used as supplied. Hydrogen peroxide (50%) and sodium hydroxide (5 M) were purchased from Sigma-Aldrich. H_2, CO and Ar used for PICVD (100% chemical purity) were obtained at Air Liquid.

Photo-initiated chemical vapor deposition

50 µL of the untreated PEG or PVA (1 mg/mL in aqueous solution) were deposited onto a copper sample holder and allowed to dry for 24 h. The copper sample holders were polished beforehand using deionized water and sandpaper (grit 1200 MX).[23] A PICVD micro-reactor equipped two UVC lamps was used for surface modification, as illustrated in Figure 1 and detailed extensively previously.[23] The lamps' peak emission was at 253.7 nm, with an irradiance of $5.5 \times 10^{-4} W/cm^2$. The PVA and PEG samples were placed inside the tubular quartz reactor 70 cm from the inlet.

Before each treatment sequence, the reactor was purged for 3 minutes using Ar. The molar ratio of syngas (H_2/CO) injected in the reactor was 0.1 (total gas flow rate of 376 ml/min). Hydrogen peroxide (H_2O_2) was added as a photoinitiator using a syringe pump at a rate of 1 mL/h. Surface treatment time was 1h. According to previous experiments to generate hydrophobic surface properties, the operating pressure in the reactor was maintained at 10 kPag for all experiments.[23] When the experiments were completed, the copper sample holders were carefully taken out of the reactor for analysis. All the samples were prepared in triplicate.

Fig. 1. Schematic of the photo-initiated chemical vapor deposition (PICVD) reactor.

Dispersion in solvents

1 mg/mL of untreated PEG was dispersed in water and mixed using a CIMAREC mixer (speed setting 6) for 0.5 h.[27] PVA dispersions in water (1 mg/mL) were prepared with the same mixer by heating at 80°C for 3 h.[28] PICVD-treated polymers were dispersed directly in water and toluene using the same mixer. The untreated and treated samples were subsequently sonicated using a Braman 5510 sonicator for 5 minutes.

Contact angle measurement

Static contact angle measurements of the polymers were done as described previously for hydrogel before and after their functionalization via chemical vapor deposition (CVD).[29] Two μL of water were placed on the copper substrate before and after coating with the polymer samples. The sessile drop contact angle being stable on the minute time frame, one measurement per location was taken

immediately using a FDS contact angle system OCA DataPhysics TBU 90E.[30] The measurements were carried out on several spots on the untreated and treated PEG and PVA.

Dynamic Light Scattering (DLS)

DLS analysis of the untreated and treated PVA and PEG in water and toluene were carried out in triplicate using a Zetasizer Nano ZSP Malvern, with analysis using the QtiPlot software.[31] Samples were sonicated with a Braman 5510 sonicator for 5 minutes beforehand.

Fourier Transform Infrared (FTIR) Spectroscopy

Using a Perkin Elmer spectrum 65 FTIR spectrometer, attenuated total absorbance probe, in the range of 600-4000 cm^{-1} FTIR spectra at 4 cm^{-1} resolution were recorded. 32 scans were co-added to improve S/N.[32]

X-ray photoelectron spectroscopy (XPS)

Survey, C1s and O1s high resolution spectra of the untreated and treated PEG and PVA were obtained on a VG ESCALab 3 Mk II, using nonmonochromated Mg Kα radiation (1253.6 eV), at a power setting of 300 W, with an instrument resolution of 0.7 eV. The samples were deposited onto silica substrates, using two-sided adhesive Cu tape. The base pressure during scanning was less than $1x10^{-9}$ torr. Electrons were detected at a perpendicular takeoff angle, using 0.05 eV steps, and spectra were analyzed using the VG Avantage software.[33]

Results and discussion

Dispersion in solvents

Untreated PEG and PVA dispersed readily in water, but would quickly settle out of suspension in toluene, these polymers being far less soluble in lower polarity solvents. This was an expected result as the polymers were hydrogels with polar molecular structures. The PICVD-treated polymers showed a reverse behavior: they were not soluble in water, but dispersed well in toluene (stable for 24 h). This indicated that the surface polarity of the polymers was changed after their surface treatment.

Contact angle measurement

The average contact angle of the copper substrate (control) was 70°. As a thick layer of PEG or PVA covered the substrate, we were sure that the measurements of contact angles of the polymers on the copper substrate were done with water. Figure 2 represents the drops of PEG and PVA dried on the copper substrates.

Fig. 2. PEG and PVA drops dried on the copper substrates.

The water contact angle values of the untreated and treated PEG and PVA are represented in Table 1 and Figure 3. The uncertainties were calculated using the standard deviation. In both cases, there is a clear change in surface wettability: PVA becomes hydrophobic, and PEG becomes less hydrophilic (but remains below the 90° threshold for hydrophobicity). This asymmetrical change is likely attributed to chemical structure differences in the polymers, affecting the reaction

mechanisms with syngas (for example, the terminal hydroxyl group in PEG may have a repulsive interaction with the gaseous species).

Table 1. Water contact angle values for PEG and PVA before and after treatment via PICVD.

Sample	Contact angle values (°)
Untreated PEG	29 ± 12
Treated PEG	65 ± 8
Untreated PVA	45 ± 11
Treated PVA	95 ± 12

Fig. 3. Sessile drop water contact angle values of (a) untreated PEG, (b) treated PEG, (c) untreated PVA, and (d) treated PVA.

Dynamic Light Scattering

The diameters of the untreated PEG in water and treated PEG in toluene were 0.90±0.04 μm and 4.5±0.4 μm and those of the untreated PVA in water and treated PVA in toluene were 0.60±0.02 μm and 1.2±0.2 μm, respectively (Figure 4). This diameter increase can be explained in two ways:

deposition or aggregation. First, a deposit may be forming on the polymers as a result of PICVD treatment. Alternatively, the PICVD treatment may be altering the charge of the polymer chains, thereby leading to aggregation. In any case, PEG appears to be significantly more impacted than PVA in this regard.

Fig. 4. Size of PEG and PVA before and after their treatment with PICVD.

FTIR analysis

For untreated PEG (Figure 5a), the peaks at 850 cm^{-1}, 950 cm^{-1} are attributed to the C-C stretching. The peaks at 1080 cm^{-1}, 1230 cm^{-1}, 1280 cm^{-1}, 1320 cm^{-1} and 2860 cm^{-1} are attributed to the C-O stretching, the C-H stretching of methylene group, respectively.[34–36] No significant differences were observed between the peaks of the untreated and treated PEG (Figures 5a and 5b) – this may be due to the thin nature of the coating deposited on the PEG (FTIR is not strictly sensitive to surface changes, which can be drowned out by the bulk).

For untreated PVA (Figure 5c), the peaks at 800 cm^{-1}, 900 cm^{-1} are attributed to the CH_2 stretching.[37] The peaks at 1080 cm^{-1}, 1230 cm^{-1}, 1300 cm^{-1}, 1400 cm^{-1}, 1560 cm^{-1}, 1650 cm^{-1} are attributed to the C-O stretching, the C-H stretching of methylene group, respectively.[34,38] The broad band in the region of 3100-3500 cm^{-1} is attributed to the O-H stretching due to the hydrogen bonding.[39] The alkyl stretching peak at 2900 cm^{-1} is splits into two peaks at 2980 cm^{-1} and 2920 cm^{-1} following treatment of PVA (Figure 5d).[38] Moreover, an intensity increase of the peaks at around 1400 cm^{-1} and 1560 cm^{-1} following treatment is observed, attributed to increased C-H stretching (methylene group).

Fig. 5. FTIR spectra of (a) untreated PEG, (b) treated PEG,(c) untreated PVA, and (d) treated PVA.

XPS analysis

In the survey spectra of untreated and treated PEG and PVA, oxygen and carbon peaks were observed (data not shown). Following PICVD treatment, a small amount of iron was also observed, which may correspond to the presence of iron pentacarbonyl in the carbon monoxide tank (a known CO contaminant)[40,41].

In Figure 6a (C1s peak for untreated PEG), the peaks at 285.0 eV and 286.3 eV were attributed to the C-C and C-O bonds, respectively. In Figure 6b (treated PEG), the peaks at 285.0 eV, 286.5 eV, 287.3 eV and 288.0 eV correspond to the C-C, C-O, C=O bonds and COOH group, respectively, respectivelyThe intensity of the C-C and C-O peaks decreased 1.9 and 1.4 times, respectively (Figure 7). Moreover, the peaks of the C=O bond and COOH group appeared in the spectrum of the treated PEG, indicating that the PICVD treatment imparts mainly additional carboxylic and carbonyl groups to the surface. The relative increase in the amount of the oxygen is attributed to an incorporation of oxygen-containing species resulting from the PICVD process (Table 2).

Table 2. Atomic percent of carbon and oxygen on the sample surfaces before and after PICVD treatment.

Samples	Chemical elements	Percentages on the surface of samples (%)
Untreated PEG	Carbon	74
	Oxygen	26
Treated PEG	Carbon	62
Treated PEG	Oxygen	35
Untreated PVA	Carbon	63
Untreated PVA	Oxygen	35
Treated PVA	Carbon	62
Treated PVA	Oxygen	37

In Figure 6c (untreated PVA), the peaks at 285.0 eV and 286.5 eV were attributed to the C-C and C-O bonds, respectively. In Figure 6d (treated PVA), the peaks at 285.0 eV and 285.5 eV correspond to the same peaks as the untreated PVA. The intensity of the C-C peak decreased 2.2 times, whereas that of the C-O peak increased 1.1 times, respectively (Figure 7). The peak at 287.2 eV and the small peak at 288.5 eV was attributed to the addition of C=O and COOH groups

appearing only after treatment. These spectral differences correspond to an attack of the polymers by the oxygen radical, possibly formed through decomposition of the hydrogen peroxide photo-initiator used.[23]

Fig. 6. XPS C1 high resolution spectra of (a) untreated PEG, (b) treated PEG, (c) untreated PVA, and (d) treated PVA.

Fig. 7. Intensity change for key peaks identified in XPS high resolution spectra of (a) PEG and (b) PVA.

Figure 8 presents a possible reaction scheme for surface functionalization of PEG and PVA. Given that certain oxidative pathways seem apparent following XPS analysis, the reaction scheme is compared to the previously reported oxidation of PEG and PVA using oxidants such as potassium dichromate or potassium permanganate [42,43].

Fig. 8. Surface functionalization of (a,c) PEG and (b,d) PVA, (a,b) by chemical reactions with potassium dichromate or manganese permanganate, (c, d) via PICVD.

Hydrophobic interactions can increase energy dissipation in hydrogel networks through the reversible disengagements of the hydrophobes from the hydrophobic associations.[44] The stiffness of hydrogels is controllable by increasing the hydrophobicity of their network.[45] Moreover, the increase of the hydrophobicity of these polymers can decrease their water uptake and increase their elastic modulus, which make hydrogels more resistant to bacterial colonization as the killing

efficiency of hydrogels depends on their surface hydrophobicity[46]. These hydrogels hold significant promise for sustained delivery of hydrophobic therapeutics.[47] The increase of the hydrophobicity of hydrogels is also helpful for the optimization of redox hydrogels for the integration of enzymes on electrodes.[48] In addition, this increase can be used in various applications that require fast separation of hydrophobic molecules from a large volume of aqueous solutions.[49] More investigation is needed to confirm the increase of the stiffness of the PEG and PVA treated via PICVD, which would make them potential candidates for these applications.

It is worth noting that hydrogels synthesized or functionalized by CVD are usually attached to solid substrates. The swelling of hydrogels attached on substrates is lower than that of unconstrained bulk hydrogels because of the substrate effect.[50] Even though PICVD appears to be a very promising technique for the surface treatment of hydrogels, the tendency of these polymers to form aggregates represents a problem. Therefore, the strategies that help avoid this should be explored in order to optimize the functionalization and swelling of these hydrogels.

Conclusions

This study confirms the efficacy of PICVD for the surface treatment of PEG and PVA hydrogels. The strength of this approach is its simplicity and rapidity in the modification of surface chemical composition. We have shown for the first time that the molecular structure of polymers affects their surface functionalization via PICVD. The difference of the surface functionalization of PEG and PVA hydrogels via PICVD may be due to the difference in their chemical structures and physicochemical properties. The hydroxyl group is found inside the polymer chain of PVA,

whereas its position is out of the polymeric chain in PEG. This may cause the difference of the repulsive interaction between the oxygen atoms of the radicals produced in PICVD with the hydroxyl group of these polymers. Therefore, the intensity of the C=O peak and COOH group on the surface of the treated PEG can be increased, whereas that of the C=O peak on the surface of the treated PVA can be decreased. Further, the surface of the polymers became more hydrophobic after their surface functionalization, evidenced by changes contact angle values. This increased hydrophobicity helped improve their dispersion in toluene – such improvement may be applied for the fabrication of hydrogel-based devices. This study shows that PICVD is an appropriate technique to treat the surface of polymers in order to increase their hydrophobicity. These more hydrophobic polymers can be used for the fabrication of polymer-based devices or targeted drug delivery vectors. More investigation is warranted to determine the effect of the duration of surface functionalization of polymers via PICVD on their surface chemical composition and dispersion in solvents, as well as further clarify the reaction scheme.

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Figure captions

Fig. 1. Schematic of the photo-initiated chemical vapor deposition (PICVD) reactor.

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