



Surface characterization of poly(vinyl chloride) urinary catheters functionalized with acrylic acid and poly(ethylene glycol) methacrylate using gamma-radiation

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ABSTRACT

Poly(vinyl chloride) (PVC) urinary catheters were modified with either a single or binary graft of acrylic acid (AAC) and/or poly(ethylene glycol) methacrylate (PEGMA) using gamma-radiation from ⁶⁰Co to obtain PVC-g-AAC, PVC-g-PEGMA, [PVC-g-AAC]-g-PEGMA, and [PVC-g-PEGMA]-g-AAC copolymers. The outer and inner surfaces of the modified catheters were characterized using scanning electron microscopy (SEM), confocal laser microscopy (CLM) and X-ray photoelectron spectroscopy (XPS). The XPS analyses, by examining the correlation between the variation of the C_{1s} and O_{1s} content at the catheter's surface, revealed that the catheter's surfaces were successfully grafted with the chosen compounds, with those that were binary grafted showing a slightly more covered surface as was evidenced by the disappearance of PVC's Cl peak. The SEM and CLM analyses revealed that catheters that had been grafted with PEGMA had a rougher outer surface as compared to those that had only been grafted with AAC. In addition, these imaging techniques showed that the inner surface of the singly grafted catheters, whether they had been grafted with AAC or PEGMA, retained some smoothness at the analyzed grafting percentages, while the binary grafted catheters showed many protuberances and greater roughness on both outer and inner surfaces.

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1. Introduction

In the area of medicine, one of most common problems affecting biomaterials is the adhesion of macromolecules – which can include proteins, platelets, and even bacteria – onto their surface [1]. In regards to this problem, urinary catheters are particularly troublesome because their use in hospital patients almost always leads to the development of a catheter-related urinary tract infection, causing not only further problems for patients, but also higher costs for the healthcare system [2–4]; leaving open the necessity to modify this material in order to improve its surface properties. The surface modification of materials can be done through both physical and chemical methods. In particular, when dealing with polymers,

grafting is an attractive method because it involves the covalent attachment of a new material with some desired properties, such as the ability to prevent macromolecules from attaching to its surface, onto the original polymer backbone, thus forming a type of brush-layer on the surface yet allowing the material to retain its original bulk properties [5]. In addition, the covalent attachment ensures that the surface modification does not wear off or is etched away, as could be the case with some coatings or physical modifications [6].

Polymer grafting is most often done by free-radical reactions, where because oftentimes the graft-polymerization is a living polymerization, the grafting process can be stopped when desired and there can be some control in regards to the grafting density [7]. Generally, grafting follows two steps: 1) the creation of active sites that will initiate the grafting process, and 2) the introduction of the compound that will participate in the graft-polymerization. More specifically, there are two ways to graft a polymer: *grafting-from*

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and *grafting-to*. In the *grafting-from* method, the active sites are created on the substrate, so that when the system is placed in contact with the monomer, this latter one can polymerize and grow from the bottom-up. In the *grafting-to* method, the active sites are tethered to the polymer chains that will be attached to the substrate [8]. Each method offers different advantages; for example, in *grafting-to* there is more control in regards to the properties of the compound that is to be attached (e.g. chain length); however, with *grafting-from*, higher grafting percentages can be obtained [8,5].

Free-radical induced grafting can be carried out through chemical means, using ozone, or by using high energy sources. Among the disadvantages of chemical polymer grafting is the need to use initiators to begin the grafting process (which could be harmful if not properly removed from medical devices), while ozone-initiated grafting is a surface-graft method – meaning it does not have a high penetration depth – that is sometimes coupled with UV-radiation to increase its grafting yield [1]. Nonetheless, one way to circumvent these problems is to use high-energy sources, such as gamma-radiation. Grafting initiated by gamma-radiation not only prevents the need to use chemical initiators, but it also offers the advantage of being a versatile method because the grafting process can be carried out in the solid, liquid, and gaseous state; it is highly reproducible; and it offers a uniform penetration depth [9]. This last point is of particular importance in this work, as the material to be modified is of a cylindrical shape and has two surfaces: the outermost surface which will be in contact with bodily tissue, and the inner surface which will be in contact with bodily fluids. In addition, it has been studied that the formation of bacteria biofilms happens on both surfaces of the device. However, one of the possible drawbacks of using gamma-radiation with PVC is that the active sites are created through a dechlorination process, with the evolution of chlorine and HCl gas as a potential drawback.

This paper will dwell into detail on how the inner and outer surface of poly(vinyl chloride) (PVC) urinary catheters changes physicochemically and morphologically after being grafted with either acrylic acid (AAc), poly(ethylene glycol) methacrylate (PEGMA), or a combination of both compounds, using gamma-rays from ^{60}Co , with the particular aim of investigating whether Cl is detected on the surface of the catheters. These compounds were chosen because poly(AAc) is a smart polymer that, due to its carboxylic acid functional group, has a swelling pH response that allows it to load and control-release drugs or other compounds; and PEG is considered one of the most biocompatible polymers and has often been used to coat drugs for an easier and longer circulation time in the body [10]. The cytocompatibility results of the modified catheters, as well as the pharmacokinetics, have been previously published [11].

2. Materials and methods

2.1. Materials

PVC urinary catheters (36.5 cm length, 3 mm diameter, 0.5 mm thickness; Biçakçilar, Turkey) were cut into 2 cm pieces, in order to be more manageable in an experimental setting, washed with methanol for 24 h, changing the washing medium three times, and dried in a vacuum desiccator for 24 h and a vacuum oven at 40 °C for 6 h. The acrylic acid (AAc; CAS 79-10-1) and poly(ethylene glycol) methacrylate (PEGMA; CAS 25736-86-1) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and distilled before using.

2.2. Grafting of AAc and/or PEGMA onto PVC

For the single graft, 2-cm PVC catheter pieces were placed inside a glass ampoule and irradiated in the presence of air with ionizing

radiation from ^{60}Co (GammaBeam 651 PT, Nordion Co., Canada). This initial irradiation step creates peroxides and hydroperoxides on the catheter, which are thermally unstable, and after heating will undergo a homolytic break to create the radicals that participate in the grafting process. After being irradiated, 5 mL of an aqueous AAc (10, 30, or 50% v/v) or PEGMA (14% v/v) solution were added to the glass ampoule and the system was bubbled with argon for 10 min, after which time the ampoule was sealed. Because AAc can homopolymerize easily, the argon bubbling process for AAc-containing ampoules was conducted in an iced water bath (5 °C) to prevent homopolymer from forming. To initiate grafting, the sealed glass-ampoule was placed in a water bath, where the reaction temperature (70–80 °C) and time (1–24 h) were varied to obtain the grafting kinetics. Once the grafting process was completed, the modified catheter pieces were washed with distilled water, for at least 48 h, changing the washing medium every 3 h, when possible, in order to remove any homopolymer formed during grafting. The cleaned modified catheters were then dried in a vacuum desiccator for 48 h and a vacuum oven for 24 h at 40 °C, which is when a constant weight was reached. Drying the samples at higher temperatures (above 50 °C) would cause a color change in the catheters, which is associated to the degradation of PVC, particularly after exposure to gamma-radiation [12,13]. The grafting percentage (G) was calculated as follows,

$$G(\%) = [(W_o - W_f)/W_o] \times 100 \quad (1)$$

where W_f and W_o are the final and initial weight, respectively, of the catheter.

The binary graft was conducted similarly; however, this time the experiments were carried out with previously grafted catheters, PVC-g-AAc or PVC-g-PEGMA, to obtain [PVC-g-PEGMA]-g-AAc or [PVC-g-AAc]-g-PEGMA.

2.3. X-ray photoelectron spectroscopy (XPS)

In order to obtain a flat surface for the analyses, the samples were left swelling in distilled water for 24 h, after which time they were cut open and placed in between two glass slides (to flatten them), left to dry in a vacuum desiccator for 24 h, and afterwards a vacuum oven at 40 °C for 24 h, which as mentioned in the previous section is when a constant weight is reached. The flattened catheters were then washed with ethanol for 3 h, to remove any surface contaminants that could have been transferred when the samples were removed from the glass slide, and dried for 6 h in a vacuum oven at 40 °C.

The XPS analyses were carried out using a RIBER LDM-32 spectrometer. The apparatus uses a vacuum generated by an ionic pump in the pressure range of 5.3×10^{-6} and 6.7×10^{-6} Pa, and a non-monochromatic Al K α radiation source ($h\nu$ 1486.6 eV). The survey spectra were obtained using a pass energy of 100 eV and energy steps of 1 eV and dwell time of 200 ms, with a time interval of 0.1 s. For each spectra 10 scans were run in the energy range of 0–1400 eV. For the high-resolution spectra the pass energy was lowered to 20 eV and the energy steps to 0.2 eV and dwell time of 200 ms. The samples were mounted on a copper sample holder (1 cm \times 1 cm) and secured using carbon tape. Two different points on the surface of each material were analyzed in order to evaluate the sample's homogeneity in regards to its chemical composition. Although similarity between these two spectra for each material were found, the spectra showing large signals assigned to copper (from sample holder) or carbon (from carbon tape) were discarded; this was taken as a measure to ensure that the sample was placed in the correct position inside the analysis chamber. The second area analyzed for each surface was used for the high-resolution spectra measurements. Spectra were acquired at 0° emission angles, normal to the sample surface, and the analyzed area was of 600 μm^2 .

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