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Immobilization of poly(ethylene glycol) or its sulfonate onto polymer surfaces by ozone oxidation

Young Gun Ko[a,b], Young Ha Kim[a,*], Ki Dong Park[a], Hee Jung Lee[a], Won Kyu Lee[a], Hyung Dal Park[a], Soo Hyun Kim[a], Gil Sun Lee[b], Dong June Ahn[b]

[a]*Biomaterials Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea*
[b]*Department of Chemical Engineering, Korea University, Anamdong 5ga-1, Seoul 136-701, South Korea*

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Abstract

A novel surface modification method has been developed to improve biocompatibility of polymeric biomaterials. This approach involves ozonation and then followed by graft polymerization with acrylates containing PEG, sulfonated PEG or by coupling of PEG derivatives. All the reactions were confirmed by ATR FT-IR and ESCA. The degree of ozonation measured by the iodide method was dependent on the ozone permeability of the polymers used. Surface hydrophilicity was investigated by measuring the contact angles. Ozonation itself yielded a slight increase in hydrophilicity and a decrease in platelet adhesion, but PEG immobilization showed a significant effect on surface hydrophilicity and platelet adhesion to confirm well-known PEG's passivity which minimize the adhesion of blood components on polymer surfaces. Both graft polymerization and coupling were effective for PU. In contrast, only grafting gave enough yields for PMMA and silicone. Platelet adhesion results demonstrated that all PEG modified surfaces adsorbed lower platelet adhesion than untreated or ozonated ones. Polymers coupled with sulfonated PEG exhibited the lowest platelet adhesion when compared with control and PEG coupled ones by virtue of the synergistic effect of non-adhesive PEG and negatively charged SO_3 groups. This PEG or sulfonated PEG immobilization technology using ozonation is relatively simple for introducing uniform surface modification and therefore very useful for practical application of blood contacting medical devices.

Keywords: PEG/PEG–SO_3 immobilization; Ozone treatment; Wettability; Platelet adhesion

1. Introduction

A variety of approaches has been undertaken to improve the blood compatibility and to minimize cell adhesion on biomaterials surfaces [1–3]. One approach involves surface modification by grafting a hydrophilic component, such as poly(ethyleneglycol) (PEG). PEG has unique solution properties and molecular conformation in aqueous solution. PEG-grafted surfaces exhibit specific non-adhesive property to proteins, blood components and cells mainly due to high surface mobility and steric stabilization effects [4–8]. In addition, sulfonated PEG, (PEG–SO_3)-grafted polymers, improved antithrombogenicity, biostability, and anticalcification in-vitro, ex-vivo, and in-vivo by the synergistic effect of the flexible hydrated PEG chains and negatively charged sulfonate anticoagulant groups [9–12].

Surface ozone oxidation is widely applied in polymer areas because it has an advantage of uniformly introducing peroxides on the polymer surface and offers an easy-to-handle, inexpensive technique [13–16]. When polymer is exposed to ozone gas, peroxides are formed in addition to carbonyl and carboxyl groups [17]. The generated polymeric peroxides are capable of initiating polymerization of vinyl monomers, resulting in surface grafting onto the ozonated polymeric materials [13].

This article describes PEG or PEG–SO_3 immobilization onto polymethylmethacrylate (PMMA), polyethylene (PE), silicone, and polyurethane (PU) by ozonation (Fig. 1). The surface structures and properties of modified polymers were investigated using attenuated total reflectance Fourier transform infrared (ATR FT-IR), electron spectroscopy for chemical analysis (ESCA), atomic force

* Corresponding author. Tel.: +82-2-958-5340; fax: +82-2-958-5308.
E-mail address: yhakim@kist.re.kr (Y.H. Kim).

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