SURFACE MODIFICATION OF POLY(ETHER URETHANE) BY CHEMICAL INFUSION AND

GRAFT POLYMERIZATION

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The surface of a commercially available poly(ether urethane), Tecoflex®, has been modified by either chemical infusion or graft polymerization techniques. The chemical infusion technique involves the physical entrapment of polymer additives in the near surface region of the sample, while graft polymerization provides chemical attachment of a polymer to the surface of the sample. The additives investigated for chemical infusion include poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG) along with iodine and silver nitrate as antibacterial agents. Graft polymerization covalently bonds polymers to the surface of the poly(ether urethane). The polymerization is initiated by photolysis of Re₂(CO)₁₀ to generate radicals on the poly(ether urethane) surface. The monomers examined for graft polymerization include N-vinyl pyrrolidone (NVP) and 2-hydroxyethylmethacrylate (HEMA), along with sulfonate containing monomers such as sodium vinylsulfonate, 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and its sodium salt (NaAMPS). The surface energies of these surface modified poly(ether urethane) samples were examined by contact angle measurements in water using the Wilhelmy balance technique. An increase in surface energy was observed following surface modification by both techniques, resulting in more hydrophilic surfaces than the untreated samples.

INTRODUCTION

Because of their good elastomeric properties, including the ability to undergo repeated flexings without failure, polyurethanes are used in a number of biomedical applications, such as flexing diaphragms or coatings on surfaces in artificial heart and ventricular assist devices.¹ In particular, poly(ether urethanes) are preferred for use in biomedical applications because of their greater hydrolytic stability as compared to poly(ester urethanes). However, poly(ether urethanes), as with other polymeric materials in contact with blood, are subject to formation of thrombus² and bacterial infections.³ These problems might be overcome by
incorporation of antithrombogenic substances and/or antibacterial agents in the surface of the polymer.

One of our approaches to surface modification uses the chemical infusion process to introduce materials into the outermost layer of the polymeric material, thereby altering the surface without changing the bulk properties of the polymer. The infused materials may slowly diffuse out of the infusion layer if they are volatile or highly mobile. However, if polymeric infusive materials are employed, they become chain entangled with the host polymer leading to a permanently modified surface. A second approach utilizes photo-initiated graft polymerization onto poly(ether urethanes) in the presence of an appropriate monomer. We have explored both of these methods by examining the infusion of poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG) into commercially available poly(ether urethane) and the graft polymerization of N-vinyl pyrrolidone and 2-hydroxyethylmethacrylate, along with sulfonate containing vinyl monomers, onto poly(ether urethane). Evaluation of the surface energies as examined by contact angle measurements is presented herein.

EXPERIMENTAL

1. Materials and Methods

The poly(ether urethane), Tecoflex EG-60D, was obtained from Thermedics, Inc., Woburn, MA. Tecoflex was injection molded into a disk-shape, 26 mm in diameter and 3.2 mm thick, and a cup-shape, 9.5 mm in diameter and height. Care was taken to avoid touching the samples, and thus introducing contaminants, by using surgical gloves when handling. The diameter of the disk was cut to 22.2 mm and the sample was rinsed several times with deionized water. The samples were air dried at room temperature prior to use. Square samples (12 x 12 mm) for contact angle measurements were cut from the disk-shaped sample and rinsed as above.

PVP (MW 10,000), Plasdone C15, was obtained from GAF. Poly(ethylene glycol) (MW 3,400), N-vinyl pyrrolidone (NVP), 2-hydroxyethylmethacrylate (HEMA), vinylsulfonic acid (sodium salt), and dirheniumdecacarbonyl (Re2(CO)10) were purchased from Aldrich Chemical, Co. NVP was purified by vacuum distillation and zone refining. HEMA was purified by vacuum distillation. Re2(CO)10 was sublimed at 40°C at 10 mm Hg prior to use. 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and its sodium salt, NaAMPS, (25% in water) were gift samples from Lubrizol Corp. and were used as received. Baker reagent grade isopropyl alcohol (IPA), Baker analyzed reagent dimethylformamide (DMF), Baker HPLC grade chloroform, and Burdick & Jackson acetonitrile (distilled in glass) were used as received.

2. Surface Treatment Procedures

A. Chemical Infusion: The infusion chamber (Figure 1) consists of two glass tubes connected by flexible tubing. One tube is filled with glass beads for static stirring to ensure complete mixing while the other holds the samples to be treated. The system uses a peristaltic pump to circulate the treatment solution and a second metering pump to add the diluent solution to the system in small increments. In this manner, the solution in the apparatus gradually becomes richer in diluent. The excess solution is collected in an overflow vessel as the volume of the reaction tube is exceeded.