Available online at www.sciencedirect.com

ScienceDirect

Sensors and Actuators B 124 (2007) 153–160

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/snb

# Anti-fouling epoxy coatings for optical biosensor application based on phosphorylcholine

Kyu Ho Chae*, Young Min Jang, Yu Ho Kim, Ok-Jae Sohn, Jong Il Rhee

*School of Applied Chemical Engineering, Chonnam National University Gwangju, Republic of Korea*

Received 19 July 2006; received in revised form 4 December 2006; accepted 5 December 2006
Available online 12 January 2007

## Abstract

Epoxy polymers containing phosphorylcholine (PC) groups were prepared by the copolymerization of glycidyl methacrylate and 2-methacryloyloxyethyl phosphorylcholine (MPC), and used as a coating material for an oxygen sensing membrane, in order to protect it against bio-fouling by microorganisms. The copolymers had good film forming properties. The cured polymer films had excellent adhesion properties and were transparent at the wavelength of more than 300 nm. The cross-linking reaction of the polymer films increased with increasing amount of MPC units in the copolymer, and the addition of an aliphatic diamine significantly enhanced the cross-linking reaction of the copolymer films. The cured epoxy copolymers show a high anti-fouling effect, which was observed by incubating *E. coli* on the copolymer films. The coatings of the cured epoxy copolymer did not interfere with the performance of the optical oxygen sensing membrane. Thus, the epoxy copolymers containing PC groups are very useful as an anti-fouling coating material for the optical biosensing membranes.

*Keywords:* Anti-fouling; Epoxy coatings; Phosphorylcholine; Optical biosensor

## 1. Introduction

Sensors have been used for the continuous monitoring of various parameters such as the pH changes, and $O_2$ or $CO_2$ concentration in bio-reactor, environmental or clinical systems. However, one of the most serious problems in such sensing systems is the surface fouling caused by various foreign materials such as proteins, cells and microorganisms, which induce a decrease in the sensitivity and life-time of the sensors. Such surface fouling finally leads to sensor failure as a consequence of the interruption of the analyte transport into the sensing layer. Therefore, it is vital to protect against or minimize the fouling of the surface of sensors caused by the build-up of foreign materials.

Several polymer systems have been reported to prevent or minimize the bio-fouling of coatings. For example, biocides embedded in a copolymer matrix [1], polymers containing phosphorylcholine (PC)-substituted methacrylate units [2], antimicrobial *N*-halamine polymer [3], fluoroalkyl diol-containing polyurethanes [4], poly(ether) grafted poly(urethanes) [5], and plasma polymers of hexamethyldisiloxane/$O_2$ [6], were found to be effective as anti-fouling coatings.

One of the most effective methods of making an anti-fouling coating is to use polymers containing PC groups, which mimic a bio-membrane surface. It is known that the major component of the outer surface of the cell membrane consists of the zwitterionic lipid PC. The PC surface provides an inert surface for the biological reactions of proteins and glycoproteins minimizing bio-fouling. Polymers containing PC groups have properties that reduce bio-fouling as well as resist protein adsorption and cell adhesion [7], and have been used in various biomedical applications to prevent bio-fouling [8].

Polymers containing PC groups were found to be suitable as a coating for devices which need to be endowed with anti-fouling properties. However, such polymers have poor mechanical properties due to the zwitterionic PC groups which absorb large amounts of water. It has generally been found that many of polymers containing PC groups possess inherently poor mechanical properties. Therefore, such polymer systems are not suitable for those devices in which the materials are exposed to mechanical forces.

---

* Corresponding author at: Chonnam National University, School of Applied Chemical Engineering, 300 Yongbong-dong, Buk-gu, Gwangju, Chonnam 500-757, Republic of Korea. Tel.: +82 62 530 1874; fax: +82 62 530 1909.
*E-mail address:* khochae@chonnam.ac.kr (K.H. Chae).

0925-4005/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2006.12.012

On the other hand, coating materials based on epoxy resins have attracted considerable attention in many areas of technology. This is due to the fact that epoxy resins can be processed relatively easily, and the cured epoxy resins have good mechanical and chemical properties. For this reason, epoxy resins have been widely used as surface coatings, adhesives, painting materials, laminates, encapsulants, polymer composites, and insulating materials for electronic devices, etc. [9,10].

In the present study, epoxy polymers containing PC groups were applied to anti-fouling optical sensor coating materials in order to improve the mechanical properties of the anti-fouling coatings, since epoxy polymers have an exceptional combination of properties such as easy processability, high safety, excellent solvent and chemical resistance, toughness, low shrinkage on curing, good electrical, mechanical and corrosion resistance along with excellent adhesion to many substrates [11]. The cured PC-containing epoxy polymers were used as a coating material for oxygen sensing membranes and their feasibility as a sensor coating material was examined.

## 2. Experimental

### 2.1. Materials and instruments

2-Chloro-2-oxo-1,3,2-dioxapholane (COP) and trimethylamine (TMA) were purchased from Aldrich Chemical Company and used without further purification. 4,4′-Methylenebis (cyclohexylamine) (MCA) and 4,4′-methylenedianiline (MDA) were obtained from the Tokyo Kasei Chemical Company and used as received. 2-(2-Oxo-1,3,2-dioxaphosphoyloxy)ethyl methacrylate (OPEMA), and 2-methacryloyloxyethyl phosphorylcholine (MPC) [12], and ruthenium(II) tris(4,7-diphenyl-1,10-phenanthroline) perchlorate (Ru-DPP) [13] were prepared by using the procedures described in the literatures.

The molecular weight was determined using a dynamic light scattering (DLS) spectrophotometer model DLS-8000HL from Otsuka Electric Co. X-ray photoelectron spectra (XPS) were obtained using a Thermo Co. instrument model Multi-Lab 2000. The optical images of *E. coli* were taken using a Hitachi model S-4700 scanning electron microscope (SEM). Fluorescence spectra were recorded using a Hitachi model F-4500 fluorescence spectrophotometer. Adhesion tests were performed using a F107 Cross Hatch Cutter KIT from Elcometer Instruments.

### 2.2. Polymerization

The reaction conditions used for preparing the copolymers are shown in Table 1. Corresponding amounts of glycidyl methacrylate (GMA), MPC, and azobisisobutyronitrile (AIBN) were dissolved in 20 mL of a THF and MeOH (7:3, v/v) solvent mixture. The mixture was charged into a cap tube and purged with nitrogen for 20 min. The tube containing the mixture was sealed under nitrogen and polymerization was carried out at 60 °C for 16 h. The resulting polymer was isolated by precipitation into *n*-hexane and subsequently redissolved in $CHCl_3$ and purified by reprecipitation into *n*-hexane. The precipitated polymer was collected by filteration, and dried in vacuo for 6 h at room temperature.

IR (KBr pellet, $cm^{-1}$): 3700–2600 (broad, medium), 3050, 2943, 1732, 1480, 1400, 1220, 1149, 1085.

### 2.3. Film preparation

A 5.0 wt.% copolymer solution was prepared by dissolving the polymer (50 mg) and diamine (2.5 mg) in $CHCl_3$ (1.0 mL). The polymer solution was filtered through a 0.45 μm Milipore filter, and spin coated on a silicon wafer or a small Confocal dish at 400 rpm for 10 s on the 1st run and 1200 rpm for 20 s on the 2nd run. The film on the silicon wafer was dried in vacuo at 40 °C for over 6 h.

### 2.4. Adhesion test

A 20 wt.% polymer solution was prepared by dissolving the copolymer-I (2.0 g) and MDA (0.1 g) in $CHCl_3$ (10 mL). The polymer solution was cast on a glass plate (20 mm × 25 mm) and the film on the glass plate was cured at 80 °C for 20 min. Thickness of the film was 58 μm. The adhesion test was performed with a cross-hatch cutter using ASTM test method B (cross-cut tape test) [14].

### 2.5. Insoluble fraction

The copolymer films on the silicon wafer, with or without the diamine, were cured at various heating temperatures for 20 min. Thickness of the film was 1.76 μm. The cured copolymer films were dipped in $CHCl_3$ for 10 min and subsequently dried in vacuo at 40 °C for 4 h. The insoluble fraction of the copolymer

Table 1
Polymer composition and physical properties

| Copolymer | Monomer[a] | | AIBN (mg) | MPC in feed (mol%) | MPC unit[b] found (mol%) | Yield (%) | $\bar{M}_n$[c] ($\times 10^5$) |
|---|---|---|---|---|---|---|---|
| | GMA (g) | MPC (g) | | | | | |
| I | 1.00 | 0.11 | 10.0 | 5.0 | 2.0 | 72 | 1.20 |
| II | 1.00 | 0.21 | 10.0 | 10.0 | 6.6 | 78 | 0.93 |
| III | 1.00 | 0.32 | 10.0 | 15.0 | 13.0 | 63 | 0.99 |

[a] Polymerization was carried out with 1 wt.% AIBN at 60 °C for 16 h.
[b] Determined from XPS.
[c] Determined from DLS-8000HL.