

THE EFFECT OF DIFFERENT POLYMER LAYERS ON PROPERTIES OF STAINLESS STEEL FOR BIOMEDICAL APPLICATIONS

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Abstract

The effect of different polymer layers (polysulfone and polytetrafluoroethylene) on mechanical properties of stainless steel plates was studied. The "in vitro" behaviour of examined samples was determined on the basis of pH variations of the Ringer fluid during the incubation, also by conductivity measurements and by sample weight variations during 10 weeks immersion in solution. Scanning electron microscopy helped to co-relate the properties of stainless steel with different polymer layers applied on its surface. Layers adhesion to stainless steel surface was observed in more detail.

Results showed that pH values of the Ringer fluid for polysulfone coated samples of stainless steel were lower than those for bare steel. Fluid conductivity presented continuous increase during incubation. The SEM micrographs showed that layers adhesion to stainless steel surface was better in the case of polytetrafluoroethylene.

Introduction

Surface properties and corrosion resistance are the most important characteristics of biomaterials among all factors that determine the biocompatibility of an implant. Several studies had demonstrated the dependence of alloy biocompatibility on surface treatments [1-5]. To solve the problem of corrosion after stenting, several coatings have been tested either in vitro or in vivo, including gold coating and polymers [6]. The degradation of bonding and inflammation are typical problems related to polymer coatings [7,8]. The studies related to polysulfone (PSU) applications in medicine started over 20 years ago. This amorphous polymer is composed of sulfone, ether and isopropylidene groups connected by aromatic rings. Due to its specific structure, polysulfone has good mechanical properties, and also good chemical and thermal resistance [9, 10]. There is enough data available on its inertness in biological environment, as well as on its biocompatibility with blood and physiological fluids [11].

Polytetrafluoroethylene (PTFE) is perhaps the most common medical polymeric fluorocarbon [12]. Commercial Teflon is a packed vinyl polymer, lacking a rigid 2D graphitic or 3D diamondoid crystalline structure. Many different kinds of Teflon are or have been in widespread use, including surface films [13, 14], wire coatings [15] and other applications. Teflon is a chemically inert, bioinactive [16], nonabsorbable [17] implant material. It is relatively stable in

the tissues and is not readily dissolved or digested by the host [18].

The aim of this study was to investigate the difference between the effects of polysulfone and polytetrafluoroethylene on the properties of stainless steel plates. The second objective was to characterize the adhesion of different polymer layers to stainless steel surface before incubation and after 10 weeks incubation in Ringer fluid, using the scanning electron microscopy to study the surface morphology.

Materials and methods

Stainless steel plates produced by Huta Baildon, Katowice (chemical composition: C 0.047%, Si 0.27%, Mn 0.38%, P 0.021%, S 0.009%, Cr 16.52%, Ni 0.14%, N 0.039%, Fe exc.) were used in this investigation. Two different polymer layers were subjected to evaluation:

1). Polysulphone (PSU) manufactured by Aldrich Chemical Company, USA; $C_{27}H_{26}O_6S$ $M=26.000$, $T_g=190^\circ C$, $d=1.24[g/cm^3]$

2). Polytetrafluoroethylene (PTFE) spray, manufactured by Kent Industries, UK.

For simulation of biological environment the Ringer Fluid was used, made by Fresenius Kabi Polska Sp. z.o.o., with the following composition: NaCl 8.6 g/l, KCl 0.3 g/l, CaCl₂ 0.243 g/l.

The PSU solution was obtained by chemical dissolution of PSU beads in CH₂Cl₂ in a ratio 1:4 (w/v) followed by a 24-hour stirring at room temperature. The steel samples were immersed in PSU solution in order to obtain different number of layers on the surface (1, 3 and 5 layers). The PTFE spray was applied on the surface of steel samples in order to obtain 1, 3 and 5 layers. In order to determine the influence of PSU and PTFE layers on properties of stainless steel, samples of bare steel and samples coated with polymer layers were incubated in the Ringer fluid and distilled water for 10 weeks at 37°C. The pH and conductivity of solutions as well as mass measurements were performed every 2-4 days using the CC-315 ELMETRON pH-meter and CC-315 ELMETRON conductivity-meter. Relative mass change was calculated using the equation:

$$\Delta m[\%] = \frac{m_s - m_o}{m_o} \cdot 100$$

where m_s [g] is a measured mass of the sample during incubation and m_o [g] is the initial mass of the sample.

The JEOL JSM 5400 scanning electron microscope was used to study the sample morphology before incubation and after 4 and 10 weeks incubation. Plates were examined at 10 kV using magnifications from 50 to 2000 in order to characterize the surface and to determine the adhesion of polymer layers to steel.

Results

The changes of fluid pH are presented in FIGs. 1a and 1b. As it can be observed, there is a decrease of pH value after week 5 for all samples. This decrease can be attributed to degradation of polymer layers. The pH values of Ringer fluid for the samples of stainless steel coated with PSU are lower than those for bare steel and PTFE-coated steel. The pH range of fluid for PSU samples was 6.2÷7.2. In the case of PTFE-coated steel, the number of layers didn't show any influence, and the pH range was 6.5÷7.5. The electrical conductivity of distilled water as a function of incubation time is presented in FIG. 2. In the case of all samples there is a continuous increase of conductivity which can be attributed to degradation of polymer layers.

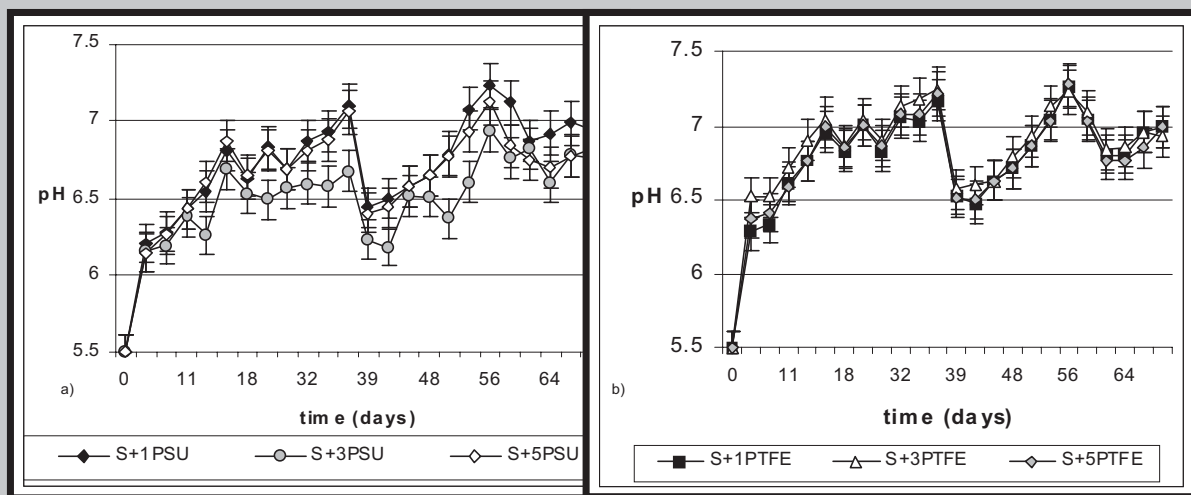


FIG. 1. Fluid pH variation as a function of time for a) bare stainless steel and PSU-coated steel and b) bare stainless steel and PTFE-coated steel (10 weeks, 37°C).

to dissolution of PTFE layer in the Ringer fluid. From all samples examined, the largest mass variation (0.4%) is presented by the samples of steel coated with PSU. Mass increase can be attributed to layers penetration by the liquid. After 5 week incubation the decrease of mass of PSU-coated samples can be observed, which can be attributed to initiation of polymer degradation. Although the process of degradation takes place, it is not very significant because of small changes of sample mass values. The number of PSU layers influences both the fluid pH and the mass variation. It can be suggested that the stress distribution is better in the case of PTFE than in the case of PSU, and this fact is also confirmed by the SEM micrographs. This leads to better adhesion of PTFE. The microstructure of samples before and after 10 weeks incubation and the adhesion of layers to steel surface are shown in FIG.4. It was observed that the protection assured by the PSU layers is better than the one by PTFE although the samples coated with PSU show worse adhesion than the PTFE-coated ones. The incubation time doesn't affect the adhesion of polymer layers to steel surface.

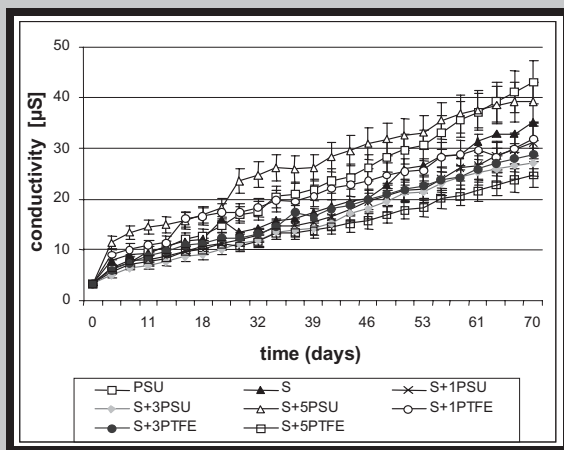


FIG. 2. Changes of electrical conductivity of distilled water (37°C) as a function of time.

Conclusions

The pH values of Ringer fluid for the samples of stainless steel coated with PSU are lower than for bare steel and PTFE-coated steel. The conductivity of distilled water presents an increase for all samples. It has been found that better adhesion and protection occurs in the case of PTFE than in the case of PSU.

The variation of mass of samples is shown in FIGs.3a and 3b. A slight negative variation of mass of samples coated with PTFE can be observed, and this fact can be attributed

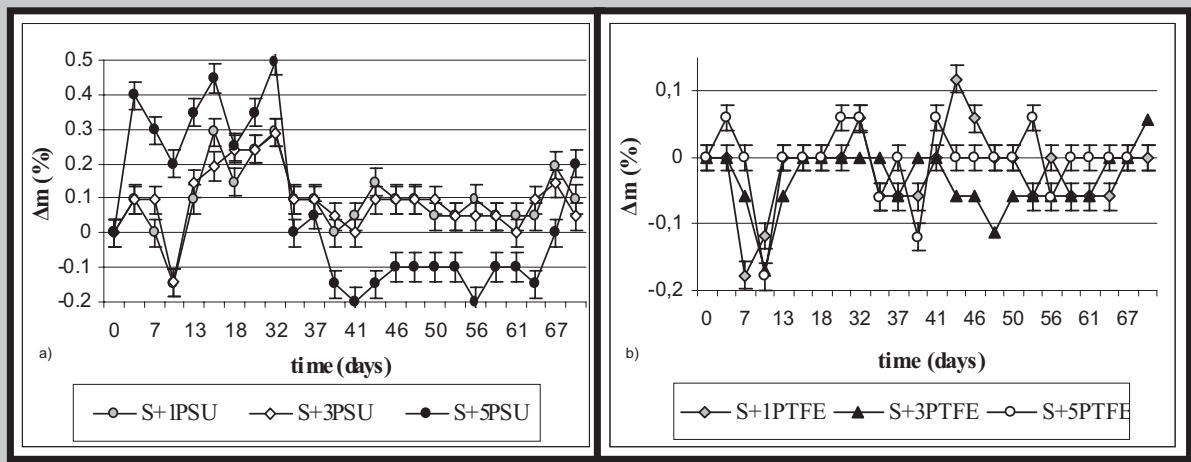


FIG. 3. The variation of samples mass as a function of time (10 weeks, 37°C, Ringer fluid).

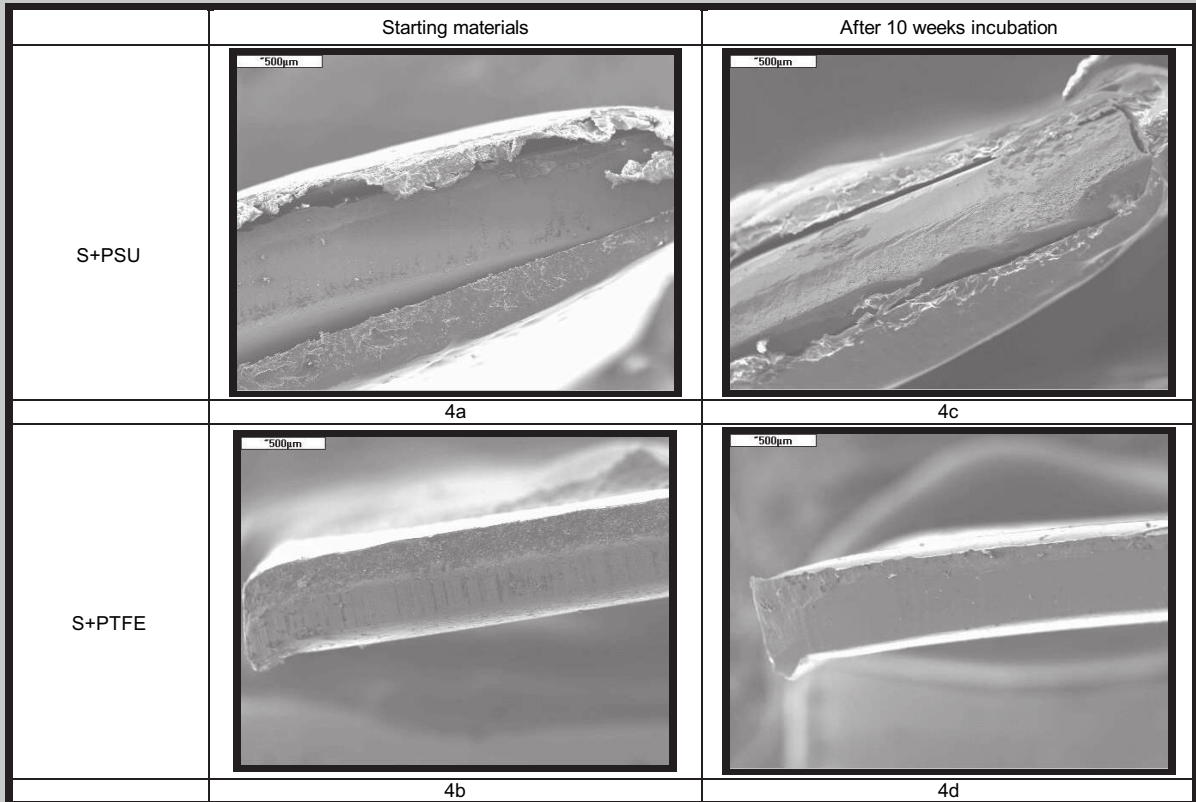


FIG. 4. The SEM micrographs of stainless steel plates surface coated with different polymer layers before (4a and 4b) and after 10-week incubation (4c and 4d).

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