



Zeta potential study of biodegradable antimicrobial polymers



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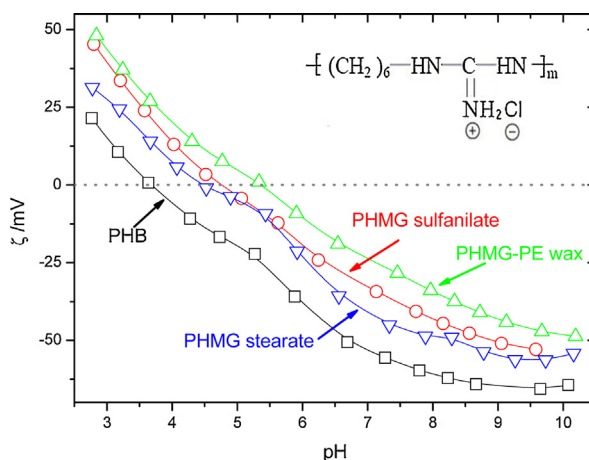
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HIGHLIGHTS

- Electrokinetic potential (ζ) vs pH of three biodegradable polymers is described.
- The polymers were poly(hydroxybutyric acid) (PHB), polycaprolactone (PCL) and poly(lactic acid) (PLA).
- They were doped with antimicrobial polyhexamethylene guanidine hydrochloride (PHMG) derivatives.
- ζ was determined from streaming current data using Smoluchowski–Helmholtz model.
- Addition of PHMG increases surface charge of the biodegradable polymers.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodegradable polymers have gained increasing interest in recent years, especially in food packaging industry. The biodegradation process is intrinsically related to adhesion of degradation-promoting bacteria on the surface of a biodegradable packaging. On the other hand, because of a direct contact with food, these materials should be resistant to colonisation by pathogenic bacteria. Thus, successful design of a biodegradable antimicrobial material critically depends on the interplay between the ability to control the strength of bacteria–polymer interactions. The aim of this work was to measure and analyse the effect of three positively charged antibacterial polyhexamethylene guanidine hydrochloride (PHMG) derivatives (sulfanilic acid salt, stearic acid salt, and polyethylene (PE) wax blend) on electrokinetic potential (ζ) of three biodegradable polymers: poly(hydroxybutyric acid) (PHB), polycaprolactone (PCL) and poly(lactic acid) (PLA). For this purpose, the streaming current vs pressure curves were recorded and analysed using the Helmholtz–Smoluchowski theory. The ζ vs pH dependency provides a simple and useful characterisation of an electrical double layer forming on the surface of biodegradable polymers in contact with an aqueous electrolyte. The undoped polymers displayed the ζ vs pH curves typical for electrically neutral polymers, with the isoelectric point, IEP = 3.5–4.0. The effect of PHMG on ζ vs pH curves depends on both the nature of the matrix polymer and the chemical form of PHMG. The stearate salt is shown to affect the curves to the smallest extent, while the most pronounced shifts towards higher pH were observed for PHMG in the form of PE wax (for PCL and PHB), or sulfanilic acid salt (for PLA). The surface of almost all PHMG-doped polymers used in this study (with exception of PLA doped with PHMG stearate) was

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more positive than the bare biodegradable polymers. From the point of view of electrostatic interactions, the addition of PHMG (especially in the form of PE wax, and especially for PHB) would thus probably enhance electrostatic polymer–bacteria interactions, possibly altering the antimicrobial activity of such polymers.

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1. Introduction

In recent years biodegradable polymers have been developed to the stage allowing for their mass production and application in an increasing number of pharmacological and food-related products. The actual biodegradation process requires a combined action of physical, chemical and biological factors, the latter involving mainly bacterial hydrolytic enzymes (proteases and esterases). For the purpose of polymer degradation especially the *Amycolatopsis* sp., *Lentzea*, *Kibdelosporangium*, *Streptoslloteichus*, *Saccharotrix* and *Brevibacillus* species were found most effective [1]. Some biodegradable polymers, e.g., poly(lactic acid) (PLA) and polycaprolactone (PCL) can be produced from renewable resources. Others, like poly(hydroxybutyrate) (PHB) – even directly by microorganisms (*Ralstonia eutropha*) [2]. This fact, in combination with the potential ability to get decomposed eventually into CO₂ and H₂O with relatively little harm to the environment, makes biodegradable polymers interesting candidates to replace their synthetic counterparts in many applications.

The classical antibacterial agents include ethanol, silver nanoparticles, ClO₂ or SO₂-releasing agents, and quaternary ammonium salts. Polyhexamethylene biguanide (PHMB) and polyhexamethylene guanidine hydrochloride (PHMG) belonging to the latter group are relatively environment-friendly, broad spectrum antibacterial agents commonly employed as antiseptic in swimming pool sanitisers, cosmetics, contact lens disinfectants, cleanser in agriculture and food handling, and recently even in wound rinsing and mouthwash solutions [3]. Chemically PHMB and PHMG are copolymers of hexamethylenediamine and dicyanamide [4], or guanidine hydrochloride [5], respectively. The presence of strongly basic biguanide groups (all being protonated at physiological pH) imparts high positive charge density of PHMB [6]. Consequently, a PHMB molecule can bind electrostatically to bacterial surface, which is typically negatively charged, mostly due to the presence of acidic phospholipids. PHMB is believed to attach to the cytoplasmic membranes through negatively charged phosphatidylglycerols. The resulting increased fluidity, lateral expansion, and higher permeability are mainly responsible for causing the subsequent bacterial cell death [7]. In Gram (–) bacteria, additional bactericidal effects are assigned to the distortion of divalent metal ions distribution near the lipopolysaccharides present on the cell surface [8]. Thanks to this non-specific and surface-located mode of membranolytic activity, PHMB remains a serious threat to the bacteria, which cannot develop any efficient resistance against species that do not pass their membranes [6]. Although little is known about the mechanism of antimicrobial activity of PHMG [9], the resemblance of its chemical structure with PHMB suggests that it may also interact in a similar way with biological membranes.

In order to effectively introduce PHMG into a polymeric network, for food-related applications its aqueous solubility should be reduced by replacing the hydrophilic chloride ions with more lipophilic ones, e.g., stearic or sulfanilic ions. Alternatively, blending with polyethylene wax was also found effective [9,10]. Richert et al. noticed that both the PE wax blend and stearate salt of PHMG slightly reduced biodegradability of PLA [10]. On the contrary, the sulfanilic acid salt of PHMG increased it by 18.8% (at 1% w/w content). A recent study of PHMG-doped PLA showed that

the bactericidal effect of PHMG additives decreases in the following order: PHMG PE wax > PHMG sulfanilate > PHMG stearate [9]. For all PHMG derivatives the antibacterial activity was found strongly correlated with concentration and the antibacterial effect was found generally stronger against *Staphylococcus aureus* than *Escherichia coli* cells.

In this paper we analyse the effect of three positively charged antibacterial PHMG derivatives (sulfanilic acid salt, stearic acid salts and PE wax blend) on electrokinetic potential (ζ) of three biodegradable polymers: poly(hydroxybutyric acid) (PHB), polycaprolactone (PCL) and poly(lactic acid) (PLA). The electrokinetic potential will be used to quantify the effect of PHMG on the surface charge of the biodegradable polymers (Table 1). This data can be further used to verify the hypothesis of the role of electrostatic interactions in controlling colonisation by pathogenic and useful (promoting biodegradation) bacteria.

2. Experimental

KNO₃, HNO₃ and KOH (puriss p.a.) were all purchased from Sigma–Aldrich. Milli-Q water (Millipore) was used to prepare all aqueous solutions. The biodegradable polymers were manufactured at the Institute for Engineering of Polymer Materials and Dyes (Toruń, Poland). The PHMG derivatives with organic carriers (polyethylene wax, sulfanilic acid, stearate) were prepared according to the Polish patent [11]. The pelleted mixture of all polymers and PHMG derivatives (composites with 1% w/w of PHMG derivatives) was prepared using a co-rotating twin-screw extruder type BTKS 20 (the diameter of the screws L' 20 mm, L/DL' 40) with segmented plasticising system (Bühler, Germany), as described in [9]. The pelletising was performed in the form of a cool extrudate in air at 25 ± 3 °C. The extruded pellets were processed into sheets with the use of a single-screw extruder type PlastiCorder PLV 151 (Brabender, Germany) with a screw diameter of 19.5 mm and $L/D = 25$.

2.1. Electrokinetic measurements

All electrokinetic measurements were performed using a SurPASS Electrokinetic Analyzer equipped with an adjustable gap cell from Anton Paar GmbH (Graz, Austria). For each measurement two pieces of a given biodegradable foil (20 mm × 10 mm) were precisely cut and installed in an adjustable gap cell of the SurPASS instrument, separated with a 100 μm – thick spacer. The channel height was set using a micrometric screw to $140 < d/\mu\text{m} < 160$, and its exact value, h_c , was determined using Hagen–Poiseuille equation:

$$h_c = \left(\frac{12\eta LQ}{H\Delta P} \right)^{1/3} \quad (1)$$

where Q – volume flow through the cell, η – dynamic viscosity, L – channel length, H – channel width, ΔP – applied pressure difference.

The cell and the tubings were carefully rinsed with the Milli-Q water prior to each measurement and the flow vs applied pressure characteristics was performed in order to verify that the two foils were installed properly in the cell. The maximum pressure difference was set at 300 mbar to assure a laminar flow. All

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