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Surface modified and medicated polyurethane materials capable of controlling microorganisms causing foot skin infection in athletes

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ABSTRACT

Foot odor and foot infection are major problems of athletes and persons with hyperhidrosis. Many shoes especially sports shoes have removable cushion insoles/foot beds for foot comfort. Polyurethane (PU) foam and elastomer have been used as cushion insole in shoes. In the present work, new insole materials based on porous viscoelastic PU sheets having hydrophilic property and antimicrobial drug coating to control foot infection and odor were developed. Bacteria and fungus that are causing infection and bad odor of the foot of athletes were isolated by microbial cell culturing of foot sweat. The surface of porous viscoelastic PU sheets was modified using hydrophilic polymers and coated with antimicrobial agent, silver sulfadiazine (SS). The surface modified PU sheets were characterized using ATR-FTIR, TGA, DSC, SEM, contact angle measurement and water absorption study. Results had shown that modified PU sheets have hydrophilicity greater than that of original PU sheet. FTIR spectra and SEM pictures confirmed modification of PU surface with hydrophilic polymers and coating with SS. Minimum inhibitory concentration studies indicated that SS has activity on all isolated bacteria of athletic foot sweat. The maximum inhibition was found for Pseudomonas (20 mm) followed by Micrococci (17 mm), Diphtheroids (16 mm) and Staphylococci (12 mm). During perspiration of foot the hydrophilic polymers on PU surface will swell and release SS. Future work will confirm the application of these materials as inserts in athletic shoes.

1. Introduction

Sweat is necessary for thermoregulation control of human body in different climate conditions. There are three types of sweat glands: eccrine, apocrine and apoeccrine. The eccrine glands are the major sweat glands of the human body and not connected to hair follicles. The highest density of eccrine glands is seen on the palms, soles, and axillae [1]. These sweat glands function throughout life by responding to elevated body temperature due to environmental heat or physical exercise. Sweat from the eccrine gland mainly consists of water (99%) and amino acids, ions, lactic acid, glycerol, urea, peptides and proteins [2]. The normal skin flora catabolize glycerol and lactic acid to short-chain (C_2–C_3) volatile fatty acids (VFA) such as acetic, and propionic acids. These bacteria also degrade amino acids into C_4–C_5 methylbranched VFA such as isovaleric acid, a common foot odorant. Foot odor is mostly due to short-chain fatty acids catabolized from components found in eccrine sweat. Isovaleric acid is an odorant derived from leucine [3].

Hyper perspiration, constitution of sweat, environmental factors such as temperature and humidity inside the shoes further encourage growth of microorganisms and their multiplication in foot skin. The metabolic end products of microorganisms such as ammonia and isovaleric acid can also be toxic to host cells [4]. The most important foot comfort properties of footwear materials are permeability and absorption of moisture. Leather is able to absorb and hold quite large quantities of water without feeling cold and clammy. But upon repeated wetting and drying leather will lose its viscoelasticity and becomes hard and stiff [5]. On the other hand most of the athletic shoes are made up of synthetic materials which have poor water absorption properties. When the rate of perspiration formation exceeds the rate of transmission, the foot skin is exposed to moisture, microorganisms and their byproducts for longer duration. Such conditions may contribute to fungal and/or bacterial infection of foot skin and cause erythema, keratolysis, umbilicated papules, tinea pedis (popularly known as Athlete's foot) [6]. Thus, the provision of an absorbent insole in athletic shoes which will also fight against multiplication of microbes by releasing antimicrobial agent will help to prevent these problems due to hyper perspiration and skin infection.

Polyurethanes foam and elastomer have been used as cushion insole material in footwear [7,8]. Surface modification is an effective way to improve the surface property of polymers and retain the bulk properties [9]. The covalent attachment of polymers or pharmaceutical agents to the polymer surface has been achieved through the use of diisocyanate bridges, such as hexamethylene diisocyanate (HMDI). This can react with urethane,

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hydroxy or amine groups at the polyurethane surface resulting in the formation of covalent bonds. The unreacted functional isocyanate (—NCO) groups can react with hydroxy or amine groups on other molecules. A large number of molecules have been grafted on the surface of polymers in this manner. Graft photo polymerization has been used to graft polyethylene glycol (PEG), polyvinyl alcohol (PVA), poly(2-hydroxyethyl methacrylate) (p-HEMA), and chitosan onto polyurethanes [10]. Radiation induced grafting of p-HEMA and other methacrylate onto polyurethane elastomer has also been achieved [11]. Wang et al. [12] had modified the surface of polyurethane with blends of stearyl polyethylene oxide coupling-polymer in chitosan as coating materials to optimize the surface biocompatibility of the intravascular catheter.

Ananthu et al. [13] have reported on surface modification of medical grade polyurethane using cyanurchloride-activated tetra ether lipid. The surface was initially modified with HMDI and subsequently treated with water or hexamethylene diamine to generate free amino groups on the surface. Jiang et al. [14] graft polymerized the zwitter ionic monomer of sulfobetaine onto polyurethane surface in a three-step heterogeneous system through the vinyl bonds of acrylic acid or HEMA, which was immobilized with HMDI. Yang et al. [15] worked on a four-step surface modification method to create a thin lubricious layer of chitosan/polyvinyl alcohol hydrogel on the segmented polyurethane urethral catheter.

Porous viscoelastic polyurethane sheets were developed and reported to have better physical and mechanical properties than that of conventional PU insoles [16,17]. Porous viscoelastic PU sheet having 3 mm thickness and 75% of porosity was prepared using the reported procedure [16] and used as base material for surface modification in this study. The surfaces of PU sheet were modified in order to incorporate water absorption and antimicrobial property in PU insole for application in athletic shoes to control sweat accumulation and subsequent foot infection. The surface of porous viscoelastic PU sheets were modified with hydrophilic polymers where the PU will act as insole material and the hydrophilic polymer on the surface will act as moisture absorbent and drug carrier. The following hydrophilic polymers were selected for modification of PU surface: poly(2-hydroxyethyl methacrylate) (p-HEMA), polyethylene glycol (PEG), polyvinyl alcohol (PVA) and chitosan. Chitosan was chosen for its antiseptic property [12].

2. Materials and methods

2.1. Materials

Polyurethane (Desmophan 1078), was obtained from Bayer materials, Mumbai, India. Toluene and N,N′-dimethyl formamide were obtained from Sisco Research Laboratory, Mumbai, India. HMDI, di-n-butyltin dilaurate (DBTDL), p-HEMA, PVA with the degree of deacetylation 99%, PEG (molecular weight 2000), and β-cyclodextrin were purchased from Sigma–Aldrich Chemicals, Germany. p-(HEMA) was 99% polymeric hydrogel for drug delivery containing 200 ppm monomethyl ether hydroquinone as inhibitor. Chitosan with a degree of deacetylation of 78% and weight average molecular weight of $3–4 \times 10^3$ and silver sulfadiazine were purchased from Srikem Laboratory, Mumbai, India.

2.2. Initial surface modification of PU sheet with HMDI

Reaction of HMDI with PU sheet will generate free isocyanate groups on PU surface through hexamethylene bridges. It is chemically based on the allophanate reaction between the urethane 'H' atoms and the HMDI-isocyanate group catalyzed by DBTDL. PU sheet and sufficient volume of toluene were taken in a three neck round bottom flask and kept in an oil bath at 55 °C under constant stirring. 10% (v/v) of HMDI to the volume of toluene was added drop wise. Then 0.1% (v/v) of catalyst was added and the reaction was continued for 2½ h [14]. The round bottom flask was removed from the oil bath and allowed to cool. The PU sheet was taken out and washed with toluene to remove unreacted HMDI. The modified PU sheet (MPU-1) was dried at 50 °C for 3 h.

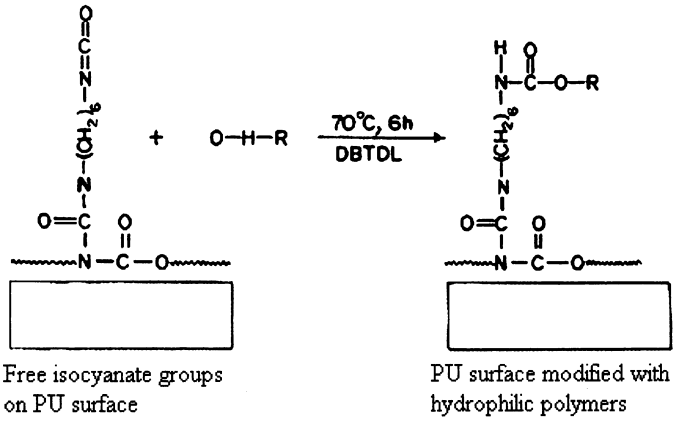

Fig. 1. Reaction of hydrophilic polymers having free active hydroxy group on HMDI modified PU surface.

2.3. Modification of HMDI modified PU sheet

The weight of the HMDI modified PU sheet was noted. The HMDI modified PU sheet was taken in a three neck round bottom flask. Toluene was added in quantity sufficient. The round bottom flask was kept in an oil bath. Then calculated amount (X g) of hydrophilic polymer (Y) was added to the reaction mixture under constant stirring. The temperature of bath was increased up to 70 °C. Then 0.1% (v/v) of catalyst was added and the reaction was continued for 6 h. The round bottom flask was removed from bath and allowed to cool. The modified PU sheet was taken out and washed with toluene and finally with methanol. Then the PU sheet was dried at 50 °C for 3 h. The schematic representation of reaction is shown in Fig. 1.

The amount of Y was calculated as follows:

$$\text{Weight of } Y = \text{Number of moles of } Y \times \text{Molecular weight of } Y = X \text{ g}$$

$$\text{Number of moles of } Y = \text{Number of moles of } PU$$

$$\text{Number of moles of } PU = \frac{\text{Weight of } PU}{\text{Molecular weight of } PU}$$

Molecular weight of polyurethane was found as 3,84,000 Da, by gel permeation chromatography method.

Whereas Y is PEG (2000)/p-HEMA/PVA/chitosan/mixture of chitosan/PVA.

The same procedure was carried out for modification of PU sheet with hydrophilic polymers (MPU-2–MPU-6). List of surface modified PU sheets prepared is shown in Table 1.

2.4. Surface modification of PU sheets by physical coating

For surface modification of PU sheets by coating with hydrophilic polymers, MPU-1 was immersed into homogeneous solution of PVA (MPU-7) or chitosan (MPU-9) or mixture of chitosan and PVA solutions (MPU-10) for 5 min and then removed. Homogenous solution of chitosan was prepared by mixing powdered chitosan with sufficient quantity of dilute acetic acid using magnetic stirrer. PVA solutions were prepared by dissolving powdered PVA in hot water under constant stirring. The surface modification of PU sheet (MPU-1) was also done by coating with cross-linked