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Preparation and characterization of a permanently antimicrobial polymeric material by covalent bonding

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ABSTRACT

A permanently antimicrobial polypropylene (PP-g-PHMG) was obtained by covalently bonding 0.5% poly(hexamethylendiamine-guanidine hydrochloride) (PHMG), a guanidine-based antimicrobial polymer, based on total weight onto polypropylene (PP) matrix using a melt grafting method in supercritical CO_2 (SC CO_2) assisted process. Attributed to the higher grafting efficiency, the hydrophilic PHMG is uniformly dispersed in PP matrix without any aggregate, which potentially enhances the antimicrobial activity. The resulting PP-g-PHMG pellets showed quickly and efficiently antimicrobial activity against both Gram-positive and Gram-negative bacteria. Furthermore, the antimicrobial activity of the PP-g-PHMG non-woven fabrics prepared by a spun-bonded method remained even after constant water washing for 10 days, indicating its permanently antimicrobial ability via a contact activity rather than a release mechanism. In addition, animal tests were conducted to evaluate the safety of the antimicrobial PP fabric in the case of direct skin contact and water washing.

1. Introduction

Currently synthetic polymeric materials have been used in many fields with the development of industries. Also, more and more polymeric materials are supposed to be equipped with antimicrobial properties because of the public health concerns. Especially, after experiencing the outbreak of both SARS and H5N1 avian influenza viruses, it reminds us to build an antimicrobial defense system to prevent reciprocal infection, to which an effective method is to wear an antivirus or antimicrobial gauze mask. However, the vast majority of the previous methods for the production of self-sterilizing surfaces have mixed organometallic biocides, such as silver, copper, tin, zinc or mercury, into the material matrix. As known to us, low molecular weight biocides are often released from the matrix or substrates during application due to the weak or unstable physical bonding. These organometallics may be suspected for reasons of toxicity or environmental effects and problems caused by their handling and are now less accepted in some of the industrial uses in which they have hitherto been employed. There is growing evidences that silver nanoparticles are highly toxic to mammalian cells [1–3], and damage brain cells [4], liver cells [5] and stem cells [1], and also cause skin disease like argyria or argyrosis [6]. Accordingly, when these toxic plastics are used, there exist the potentials of human toxicity and environmental pollution through leaching and landfill disposal, which cannot be tolerated for the uses of food contact, baby toys and the gauze masks.

Therefore, the immobilization of biocides by chemical bonding, which can effectively deactivates microorganisms on contact without toxicity and releasing biocides, represents a modern approach towards permanently sterile materials. Non-leaching antimicrobial polymeric surface, where the antimicrobial agent is permanently fixed on the matrix through covalent bonding, can be achieved through the chemical bonding of antimicrobial polymers, such as N-alkylated poly(4-vinylpyridine) [7], quarternized

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polyethylenimine [8], and methacrylic acid derivatives with quaternary amines [9], to numerous common material surfaces. Furthermore, the common bacterial strains *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) do not develop noticeable resistance against these polymer surfaces [10]. Recent literature data described a number of procedures leading to an evaluation of antimicrobial activity of a solid surface [7,11,12]. Organosilicon quarternary ammonium salts (QAS), such as 3-(trimthoxysilyl)propyldimethyloctadecylammonium chloride, have often been used as biocides and can be immobilized on surfaces of a variety of substrates with active groups [13–18]. However, a particularly vexing challenge is to covalently couple biocides to the inert surface of polymers (e. g., PP and polyethylene (PE)) efficiently. As an example of the preparation of an antimicrobial polymer with inert surface, polyamide fibers [19] with antibiotics (penicillin, neomycin and gentamycin) were firstly activated with a benzene solution of benzoyl peroxide, and then treated with a grafting bath containing acrylic acid; finally, modified with the antibiotics. Antimicrobial PAN [20] and PET [21] fibers were respectively obtained by the similar method. In addition, Polycationic biocides with phosphonium salts were immobilized on the surface of PP film by means of surface photografting method [22]. Also, metal-complexed PP [23] fabirics were prepared by irradiation of PP fabric using ^{60}Co followed by the immersion of irradiated fabrics in acrylic acid monomer and then in various metallic solutions. Metal-complexed sulfonated styrene-grafted PP fabrics were prepared by a method to the one described above. In general, most of the current methods utilize the plasma [24,25], coating [26,27], or atomic transfer radical polymerization (ATRP) [28–30] techniques to introduce antimicrobial groups on the surfaces of polymer surfaces. However, these described methods seem not to be entirely satisfactory for a future industrial routine check. Furthermore, although the biocides are bonded covalently with the surfaces, it is often less durable than the substrate to which it is applied and is prone to mechanical wear or harsh, abrasive chemical cleaning. Once the surface coating is worn off, all antimicrobial protection is lost.

The objective of this study was to develop a feasible method that renders the general polyolefin substrate permanently contact-actively antimicrobial through a chemical bonding method, in which a guanidine-based antimicrobial polymer, i.e., PHMG, was melt grafted onto the polyolefin substrate. The fixed nature of the PHMG biocides is important where toxicity, taint and other organoleptic aspects are of concern. PHMG has broad-spectrum activity against Gram-positive and Gram-negative bacteria, fungi, yeasts [31] and viruses including human immunodeficiency virus [32]. PHMG has been widely used as an antiseptic in food industry and medicine, as a mouthwash [33], as a disinfectant for a variety of solid surfaces [34]. PHMG is odourless, colourless and noncorrosive [35], and is significantly less toxic and harmless than currently used disinfectants [31] to humans and animals at a concentration $\leqslant$1%. Therefore, the antimicrobial PP prepared by the method will provide contact-actively antimicrobial ability without any leaching of PHMG molecules. Besides, unlike some antimicrobial materials filled with inorganic metallic nanoparticles, which provides antimicrobial ability by the migration of some metallic ions and will be deactivated with the loss of nanoparticles, the antimicrobial activity of the resulting polymeric material can still remain in a long term until PHMG molecules depart from the matrix of polymer by some chemical actions. In comparison with the surface treatments described above, the antimicrobial polymer prepared can continuously expose a new surface containing the same antimicrobial concentration as when it was new, affording antimicrobial protection for the lifetime of the material, that is, permanently antimicrobial activity. In addition, the melt spinning processability of the resulting PP-g-PHMG was characterized by GPC, thermogravimetrical analysis (TGA), and elongational viscosity test. The PP-g-PHMG non-woven fabrics prepared by a spun-bonded method can be anticipated to use as bed sheets, hospital garments, and wound gauze due to the non-leaching property and broad-spectrum antimicrobial potential. It is expected that the wound gauze would have the capability to kill various bacteria by simply wrapping the wound and could be reused after washing with water in the case of emergency. In order to ensure that the antimicrobial fabrics are safe for direct skin contact, animal skin irritation test was conducted as a preliminary evaluation. Furthermore, taking into account the usage repeatability of the fabrics, the *in vivo* biological safety of its washing water was also evaluated.

2. Materials and methods

2.1. Materials

Hexamethylenediamine and guanidine hydrochloride were purchased from Sinopharm Chemical Reagents Co. Ltd. Dicumyl peroxide, glycidyl methacrylate (GMA), and styrene were used as received from Aldrich. The antioxidant, Irganox 1010 (Ciba), was used as received from the company. The commercial polypropylene, Z30S (MFR = 25 g/10 min, Zhenhai Petrochemical Co.), was dried in an oven at 80 °C for 12 h prior to use.

2.2. Synthesis of PHMG

58.1 g (0.5 mol) of hexamethylenediamine and 47.75 g (0.5 mol) of guanidine hydrochloride were added to a three-necked round-bottom flask, respectively. A vacuum system was equipped for removing the ammonia, which is a by-produce produced during the condensation polymerization. The two monomers reacted for 1 h at 100 °C, and ammonia as a by-produce was absorbed by a lot of water. Then, the reaction temperature was increased to 170 °C to keep reacting for several hours, during which the by-product ammonia was removed by the vacuum system equipped to further increase the molecular weight of the PHMG (92.5 g, 87.4%). At the end of the reaction, the reaction temperature was decreased to 110 °C and 28.4 g (0.2 mol) of GMA was added to the reaction system to react with the primary amine groups at the two ends of the resulting PHMG, thus introducing unsaturated bonds on