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Antimicrobial and insect-resist wool fabrics by coating with microencapsulated antimicrobial and insect-resist agents

Mohammad Mahbubul Hassan*, Matthew Sunderland

Textile Science and Technology Team, Food and Bio-based Products Group, AgResearch Limited, Private Bag 4749, Lincoln, Christchurch 8140, New Zealand

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ABSTRACT

In this work, various types of antimicrobial and insect-resist agents were microencapsulated by several techniques to minimise their toxicity to humans. The microencapsulated antimicrobial and insect-resist agents were applied to wool fabrics by a pad-dry-bake method, and their performance was assessed in accordance with standard methods. The durability of the treatments to ageing and washing was evaluated. It was found that the antimicrobial and insect resist agents migrated to the outer surface of the capsules during ageing. Of the antimicrobial agents investigated, poly(N,N-dimethyl-2-hydroxypropylammonium) chloride or Barquat PQ 2 encapsulated with polylactic acid showed the best overall antibacterial performance after 10 cycles of International Wool Secretariat (IWS) 7A washing and also after ageing. The clothianidin insecticide encapsulated with polylactic acid showed the best insect-resist performance according to Wools of New Zealand Test Method 25 at a level of 50 ppm, passing this test method even after 10 cycles of washing. The washed fabric showed 85% insect mortality and the mean wool mass loss was only 4.6 mg. The fabric handle properties were only slightly affected by the treatments. The developed methods may find application in industry as they are quite durable to washing.

1. Introduction

Previous studies showed that consumers want to have various functionalities in their apparel, and that one of the key attributes they wanted is antibacterial activity [1–4]. This was not surprising as modern consumers are increasingly concerned about health and wellbeing [5]. Wool textiles generally do not allow bacteria to adhere to their surface, but in contact with the human body offer a favourable environment for bacterial growth [6]. Microbes present in the fabric can not only affect the health and wellbeing of the wearer, but some species can create unpleasant smells and can even degrade fabric materials. Various antibacterial agents, such as quaternary ammonium compounds, hexamethylene biguanide hydrochloride, and triclosan have been investigated for making textile products antibacterial [7–10].

Another antimicrobial agent is silver, which is a broad spectrum antimicrobial agent with a long history in the treatment of burns. While metallic silver is relatively inactive, silver ions are effective against a wide range of bacteria [11]. Silver compounds produce their antimicrobial effect by the time-dependent release of silver ions and their clinical efficiency is directly related to the constant presence of free silver ions in the local microbial environment [12]. Recent advances in nanotechnology have led to the introduction of fabrics treated with silver nanoparticles, and such fabrics have been widely embraced by sportswear manufacturers, although environmentalists and toxicologists have raised concerns about the effects on the aqueous environment and human health of silver leached from such fabrics during wear and washing [13,14]. In addition to toxicity of silver nanoparticles, the binding of silver nanoparticles to the surface of fibres, particularly wool, is problematic. Therefore alternatives to silver are needed.

Quaternary ammonium compounds are proven antimicrobial agents and have been investigated [15,16] for use on wool to impart antibacterial functionality. However, the quaternary ammonium compounds slowly wash away during laundering, resulting in a considerable loss of antimicrobial activity. Zhu and Sun applied three quaternary ammonium compounds, cetylpyridinium chloride, cetyltrimethylammonium bromide and benzyldimethylhexadecylammonium chloride to wool but found that after 10 washings the percentage of *Escherichia coli* mortality dropped from 99.3%, 100% and 97.3% to 79.3%, 10.3% and 0% respectively [16]. As all quaternary ammonium compounds and triclosan are relatively toxic, their contact with the human body at high concentrations could be harmful. Encapsulation of antibacterial agents would be an

* Corresponding author. Tel.: +64 3 321 8755; fax: +64 3 321 8811.
E-mail address: mahbubul.hassan@agresearch.co.nz (M.M. Hassan).

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ideal method to overcome this problem as the antibacterial agents would be inside the capsules and their release will be controlled, substantially diminishing the chance of a damaging effect on skin. Micro-encapsulated copper oxide and herbal extracts have been investigated for textile applications [17]. Encapsulation also allows the use of antibacterial agents that are highly water-soluble that would otherwise leach out quickly from fabric during washing and sweating.

Wool products can be eaten and digested by larvae of particular insects, such as the common clothes moth *Tineola bisselliella*. Not only are the aesthetic properties of wool apparel attacked by moths compromised, but the damage may be extensive enough to render the product unusable. To protect wool apparel from insect damage, they are sometimes treated with insect-resist agents. The application of insect-resist agents to wool apparel may be perceived negatively by some consumers, despite the agents' low mammalian toxicity. Encapsulating these insecticides may give extra reassurance to these consumers. The research carried out in this area is quite negligible. Kettel et al. coated wool fabrics with permethrin-embedded β-cylodextrin nanogel with controlled release of permethrin [18]. Encapsulated citronella oil also has been investigated as a mosquito repellent for cotton fabrics [19].

Encapsulation would allow the application of water-soluble antimicrobial agents and insecticides with low to no affinity for wool (i.e. they would not be absorbed into fibre), would reduce their potential dermal toxicity, increase ease of handling, and also would prolong their durability to washing. Moreover, conventional antimicrobial and insect-resist treatments can produce an environmental problem from the toxicity of aqueous effluent. This is because the applied quaternary ammonium compounds only 50–95% are absorbed into wool depending on their chemical structure [15,16] and also insect-resist agents are not 100% absorbed into the wool and the residual active in the effluent can be toxic to some aquatic life [20]. Some effluent may need treatment before discharging to main sewer or into a watercourse [21], but encapsulation has the potential to reduce contamination of this effluent. Insecticides require low water solubility to be well absorbed by wool in an aqueous dyebath by current methods. Some insecticides with high water solubility, such as the neonicotinoid imidacloprid, can be effective against wool-digesting insects [22]. This class of insecticide could be practical if it could be applied to wool using an application system not relying on aqueous dyebath uptake. Recent investigations into alternative non-insecticidal insect-resist compounds also indicate advantageous new approaches are possible using encapsulation [23]. It is therefore clear that application of insecticides in an encapsulated form may overcome many problems.

In this work, a neonicotinoid insecticide (clothianidin), and also a synthetic pyrethroid (permethrin) in combination with a neonicotinoid (imidacloprid) were microencapsulated and applied to wool fabrics to achieve durable insect-resist performance. Four antibacterial agents including triclosan, dodecyltrimethylammonium chloride (DTAC), PDPAC and chlorhexidine gluconate were microencapsulated and applied to wool fabrics as they are proven antibacterial agents with low toxicity. Several polymers including chitosan, ethyl cellulose and polylactide have been investigated as an encapsulating agent. The antimicrobial and antifungal activity of the wool fabrics treated with these various microcapsules were studied.

2. Experimental

2.1. Materials

The 100% wool fabric used was a 2/2 twill, having 34 ends/cm and 24 picks/cm and weighed 210 g/m^2. Teric GN12 (non-ionic detergent), and Sandozin MRN (wetting agent) were purchased from Huntsman (USA) and Clariant Chemicals (Switzerland) respectively. The selected insect-resist agents were clothianidin and imidacloprid supplied by Sumitomo Chemical (Japan) and Meghmani Organics Limited (India) respectively, and permethrin supplied by Chemcolour Industries Limited (NZ). The antibacterial agents used were triclosan or 5-chloro-2-(2,4-dichlorophenoxy) phenol, dodecyltrimethylammonium chloride (DTAC), poly(N,N-dimethyl-2-hydroxypropylammonium chloride) or PDPAC (commercial name: Barquat PQ 2), and chlorhexidine gluconate (CHG); the first two were supplied by Sigma-Aldrich Chemicals Ltd. (USA) and the others were purchased from Lonza Ltd. (Switzerland). Basolan MWP, a silicone resin, was purchased from BASF Chemicals (Germany). Polylactide (PLA, M_n = 20,000, melting temperature = 167 °C and polydispersity = 1.1) was supplied by Dow-Cargill (USA). Hercosett, an epoxy polyamide resin, was supplied by Ashland Inc. (USA). Span 20 (sorbitan monolaurate), ethyl cellulose (viscosity = 170 mPa s of 5% solution in 80/20 mixture of toluene/ethanol at 25 °C, ethoxyl content = 48.0–49.5% (w/w) and glass transition temperature = 129–133 °C) and chitosan (85% deacetylated) were purchased from Sigma-Aldrich Chemical Ltd. (USA).

Prior to treatments with encapsulated insect-resist and antimicrobial agents, the wool fabrics were scoured with 2 g/l Teric GN12 at 50 °C for 20 min to remove processing oils and contaminants.

2.2. Encapsulation of antimicrobial and insect-resist agents

2.2.1. Encapsulation of DTAC

Chitosan was used to microencapsulate DTAC. A required quantity of chitosan was dissolved in 20 ml of 1% acetic acid solution. The required quantity of DTAC was added to it and was completely dissolved. The ratio of DTAC to chitosan in the solution was 2:1 by mass. The solution was then added to 100 ml of 1% dodecyl sulphate solution drop-wise with vigorous stirring. Then 1 ml of glycerol diglycidyl ether was added to crosslink the chitosan. After completion of the reaction, the capsules were recovered by centrifuging at 4000 rpm for two min.

2.2.2. Encapsulation of permethrin/imidacloprid

Ethyl cellulose was used to encapsulate the combination of insecticides used in this work as both ethyl cellulose and the insecticides are soluble in ethyl acetate, which made encapsulation easy. The mass ratio of permethrin to imidacloprid in the capsules was 3:1. A required quantity of ethyl cellulose was dissolved in 15 ml of ethyl acetate. The required quantity of permethrin and imidacloprid was added to it and was completely dissolved by stirring. The ratio of permethrin/imidacloprid to ethyl cellulose was 2:1. The solution was then added to 100 ml of 1% Span 20 solution drop-wise. After completion of capsule formation, 1 ml of glycerol diglycidyl ether was added to crosslink the ethyl cellulose. After 2 h, the reaction was completed and the capsules were separated by centrifuging at 4000 rpm for 2 min.

2.2.3. Encapsulation of clothianidin, triclosan, PDPAC, and CHG

PLA was used as an encapsulating material to encapsulate clothianidin, triclosan, PDPAC, and CHG. A required quantity of PLA was dissolved in 40 ml of dichloromethane to make a solution. In each case the antibacterial or insect resist agent was added to the solution drop-wise and a solution was made by stirring. The ratio of insecticidal and antimicrobial agents to PLA in the solution was 2:1 by mass. After formation, the microcapsules were separated from solution by centrifuging at 4000 rpm for 2 min, and were re-dispersed in water to apply them on wool fabric samples.