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Gallnut extract-treated wool and cotton for developing green functional textiles

Eunmi Koh [a], Kyung Hwa Hong [b,*]

[a] Department of Food and Nutrition, Seoul Women's University, Seoul 139-774, South Korea
[b] Department of Fashion Design and Merchandising, Kongju National University, Chungnam 314-701, South Korea

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ABSTRACT

Gallnuts are known to exert various pharmaceutical effects, including anti-inflammatory, antimicrobial, antioxidant, and detoxifying effects. In particular, the gallnut extract is thought to be a safe antimicrobial agent for textile application, since it is of natural origin. Hence, wool and cotton fabrics were treated with the gallnut extract, by using a pad-dry-cure process to develop multi-functional clothing material with no harmful effects. Additionally, fabrics were plasma-treated to improve the finishing effect. This study thoroughly investigated the surface appearance, mechanical properties, antimicrobial ability, and antioxidant performance of gallnut extract-treated wool and cotton fabrics. Gallnut extract treatment was found to impose the antimicrobial and antioxidant properties on the wool and cotton fabrics.

1. Introduction

Various antimicrobial technologies have been developed to protect various textile materials from microbial damage, and to prevent cross-transmission of infectious diseases through direct contact. Textiles are known to be susceptible to microbial attack since they have a large surface area and absorb moisture, both of which can promote microbial growth [1]. Moreover, natural fibers allow bacterial growth and multiplication, by providing basic requirements such as nutrients (in the form of protein or cellulose), moisture, and appropriate conditions of oxygen and temperature [2]. Hence, textiles are treated with various compounds, including organic compounds such as triclosan, quaternary ammonium compounds, polybiguanides, N-halamines, chitosan, and inorganic materials such as silver and titanium oxide (TiO_2) [3–11], for antimicrobial functionality. The chemicals used in textile treatment include inorganic salts, organometallics, iodophors, phenols, thiophenols, heterocyclics with anionic groups, nitro compounds, urea, formaldehyde derivatives, and amines, among others [8]. Many of these chemicals, however, are toxic to humans and are difficult to degrade naturally [12–15]. Therefore, the development of new and improved antimicrobials is an area of active research, and much interest has been generated in development of potential naturally derived antimicrobials [11,16]. Ali and El-Mohamedy reported that wool fabrics dyed with the extract from the red prickly pear plant showed antimicrobial activity against *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and others [17]. Mahesh et al. found that cotton fabrics treated with a pomegranate extract showed antimicrobial properties that can be attributed to natural tannin compounds present in the extract [18]. Ben-Fadhel et al. reported the manufacture of antibacterial textiles by treating wool and cotton fabrics with an extract of the Eucalyptus leaf [19]. In the previous study, it was recently identified certain natural materials with antimicrobial activity and applied these materials to textiles [2]. Among these natural materials, the gallnut extract was found to be an attractive candidate for textile application, as it displayed excellent antioxidant and antimicrobial activities when applied to textiles. Galls are outgrowths of plant tissues produced when irritants are released by the larvae of gall insects such as those of the Cynipidae family, the gall wasps. This extract contains the highest naturally occurring levels of tannin (gallotannin, 50–75%), as well as smaller molecules such as gallic acid and ellagic acid. Additionally, this extract is known to possess pharmaceutical properties, including anti-inflammatory, antibacterial, and detoxifying properties [20].

Therefore, in this study, the gallnut extract was applied to a wide range of textile materials, including those containing cellulose or

* Corresponding author. Tel.: +82 41 850 8305; fax: +82 41 850 8301.
E-mail address: hkh713@kongju.ac.kr (K.H. Hong).

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protein fibers, by using a pad-dry-cure process. Additionally, it was attempted to improve the finishing effect of the fabric by using the plasma sputtering technique; this technique can modify the textile surface, thus improving the finishing effect of the treatment.

2. Experimental

2.1. Materials

Bleached and de-sized cotton fabric (No. 400) was purchased from Testfabrics Inc. (West Pittston, PA); scoured wool fabric (KS K 0905) was purchased from Sombe Co. (Cheongju-si, Korea). Gallnuts were acquired from a local market in Korea in the flake form. 1,1-Diphenyl-2-picrylhydrazyl (DPPH, a free radical generator) was purchased from Calbiochem (Darmstadt, Germany). Methanol (C99.8%) was purchased from Samchun Chemical Co., Ltd (Gyeonggi-do, Korea). All other reagents were used as received, without any further purification.

2.2. Sample preparation

2.2.1. Extraction of natural functional material

Gallnuts (100 g) were dried and ground to powder form. Next, the powder was mixed with 1 L of deionized water and boiled for 1 h. The extract was cooled to room temperature and filtered to remove insoluble residues. The resulting filtrate was then diluted to 50 vol %, and the diluted solution was used as a stock finishing solution (pH 4.43) for textile treatment.

2.2.2. Fabric finishing process

Cotton and wool fabrics, each cut into pieces approximately 30 cm × 30 cm in size, were first treated with plasma for 10 min, by using the CD 400 MC/PC system (Europlasma, Oudenaarde, Belgium) and the gases O_2 (under 100 sccm, 40 mTorr, 200 W) and Ar (300 sccm, 40 mTorr, 250 W). Immediately (within 1 h) after plasma treatment, fabrics were processed using the following procedure: they were immersed in the gallnut extract for 30 min (bath ratio = 1:18), the damped fabrics were squeezed through a laboratory padder until a wet pick-up rate of approximately 100% was reached, and then, they were wet-fixed by placement in plastic sealing bags. The storage bags were placed in a convection oven for 30 min at 60 °C. Subsequently, the fabrics were cured at 120 °C for 15 min, and then washed with deionized water and tumble-dried.

2.3. Characterization

The surface morphologies of the fabric samples were examined using a high-resolution field emission scanning microscope (Tescan, Brno, Czech Republic). Color changes, estimated using the L^*, a^*, and b^* values, and yellowness (ASTM E 313) in the treated fabrics were obtained using the Color i7 Benchtop Spectrophotometer (X-rite Inc., Seoul, Korea). Fourier transform infrared (FTIR) spectroscopy was performed using the Spectrum 100 Optica FTIR instrument (PerkinElmer, Waltham, MA), with a resolution of 4 cm^{-1}. Measurements were carried out using an attenuated total reflectance (ATR) technique. The tensile strength of the fabrics was measured by the cut strip method (KS K 0520-1995), using the Instron 5543 system (Norwood, MA). The ability of the fabric samples to impede microbial growth and retention was tested using *Staphylococcus aureus* (ATCC 6538; a gram-positive bacterium) and *Klebsiella pneumoniae* (ATCC 4352; a gram-negative bacterium) cultures, according to an established protocol to test the antibacterial activity of textiles (KS K 0693). During the antimicrobial test, all fabrics were inoculated with bacteria cultures, and then incubated under ambient conditions for 18 h. After the time allotted for contact had elapsed, the inoculated fabrics were immersed in 20 mL of quenching solution (distilled water), and the containers were strongly agitated to transfer the bacteria from the fabric to the quenching solution. Next, the fabrics were removed, and 1 mL of the quenching solution containing the transferred bacteria was serially 10-fold diluted with distilled water. A fixed volume of each dilution (100 μL) was inoculated on agar plates and the plates were incubated at 35 °C for 24 h. Bacterial reduction was calculated according to the following equation:

$$\text{Reduction of bacteria } (\%) = \frac{(B - A)}{(B)} \times 100 \qquad (1)$$

In the above equation, *A* and *B* represent the surviving bacterial cells (colony-forming unit mL^{-1}) on the plates inoculated with test samples derived from treatment of gallnut extract-treated fabrics and the control untreated fabrics, respectively. The dyed cotton fabrics were exposed to DPPH radicals (DPPH•) to measure the antioxidant activity, using a previously reported method [21]. DPPH• is a well-known radical and acts as a trap ("scavenger") for other radicals. Therefore, a reduction in the reaction rate upon the addition of DPPH• is used as an indicator of the radical nature of that reaction [22]. The evaluation was conducted as follows: 500 mg of the fabric was immersed in a container containing 30 mL of 0.15 mM DPPH•/methanol solution. After the solution had been allowed to stand in the dark for 1 h, the absorbance at 517 nm was measured using a UV–Vis spectrophotometer (SINCO S-3100; SCINCO Co., Ltd. Seoul, Korea). A reduction in the absorbance of the reaction mixture indicated a higher DPPH• scavenging activity. DPPH• scavenging activity was calculated using the following equation:

$$\text{DPPH}\cdot\text{scavenging activity } (\%) = \frac{C - S}{C} \times 100 \qquad (2)$$

In the above equation, *S* and *C* represent the absorbance of sample and control, respectively.

3. Results and discussion

3.1. Surface appearance of gallnut extract-treated fabrics

Table 1 shows the color properties of wool and cotton fabrics after gallnut extract treatment. The three coordinates of CIELAB represent the color shade ($L^* = 0$ indicates black, while $L^* = 100$ indicates a diffuse white color; the L^* value for specular-white may be higher), the color position between red/magenta and green (negative a^* values indicate green, while positive a^* values indicate magenta), and its position between yellow and blue (negative b^* values indicate blue, while positive values indicate yellow) [23]. Additionally, the yellowness index indicates a yellow shade detected on the fabric surface. Overall, following treatment of both cotton and wool fabrics with the gallnut extract, a^* and b^* values as well as the yellowness index increased, while L^* values decreased.

Table 1
Color appearance of wool and cotton fabrics.

	L^*	a^*	b^*	Yellowness index
Untreated wool	88.87	−1.16	12.63	19.24
Gallnut-treated wool	84.24	1.45	14.52	23.12
Ar plasma + gallnut-treated wool	83.86	1.20	15.25	24.25
O_2 plasma + gallnut-treated wool	84.21	1.29	14.80	23.48
Untreated cotton	94.99	−0.52	3.25	4.85
Gallnut-treated cotton	90.90	−0.28	9.67	14.80
Ar plasma + gallnut-treated cotton	91.25	−0.29	9.73	14.86
O_2 plasma + gallnut-treated cotton	91.21	−0.27	9.29	14.22