Antimicrobial Finishing of Polypropylene Nonwoven Fabric by Treatment with Chitosan Oligomer

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ABSTRACT: Water-soluble chitosan oligomer was prepared for finishing polypropylene nonwoven fabrics to impart antimicrobial activity. The weight average molecular weight was 1814 and its degree of deacetylation was 84%. Polypropylene nonwoven fabrics were treated with chitosan oligomer solution by the pad-dry method. Antimicrobial activity was measured by the shake flask method. The chitosan oligomer showed high antimicrobial activities against *Proteus vulgaris, Staphylococcus aureus,* and *Escherichia coli* at 0.01% and 0.05% level, respectively, showing above 90% of reduction rate. Chitosan oligomer was the most effective against *Proteus vulgaris.* However, it was not effective against *Klebsiella pneumoniae* and *Pseudomonas aeruginosa* below the treatment concentration of 1.0%. Fabrics became stiffer and less air permeable with the increase of treatment concentration. Tensile strength of the treated samples was lower than that of the untreated one. Liquid strike-through time of the sample treated with 0.5% chitosan oligomer solution (3.0 s) was comparable with that of a hydrophilic finished sample available commercially (2.6 s). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2911–2916, 1999

Key words: chitosan oligomer; polypropylene nonwoven; shake flask method; antimicrobial activity; liquid strike-through time

INTRODUCTION

Textile materials used in the medical and related healthcare and hygiene sectors are an important and rapidly growing segment of the textile industry. Nearly 70% of the products are disposable nonwoven whereas the remaining 30% are reusable.[1] The applications of nonwoven fabrics vary in a wide range from disposable hygienic products to sophiscated medical fabrics along with industrial uses. The fabrics selected for this study is polypropylene (PP) nonwoven used for coverstock. Coverstock is the topsheet of diaper, incontinence, and sanitary products and thus it is contacted directly with skin. Skin troubles, such as diaper dermatitis, are often caused by wearing disposable diaper and hygienic products. Currently, there is an increasing necessity for antimicrobial finishing due to consumers' great interest in healthcare.

It is well known that chitosan inhibits the growth of many bacteria including gram-negative and gram-positive ones.[2–4] Recently, chitosan oligomer has received much attention because of higher antimicrobial activity and water solubility compared with chitosan of high molecular weight.[3] Chitosan itself is known to induce little skin reaction over a wide range of biomedical investigation.[2] This is an important advantage, especially for its application onto next-to-skin fabrics.

In the present study, water-soluble chitosan oligomer was prepared and its efficacy to impart antimicrobial properties was investigated. The antimi-

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crobial activity of nonwoven fabrics treated with chitosan oligomer was tested against various strains of bacteria. Additionally, performance properties of the treated nonwoven fabrics including strength, elongation, stiffness, air permeability, and liquid strike-through time were measured.

EXPERIMENTAL

One hundred percent PP nonwoven fabric (thermal bonded, 26 g/m^2, 0.13-mm thickness) for coverstock was used.

Chitosan oligomer was prepared by acid degradation from a chitosan [degree of deacetylation (DDA), 85%] obtained commercially. Briefly, 100 g of chitosan was dispersed in 1.5 L of deionized water and then 100 cc of 0.1*N* acetic acid was added dropwise with stirring to dissolve chitosan. To depolymerize chitosan, the pH of the chitosan solution was adjusted to 2.8 with acetic acid and it was held for 24 h at 70°C under stirring. After confirming the appearance of chitosan oligomer by thin layer chromatography and column chromatography using a series of standard compounds (chitosan oligosaccharides 1 ~ 6: Koshin Co., Japan), it was crystallized by the addition of acetone and filtered to obtain chitosan oligomer powder. This chitosan oligomer was dissolved in distilled water and neutralized with $NaHCO_3$. Then, recrystallization was performed with acetone. The chitosan oligomer powder obtained was washed with ethanol and ether in turn three times and freeze-dried.

The molecular weight of chitosan oligomer prepared was determined by gel permeation chromatograph (JASCO, LCSS-905, Jasco Co., Japan) with a Shodex OHpak SB-801 + SB-802 + SB-803 column using 0.1*M* NaCl in 0.2% acetic acid as a mobile phase at 1 mL/min flow rate. Pullulan (M_w, 853,000, 95,400, 23,700, 5800) and chitosan oligosaccharides (M_w, 322, 483, 706, 876) were used as standard compounds.

Colloid titration technique[5] was used to estimate DDA. Colloid solution was made by dissolving 1 g of chitosan oligomer in 100 mL of deionized water and 100 mL of 0.4*M* acetate buffer (18 mL of 0.4*M* acetic acid/82 mL of 0.4*M* sodium acetate). One gram of colloid solution mixed with 30 mL of deionized water was titrated with 1/400*N* potassium polyvinyl sulfate solution by using toluidine blue as an indicator. End point was determined by the color change from blue to reddish purple.

Infrared (IR) spectra of chitosan (Sigma Chemical Co.) and chitosan oligomer prepared were collected with a Nicolet Fourier transform infrared (FTIR) spectrometer using the KBr pellet method.

Fabric samples were padded with chitosan oligomer solution of various concentrations to give 100% pick-up. The padded samples were dried at 100°C for 3 min. Antimicrobial activity of the treated fabrics was evaluated by the shake flask method[6] in terms of bacteria reduction rate. Bacteria used were *Staphylococcus aureus* (ATCC 6538), *Escherichia coli* (ATCC 8473), *Proteus vulgaris* (ATCC 6059), *Klebsiella pneumoniae,* and *Pseudomonas aeruginosa* (ATCC 13388).

Performance properties of the treated samples were evaluated using published standard procedures including tensile strength and elongation in both machine and cross direction, IST (INDA standard test) 110.4; stiffness, IST 90.1; air permeability, IST 70.1; liquid strike-through time

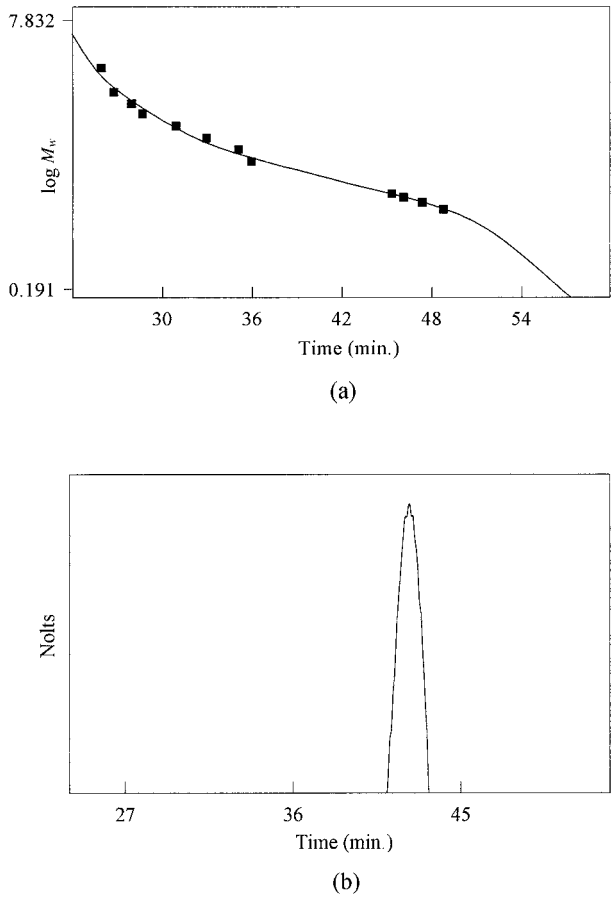

Figure 1 Gel permeation chromatographic (GPC) calibration curve (a) and trace (b) of chitosan oligomer.

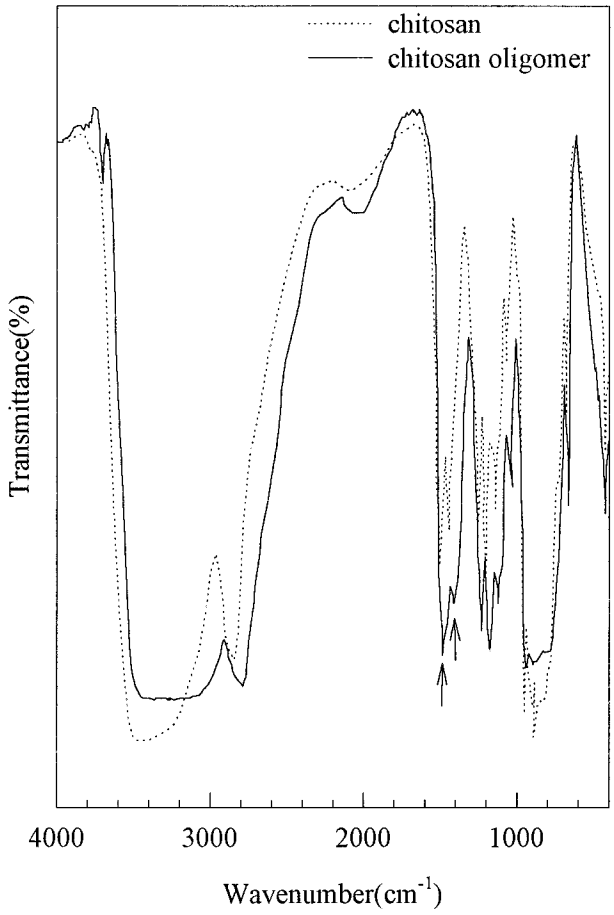

Figure 2 IR spectra of chitosan and chitosan oligomer.

using simulated urine (9 g NaCl/1 L of distilled water), ERT 150.2-93.

RESULTS AND DISCUSSION

Analysis of Chitosan Oligomer

Gel permeation chromatographic data are shown in Figure 1. The molecular weight of chitosan oligomer is in the range of 1400–2300 and its weight-average molecular weight is 1814. Its DDA determined by the colloid titration technique was 84%. Figure 2 shows the IR spectra of chitosan and chitosan oligomer prepared. As in a typical chitosan, chitosan oligomer shows a C═O stretching (amide I) band at 1650 cm^{-1}, NH_2 deformation band at 1590 cm^{-1}, and OH stretching at 3450 cm^{-1}.

Antimicrobial Activity of Treated Fabrics

Figure 3 shows the effect of chitosan concentration on antimicrobial activity of the fabric treated with chitosan oligomer. The untreated sample shows 15–38% of reduction rate depending on the strains of bacteria. Effectiveness of chitosan on antimicrobial activity depends on the strains of bacteria. Chitosan oligomer is the most effective against *P. vulgaris,* exhibiting above 90% of reduction rate at a 0.01% level. *P. vulgaris* is known to rapidly decompose urea in urine into ammonia causing unpleasant odor and diaper dermatitis. It was established that pH elevation of the skin in the diaper area resulting from ammonia production increased the probability of skin irritation because of activation of fecal enzymes.[7] The wool fabric treated with chitosan exhibited 85–95% ammonia reduction rate, resulting in a 30–40% higher deordoring rate compared with untreated fabric.[8] We expect that chitosan oligomer, to some extent, would control unpleasant odor as well as skin problems caused by ammonia. More detailed studies on these subjects are necessary. Chitosan oligomer also shows above 90% of reduction rate against *S. aureus* and *E. coli* at a 0.05% level. *S. aureus* has been known to aggravate atopic dermatitis or prevent resolution of the disease.[9,10]

We tested antimicrobial activity against *K. pneumoniae* and *P. aeruginosa* up to 1.0% treatment concentration. Chitosan oligomer was not effective against them showing only about a 30% reduction rate. Seo et al.[2] reported that minimum inhibitory concentration of chitosan (M_w 3 × 10^5, DDA 80%) was different depending on the strains

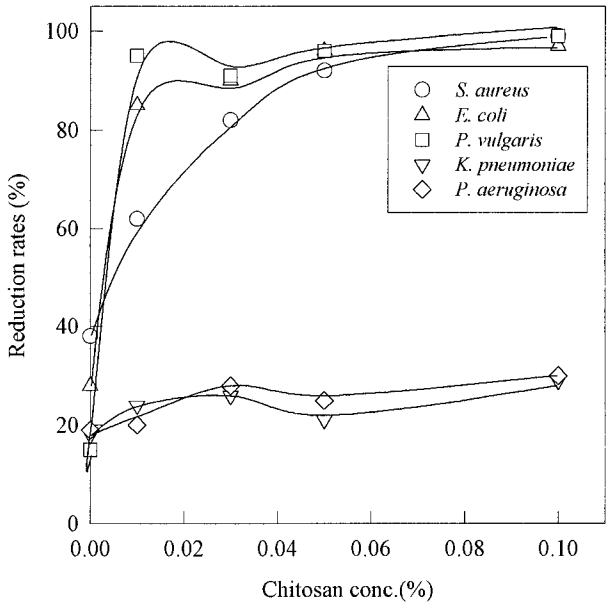

Figure 3 Antimicrobial activity of fabrics treated with chitosan oligomer.

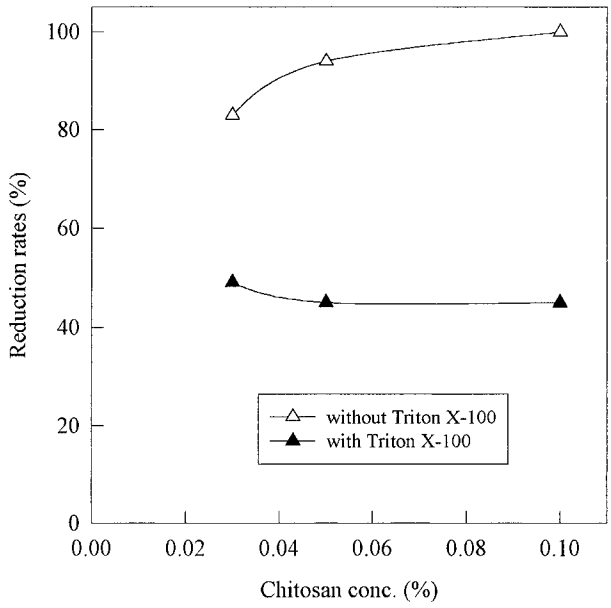

Figure 4 Effect of wetting agent on the antimicrobial activity against *S. aureus.*

of bacteria and some bacteria were not inhibited significantly. In the case of *K. pneumoniae* and *P. aeruginosa,* the mechanism of growth inhibition seems to be different from the other three bacteria according to the results in this study. There are two proposed mechanisms of antimicrobial activity by chitosan. In one mechanism, the polycationic nature of chitosan interferes with bacterial metabolism by stacking at the cell surface.[11] The other mechanism is the binding of chitosan with DNA to inhibit mRNA synthesis.[12] In the latter mechanism, chitosan must be hydrolyzed to a molecular weight less than 5000 which is easy to permeate into the cell.[13] We obtained about 80% reduction rate against *K. pneumoniae* and *P. aeruginosa* by using chitosan of M_w 180,000 (DDA 85%) at above 0.5% concentration in the preceding study.[14] From the results, we speculate that the growth of *K. pneumoniae* and *P. aeruginosa* is more effectively inhibited by the chitosan molecules of large size than those of small size by stacking on the cell wall. Uchida et al.[3] studied the effect of molecular weight of chitosan oligomer on antimicrobial activity and found that the chitosan oligomer consisting of 4–7 repeat units inhibited the growth of *E. coli,* whereas oligomer mainly consisting of 3–4 repeat units did not retard the growth of *E. coli.* On the other hand, Tokura et al.[13] reported that chitosan oligomer of M_w 9300 was the growth inhibitor of *E. coli,* whereas chitosan oligomer of M_w 2200 was not a growth inhibitor. The dependence of molecular weight on the antimicrobial activity of chitosan is still controversal.

Wetting agent is generally added in the finishing formulation to improve the penetration of finishing solution. Thus, we tested the effect of wetting agent on the antimicrobial activity of chitosan oligomer. Although the alkylaryl polyether alcohol (Triton X-100) used in this study is nonionic, the reduction rate of *S. aureus* decreases up to 30–40% at the concentration of 0.1% as shown in Figure 4. This seems to be due to interactions between cationic groups in chitosan oligomer and weak anionic ethylene oxide groups in the wetting agent, resulting in the decrease of antimicrobial activity imparted by amino groups in the chitosan oligomer. Therefore, it is very important to select a compatible wetting agent with chitosan oligomer, if wetting agent is necessary.

Performance Properties of Treated Fabrics

Table I shows the physical properties of the treated nonwoven fabrics. Stiffness of samples

Table I Physical Properties of Treated Fabrics

Chitosan Concentration (%)	Stiffness (cm)	Tensile Strength[a]		Elongation (%)	
		MD[b]	CD[c]	MD	CD
—	2.55	5.55	1.28	49	88
0.01	2.63	5.27	1.12	47	90
0.05	2.75	4.29	1.24	41	87
0.50	2.87	4.68	1.23	44	85
1.00	2.98	4.43	1.23	38	86

[a] kg/5 cm.
[b] Machine direction.
[c] Cross direction.

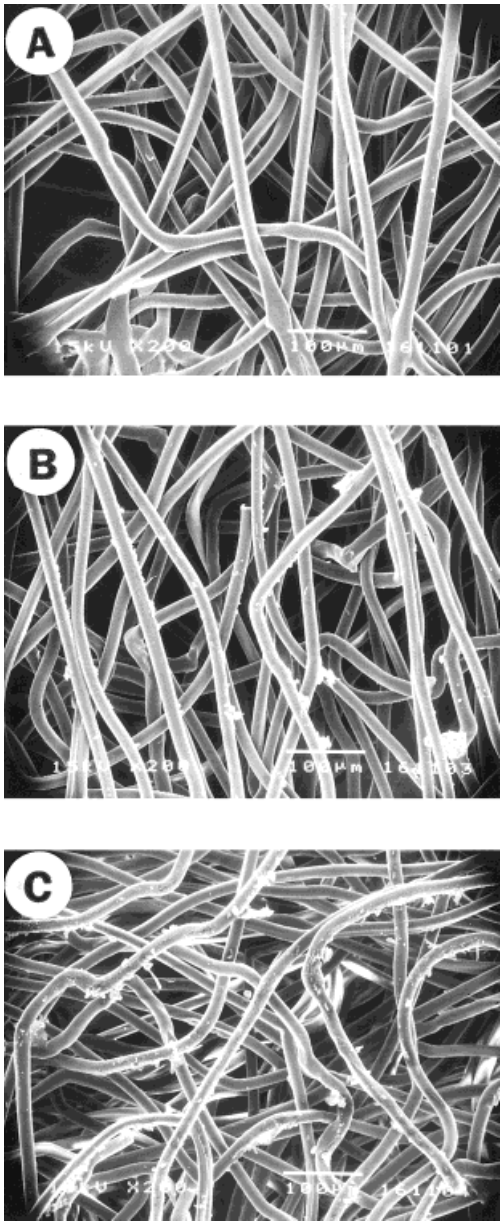

Figure 5 SEM pictures (original magnification, ×200) of control and fabrics treated with chitosan oligomer (A, control; B, 0.05%; and C, 0.1%).

increases with the increase of treatment concentration due to surface deposition of chitosan molecules, as seen in SEM pictures (Fig. 5). Tensile strength decreases slightly in machine direction. Strength in machine direction, corresponding to strength in the warp direction of woven fabric, is important in diaper manufacturing by continuous process; 3.5–4.0 kg/5 cm is generally required. Strength in cross direction, corresponding to strength in the fill direction of woven fabric, should be enough to prevent diaper material from tearing at the side of the adhesive tape. This side-tearing is one of the most common complaints from consumers. A strength of 0.6–1.1 kg/5 cm is usually required for cross direction. Although tensile strength slightly decreases after treatment with chitosan oligomer, it is sufficient for using diaper coverstock. Elongation in the machine direction decreases slightly, but no significant change occurs in cross direction.

Figure 6 shows the effect of chitosan concentration on air permeability. Air permeability of the treated samples decreases as chitosan concentration increases. This is because chitosan molecules deposit on the fiber surface to block pores rather than penetrate into PP fiber and change the porous structure of nonwoven fabric. A decrease in air permeability might adversely affect the comfort of hygienic products.

The dependence of liquid strike-through time on chitosan concentration is shown in Figure 7. The liquid strike-through test measures the time taken for a specified quantity of test fluid (5 mL of simulated urine in this study) to be absorbed by a test piece of nonwoven coverstock, which is in contact with an underlying standard absorbent pad. Liquid strike-through time of the treated samples decreases with the increase of treatment concentration to 0.5% and reaches to equilibrium thereafter. The increase in absorbancy of the treated samples is attributed to hydroxyl and

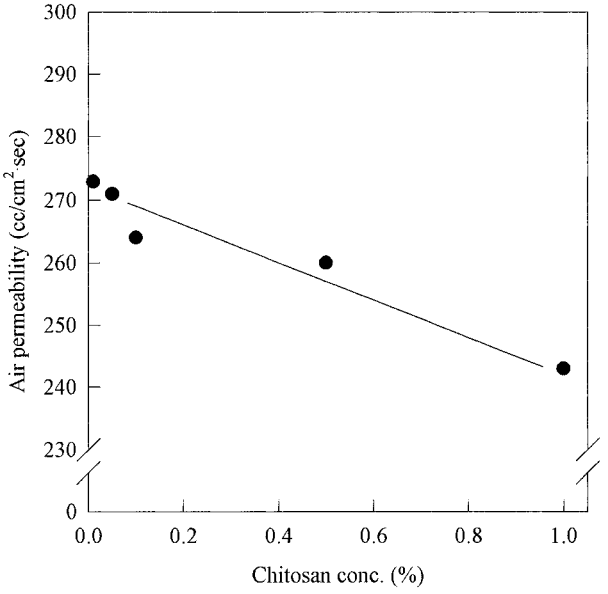

Figure 6 Air permeability vs chitosan oligomer concentration.

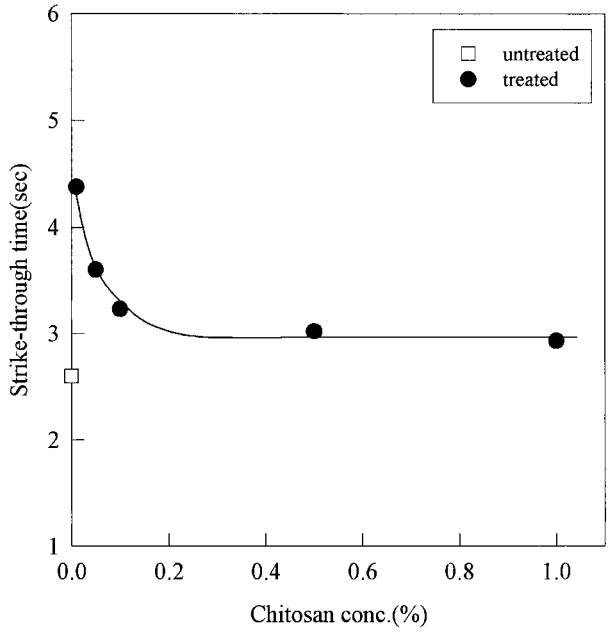

Figure 7 Liquid strike-through time vs chitosan oligomer concentration.

amine groups in chitosan providing reactive sites with water. Liquid strike-through time of a hydrophilic finished sample, which is commercially available, is 2.6 s. On the other hand, liquid strike-through time of the sample treated with 0.5% of chitosan oligomer, shows that the 100% reduction rate against *S. aureus, E. coli,* and *P. vulgaris,* is 3.0 s. This is comparable with 2.6 s of a hydrophilic finished sample commercially available. Cottenden[15] reported that pads with fast strike-through times generally had the best wet comfort. Because coverstock requires less than 3.0 s of liquid strike-through time, the samples treated with chitosan concentration above 0.5% are acceptable for coverstock use.

SUMMARY

Water-soluble chitosan oligomer was prepared to apply as an antimicrobial finishing agent for PP nonwoven fabric used as coverstock. Fabrics were treated with chitosan oligomer solution by the pad-dry method. The treated samples show high antimicrobial activity against *P. vulgaris* at 0.01%, *S. aureus* and *E. coli* at 0.05% level showing above 90% reduction rate. But chitosan oligomer is not effective against *K. pneumoniae* and *P. aeruginosa* below 1.0% treatment concentration. Nonwoven fabrics become stiffer as treatment concentration increases. Tensile strength decreases slightly, but it is enough to use as coverstock. Air permeability decreases as treatment concentration increases. Liquid strike-through time decreases to 0.5% of treatment concentration and reaches to equilibrium thereafter. Liquid strike-through time of the samples treated with 0.5% of chitosan oligomer solution, showing 100% reduction rate against *S. aureus, E. coli,* and *P. vulgaris,* is 3.0 s, which is comparable with 2.6 s of a hydrophilic finished sample commercially available.

It is concluded that chitosan oligomer is applicable to impart antimicrobial properties for PP nonwoven coverstock of diaper and hygienic uses. However, the optimum molecular weight of chitosan should be selected according to the end use of products.

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