A Simple Method of Simultaneously Endowing Paper or Fluff Pulp With Both High Softness or Appropriate Fluffing Properties and Antimicrobial Properties

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Abstract

As the living standard improve, disposable sanitary and living paper requires not only softness or easy to
fluff in a dry state, but also good antibacterial property. In this study, a series of alkyl quaternary
ammonium salts (AQAS), a kinds of antibacterial-debonding agents, were synthesized by using a two-
step process. The SN2 nucleophilic substitution reaction was designed between triethanolamine and
sulfoxide chloride, and followed subsequent quaternization by tertiaryamines with different long alkyl
chains. The obtained products can be used as an antibacterial and softening/debonding agent for
improving the performance of paper or fluff pulp. The results showed that these new compounds can
endow antibacterial function and high softness to paper or control appropriate burst strength to fluff pulp
board. These AQAS products can be not only used in daily disposable sanitary products, but also have
potential applications in other products such as glass spacer paper, advanced household paper, or
antibacterial tissue products to prevent microbial contamination.

1. Introduction

With an improvement in people's living standard, there has been an increasing demand for disposable
sanitary—such as women's sanitary napkins, baby diapers and adult incontinence products (Cordella et al.
2015; Ajmeri and Ajmeri 2016; Widen et al. 2017; Mendoza et al. 2019)[2-5]. Since most disposable
sanitary products have close contact with human body, high antibacterial activity during uses is usually
desired. However, in most cases, the main material, fluff pulp, used to prepare these disposable sanitary
products has no antibacterial activity (Forsgren-Brusk et al. 2017). In addition, a large number of
microorganisms exist in the natural environment and they can mass propagate once the conditions are
suitable, which can cause bacterial infection and create health problem for people (Asri et al. 2014;
Paterson and Harris 2016; Mc Carlie et al. 2020; Wang et al. 2020). Therefore, the development of
materials with antibacterial activity has attracted significant interest in new material research (El-Naggar
et al. 2018; Noorian et al. 2020).

In addition, with the increasing demand for household papers, such as toilet paper, napkins, beauty paper
and paper towels, there are increasing requirements for quality and performance of these products,
especially the softness (Gashti and Adibzadeh 2014). However, in the manufacturing process of
household papers, in order to reduce the production costs, a large number of non-wood and secondary
fibers used (Guan et al. 2019; An et al. 2020), which usually makes such products dense and their surface
stiff (Illeez et al. 2015; Liu et al. 2020). Although creping is an effective way to increase the softness, it
has limited impact. Hence, much attention has been paid to develop novel paper softeners (Tang et al.
2017; Mazzon et al. 2019). In the textile industry, softeners are used widely, but textile softeners are
seldom used in papermaking due to some disadvantages, such as the large loading, high cost and poor
effectiveness. Therefore, there is a clear need to develop special softening agents for this kind of papers
or debonding agents for fluff pulp board. In order to make the final tissue products possess high
antibacterial activity and at the same time create enough softness or appropriate burst strength,
antibacterial agents (Hayashi et al. 2019; Xu et al. 2020) and softening/debonding agent (Igarashi et al.
2016) are usually added together during the papermaking process. However, there are few reports on chemical additives which have both antibacterial and softening/debonding effects. Hence, it is imperative to come up with a concoction as antibacterial-debonding agent to endow paper or fluff pulp with antibacterial and softening/debonding effects.

At present, antibacterial agents have two main types: inorganic and organic agents. Inorganic antibacterial agents such as Au (Lai et al. 2015), Ag (Alahmadi et al. 2018; Caschera et al. 2020; Rabbi et al. 2020; Yousaf et al. 2020), Cu (Jose et al. 2020; Li et al. 2021), TiO2 (Alizadeh-Sani et al. 2020) and Zn (Zhao et al. 2017; Lallo da Silva et al. 2019; Farooq et al. 2020) and other metal nanoparticles have the advantages of low cost and good antibacterial properties, but at the same time there are disadvantages such as easy discoloration, manufacturing difficulties, and complex processing processes that limit their application in real life. Organic antibacterial agents such as chitosan (Salari et al. 2018; Tu et al. 2019), chlorhexidine (Bashir et al. 2019), triclosan (Alfhili and Lee 2019), polyethyleneimine (Wahid et al. 2019), quaternary ammonium salts (Quinlan et al. 2015; Jiao et al. 2017; Li et al. 2018) have the advantages of fast sterilization speed, strong sterilization ability, convenient processing, and good color stability. The quaternary ammonium salts have been studied by a large number of researchers because of their convenient synthesis and excellent antibacterial ability, and have been greatly developed. Li et al. (Li et al. 2018) achieved functionality by surface modification of cellulose nanocrystals grafted 2-(dimethylamino) ethyl methacrylate (DMAEMA) onto the surface of CNCs to prepare CNCs-g-dmaema. Subsequently, the tertiary amine group of CNCs-g-PDMAEMA was transferred to the quaternary ammonium group by adding alkyl bromide (C10-C18) with different carbon chain lengths. The results of the study showed that the antimicrobial activity of the prepared antimicrobial materials was related to the alkyl chains of the prepared materials. The best antimicrobial effect was observed for the materials containing C10 alkyl groups in the quaternary ammonium salts.

In a word, compared with other antibacterial agents, organic antibacterial agent with quaternary ammonium group has been widely studied by researchers worldwide because of its advantages of low cost, high antibacterial efficiency, good safety and convenience for applications (Ma et al. 2012; Liu et al. 2015; Jung et al. 2020). Also, the alkyl group on the side chain of QAS has a certain hydrophobicity, which can improve the softness of tissue products (Gao et al. 2019) and may weaken the bonding strength between fibers as debonding agent for fluff pulp board.

In this work, a series of multibranched long-chain alkyl quaternary ammonium salt compounds (AQAS), a kinds of antibacterial-debonding agents, were synthesized, which played double roles in fluff pulp board or paper preparation. Subsequently, the effect of the amount of AQAS on the physical properties of fluff plup board and paper were evaluated and analysed. The softness is changed mainly due to an increase of the length of alkyl chains and the number of long alkyl chains on the side chains in the AQAS molecules. The antibacterial effect is mainly due to an increase of the number of nitrogen positive ions in the AQAS molecules, and the antibacterial properties of the product are measured by the inhibition circle method based on the antibacterial mechanism of nitrogen positive ions. These AQAS products have potential applications in daily disposable sanitary products and other antibacterial tissue products to
prevent microbial contamination. These AQAS products have potential applications in daily disposable sanitary products and other antibacterial tissue products to prevent microbial contamination. The research results have important application value for developing compound functional chemicals and improving the quality of disposable sanitary products, household paper and industrial paper for special needs.

2. Material And Methods

2.1 Materials

Triethanolamine, ethyl acetate and absolute ethanol were obtained from Tianjin Tianli Chemical Reagent Co., Ltd. Sulfoxide chloride, chloroform, and N,N-dimethylhexadecylamine were obtained from Sinopharm Chemical Reagent Co., Ltd. N,N-dimethylloctylamine was obtained from Aladdin Reagent Co., Ltd., China. N,N-dimethyltetradecylamine was obtained from TCI Tokyo Chemical Industry Co., Ltd, and all chemicals and reagents were used as received. Bleached softwood and hardwood pulps (in dry lap form) were all provided by Guangxi Fenghuang Co., Ltd., China. In addition, nutrient agar used for antibacterial test was obtained from Beijing Aofox Biotechnology Co., Ltd.

2.2 Methods

The synthesis schematic of AQAS

The AQAS with different long alkyl chains was synthesized by using a two-step process. The SN$_2$ nucleophilic substitution reaction was carried out first via the reaction between triethanolamine and sulfoxide chloride, resulting in tris(2-chloroethy)amine and then long-chain alkyl groups were introduced to the molecule of tris(2-chloroethy)amine by the quaternization reactions with different alkyl tertiaryamines (Scheme 1).

The synthesis of tris(2-chloroethy)amine

Chloroform (0.3 mol) and triethanolamine (0.075 mol) were added into a 250 mL three mouth flask, and then sulfoxide chloride was dropped into the reaction mixture. The above solution was stirred in an ice-water bath. During reaction, there was a slow release of gas, which was absorbed by the sodium hydroxide solution. After the addition, the reaction temperature was slowly raised to 30°C and the reactor was kept stirring for 3h, and then heated up to 60°C and stirred until no gas was released. Finally, the flask was cooled in ice-water and a large amount of white solid was precipitated, which was then filtered and repeatedly washed with chloroform and ethanol absolute and dried at 50°C to obtain the intermediate product tris(2-chloroethy)amine hydrochloride white crystals.

The synthesis of AQAS
Tris(2-chloroethyl)amine (0.0083mol) was first added into a 250 mL glass flask. Dilute sodium hydroxide solution was added dropwise into aqueous emulsion to adjust the pH value of the system within a certain range. After heating up to 60°C, and N,N-dimethyl-octylamine (N,N-dimethyl-tetradecylamine and N,N-dimethyl-octadecylamine) (0.0332 mol) were gently dropped into the three flask to react with the intermediate product. Afterwards, the mixture was stirred at 90°C for 7 h. Finally, the flask was cooled in ice water bath and a large amount of yellowish solid was separated out, which was then filtered and washed with ethyl acetate and ethanol absolute several times and dried at 50°C to obtain the product. The products were named as AQAS 2a, AQAS 2b and AQAS 2c.

The preparation of antibacterial paper (or fluff pulp board)

AQAS 2a, AQAS 2b and AQAS 2c with concentration of 0.01 g·ml⁻¹ were added into the pulp suspensions at 0, 0.25%, 0.5% and 0.75%, respectively. A thorough mixing was provided and paper sheets (or fluff pulp board) with the basis weight of 60 g·m⁻² (660 g·m⁻²) were then prepared. The wet sheet was pressed three times under 4 MPa for 2 min, and then the two sides of wet paper was dried for the same time at 105°C in the glazing machine, to ensure the moisture content of the sheet or pad is between 8%~12%. Finally, the dried papers (fluff pulp boards) were conditioned in sealable bags for 12 h to stabilize the moisture content (Scheme 2).

2.3 Characterization

The ¹H nuclear magnetic resonance (¹H NMR) spectrum of AQAS were recorded using an AVII-500 MHz spectrometer (Bruker, Germany) with deuterated chloroform (CDCl₃) as the solvent.

Fourier transform infrared spectroscopy (FTIR) of AQAS were recorded on a spectrometer (VECTOR22, Bruker, Germany) in the range of 400 ~ 4000 cm⁻¹, with 4 cm⁻¹ resolution. The samples were ground with potassium bromide (KBr) and pressed into transparent pellets.

The burst strength index of fluff pulp board was performed on a bursting strength tester (DCP-NPY5600, Changjiang Papermaking Instrument, Sichuan, China) according to GB/T 1539-2007. The fluff-specific volume, absorption rate and absorbility were determined according to GB/T 21331-2008. The mechanical performance of each specimen was determined parallely for three times. The fluff-specific volume (A), absorption rate (B), and absorbility (C) were calculated according to the formula as follow:

\[ A = s \cdot h / (10 \cdot x) \]
\[ B = (y - x) / t \]
\[ C = (y - x) / x \]
Where \( s \) is the area of specimen (19.64 cm\(^2\)), \( h \) is the initial height of pulp specimens (cm), \( x \) is a constant weight (3.00 g) for specimen, \( y \) is the weight of specimen with sufficient absorption (g), \( t \) is the penetrating time of water from the bottom to top of specimens (s).

The softness of the prepared antibacterial paper was performed on a Tissue Softness Analyzer apparatus (Drake Co. Ltd, Shandong, China).

The surface morphology of antibacterial paper was observed with a scanning electron microscopy (SEM, VEGA 3 S-4800, HITACHI, Tokyo, Japan). All samples were sputtered with a layer of gold in vacuum for 60 s before analysis.

The antibacterial capability of the prepared antibacterial paper was investigated using the inhibition zone method which is also called the agar disk diffusion method. \( E. \ coil \) and \( S. \ aureus \) were used in the antibacterial experiment as typical Gram-negative and Gram-positive bacteria, respectively. The medium was prepared as follows: 0.5 g beef extract, 0.5 g sodium chloride, 1.0 g peptone and 1.5 g agar were added into 100 mL distilled water and autoclaved at 121°C for 15 min. Then 20 mL medium was poured into the sterilized petri dish. After the medium was solidified, 50 mL bacterial suspensions were uniformly smeared over the dish. Then, the cellulosic specimens were cut into circles with a diameter of 12 mm and then were gently placed on Petri dishes. After being incubated for 24 h at 37°C, the diameter (mm) of the inhibition zone was calculated using the following formula:

\[
H = (D - d) / 2.
\]

Where \( H \) is the bacteriostatic belt width, \( D \) is the average outside diameter of inhibition zone, and \( d \) is the diameter of the specimens or the control ones.

3. Results And Discussion

3.1 The \(^1\)H NMR and FT-IR spectra analysis of AQAS 2a

The \(^1\)H NMR spectra (500 MHz, CDCl\(_3\), 25°C) of AQAS 2a is shown in Fig. 1. The peaks at 0.88, 1.26 and 1.74 ppm originate from the AQAS 2a and are attributed to the terminal methyl of -CH\(_2\)-CH\(_3\), side chain methylene group \((\text{CH}_2\)'\(_5\)) of AQAS 2a and methylene of N\(^+\)-CH\(_2\)-CH\(_2\)-, respectively. The peak at 3.35 ppm belongs to methyl of N\(^+\)-CH\(_3\), the peak at 3.42 ppm is attributed to the methylene (N\(^+\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-(Kang et al. 2016)), indicates that the target product has been successfully synthesized (Fig. 1). However, the methyl peak (2.79 ppm) in -CH\(_2\)-CH\(_3\), methylene peak (2.94 ppm) in N\(^+\)-CH\(_2\)-CH\(_2\)-, and the peak of N\(^+\)-H at around 2.21 ppm are also weakly observed in Fig. 1, which indicates the presence of by-products (tertiary ammonium hydrochloride) in terminal product.

Fig. 1. \(^1\)H NMR spectra of (1) tris(2-chloroethyl)amine, (2) N, N-dimethyloctylamine and (3) AQAS 2a.
The AQAS2a was further characterized by FT-IR spectra (Fig. 2). The strong absorption peak at 1470 cm\(^{-1}\) belongs to methyl bending vibration peak in N\(^+\)-(CH\(_3\))\(_2\), and the symmetric bending vibration absorption peak of methyl in -CH\(_2\)-CH\(_3\) could be observed at 1379 cm\(^{-1}\), which is a characteristic absorption peak of moderate intensity. The weak absorption peak near 1040 cm\(^{-1}\) is the characteristic absorption frequency of quaternary ammonium salt, which confirms the formation of AQAS2a. Compared with Line 2 in Fig. 2, the characteristic absorption peaks of methyl and quaternary ammonium salt group appear for the first time. Besides, there still exist the methylene asymmetric and symmetric stretching vibration absorption peaks at 2927 cm\(^{-1}\) and 2870 cm\(^{-1}\) region in NR\(_2\)-CH\(_2\)-R. In addition, the strong absorption peak at 760 cm\(^{-1}\) is weakened, which indicates the weakened C-Cl stretching vibration peak in -CH\(_2\)-Cl. This may be attributed to the presence of by-products that incomplete quaternary ammonium salt in the product. We successfully synthesized AQAS2b and AQAS2c by using a similar method to AQAS2a. For detailed characterization and spectra please refer to the supporting information (Fig. S1, Fig. S2, Fig. S3, Fig. S4).

Fig. 2. FT-IR spectra. 1. N,N-dimethyl-octylamine, 2. tris(2-chloroethy)amine and 3. AQAS2a

### 3.2 The properties of the fluff pulp board and fluff fiber

**The apparent density and burst strength index**

As shown in Fig. 3a and b, the apparent density and burst strength index of the fluff pulp boards decrease with increasing the addition of AQAS, and the decrease is more significant with the increase of the addition. The decreasing trend of the apparent density and burst strength index becomes flat after the amount of AQAS is more than 0.75%. From this experimental results it was deduced that the bonding force becomes weak because of the increase in spacing between the fibers in fluff pulp boards and decrease in hydroxyl with the addition of AQAS. The effect of long alkyl chain is more obvious.

**The water absorbility and water absorption rate of fluff pulp**

As the amount of AQAS increased, the water absorbility and water absorption rate of fluff pulp show a decreasing trend (Fig. 3c and d). When the amount of AQAS is up to 0.5%, the decreasing trend is gradually leveled off. The alkyl chain in AQAS plays the role of shielding hydroxyl group, and with the increase of AQAS, the shielding effect becomes more obvious. The longer the alkyl chain, the greater the shielding effect of the hydroxyl group. More alkyl groups with hydrophobic effect are attached to the surface of the fluff pulp fibers, resulting in less absorbency of the fibers and consequently less water absorption rate of the fluff pulp.

**The fluff-specific volume of fluff pulp**

As shown in Fig. 3e, with increasing the addition of AQAS, the fluff-specific volume tends to rise first and then fall. The three hydrophobic alkyl chains in AQAS on the fiber surface hinder the combination between fibers, making the gap between fibers increase and become fluffy, so that the fluff-specific
volume of the fluff pulp board is on the rise; and when the amount of AQAS is high, the three long alkyl chains in AQAS are easy to cross and tangle with each other, so that when the pulp board is dry dissociated, the fiber pile is uneven and appears to be knotted and fall off in pieces. It affects the fluff-specific volume of antibacterial pulp fiber.

The surface morphology of fluff pulp fibers

Surface morphology of antibacterial fluff pulp fibers with AQAS 2c was examined using SEM as shown in Fig. 4, we can see that the surface of fibers in the blank sample is very rough, and some microfibrils are broken away from the surface. This would have an adverse impact on the softness of fluff pulp board. However, the SEM images of fluff pulp fibers treated by AQAS 2c show that the fiber surface is smoother with the increase of the loading of AQAS 2c. Therefore, adding proper amounts of AQAS 2c to pulp fiber is an effective way improve the softness of antibacterial paper.

3.3 The softness and air permeability of antibacterial paper

In order to explore the effect of AQAS 2a, AQAS 2b and AQAS 2c on the air permeability and softness of antibacterial paper, the different amounts of AQAS were added into pulp suspension to make paper that the basis weight is 60 g m\(^{-2}\) (Scheme 2), and the testing results are shown in Fig. 5.

The air permeability of paper gradually increases with the amount of AQAS increases, the shielding effect of alkyl chains on fiber hydroxyl groups also increases, and the bonding force between pulp fibers decreases (Fig. 5a). The reason is that the hydrogen bonds between fibers can not form when the AQAS was used. On the other hand, the three hydrophobic alkyl chains in AQAS on the fiber surface hinder the combination between fibers, and when the amount of AQAS increases, the three long alkyl chains in AQAS are easy to cross and tangle with each other, which make the gap between fibers increase and the paper become bulky.

As shown in Fig. 5b, the softness of control sample is 2428.5 mN. However, the softness of paper decreases with the amount of AQAS increases, indicating that the softness is constantly improved. The result supports the conclusion that AQAS 2a, AQAS 2b and AQAS 2c also have softening effect. Moreover, it is found that the softness of all samples decrease slowly with the AQAS loading up to 0.25wt%. When their loading is more than 0.25wt%, the softness of paper adding AQAS 2a or AQAS 2b also drops slowly, but the decreasing trend is clear for adding AQAS 2c. This indicates for AQAS 2c can endow paper the best softening effect. It may be attributed to the alkyl groups with hydrophobicity of AQAS 2c which are more than that of AQAS 2a and AQAS 2b. The alkyl groups can form hydrophobic external reverse adsorption on the surface of fibers, and reduce the dynamic and static friction factors of paper fiber. Therefore, the AQAS 2c can be used as a softener with antibacterial activity for tissue papermaking.

3.4 The antibacterial activity of fluff pulp board and paper
The antibacterial activity testing results are shown in Fig. 6. It was found that no inhibition zone appeared around the blank sample, indicating the poor antibacterial activity for original fiber. However, the inhibition zone appeared for other samples of paper made with \textit{AQAS} 2a (\textit{AQAS} 2b, \textit{AQAS} 2c), and the inhibition zone increased with the increase of the loading amount of \textit{AQAS}, which all confirmed the addition of 2a (2b, 2c) afforded fluff pulp board with antibacterial activity. \textit{AQAS} 2a, \textit{AQAS} 2b and \textit{AQAS} 2c are excellent antibacterial agents against \textit{S. aureus} and \textit{E. coli}.

The comparison of antibacterial activity of different \textit{AQAS} is shown in Fig. 7. As can be seen on the two plates, the diameter of inhibition zone around the samples decreased significantly with the increase of alkyl group on the side chain of \textit{AQAS}, which means the antibacterial activity of \textit{AQAS} 2a is the strongest against either \textit{S. aureus} or \textit{E. coli}, the second is \textit{AQAS} 2b, and the antibacterial activity of \textit{AQAS} 2c is the weakest. Furthermore, compared with \textit{E. coli}, the antibacterial activity of fluff pulp with different \textit{AQAS} against \textit{S. aureus} is better, which is consistent with the above conclusion in Fig. 3.

3.5 The antibacterial and softening mechanism of \textit{AQAS}

\textit{As shown in Scheme 3, when a certain loading of AQAS is added to the pulp fiber, the AQAS can be attached to the fiber surface by electrostatic adsorption to form something like water film. Then it hinders the bacteria from getting closer to achieve certain antibacterial effect. Besides, the AQAS contacts with the surface of bacteria, and the structure of bacteria cell membrane is destroyed, so that the bacteria die (Jung et al. 2019), to achieve the purpose of sterilization. However, the softening effect can be attributed to: (1) the quaternary nitrogen positive ions combine with free hydroxyl groups on the surface of fibers, reduce the formation of hydrogen bonds, weaken the bond between fibers, decrease the static friction coefficient between fibers, and then the surface of the fibers became smoother, (2) long alkyl chains have a certain hydrophobicity, which reduces the formation of hydrogen bonds between fibers and makes the structure of fibers more loose. Therefore, both of them can make the antibacterial products have certain softening effect, and control the burst strength of fluff pulp board suitable for dry disintegration.}

4. Conclusions

The antibacterial effect is mainly by increasing the number of nitrogen positive ions in the \textit{AQAS} molecule, based on the antibacterial mechanism of nitrogen positive ions to achieve the purpose of product antibacterial. And the softness is mainly by increasing the length of alkyl chains and the number of long alkyl chains on the side chains of \textit{AQAS} molecules, relying on the hydrophobicity of alkyl chains, reducing the hydrogen bonding, and using electrostatic adsorption to attach to the fiber surface, reducing the static friction coefficient between fibers, so that the product has a certain degree of softness.

A series of \textit{AQAS} products were successfully synthesized and evaluated as antibacterial and softening agents in paper making and debonding agents in fluff pulp board. The obtained fluff pulp and paper with these \textit{AQAS} products showed excellent antibacterial activity against \textit{S. aureus} and \textit{E. coli}. At the same
time, the softness for the antibacterial tissue and the burst strength for antibacterial fluff pulp board has been improved. These AQAS products can be used in daily disposable sanitary products, but also have potential applications in other products such as Liquid Crystal Display (LCD) glass spacer paper, advanced household paper, or antibacterial tissue products to prevent microbial contamination.

**Declarations**

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**Figures**
Figure 1

1H NMR spectra of (1) tris(2-chloroethyl)amine, (2) N, N-dimethyloctylamine and (3) AQAS 2a
Figure 2

FT-IR spectra. 1. N,N-dimethyl-octylamine, 2. tris(2-chloroethyl)amine and 3. AQAS 2a
Figure 3

The properties of fluff pulp board with the loading amounts of AQAS. a. apparent density, b. burst strength index, c. water absorbility, d. water absorption rate, e. fluff-specific volume
Figure 4

The surface morphology of paper with different loading amounts of AQAS 2c

Figure 5

The properties of paper with different loading amounts of AQAS. a. air permeability, b. softness
Figure 6

Antibacterial activity of fluff pulp board with different loading amount of AQAS 2a, AQAS 2b and AQAS 2c. S0, S1, S2, S3 and S4 stand for the amount of 0, 0.25%, 0.5%, 0.75% and 1.0%, respectively.
Figure 7

Antibacterial activity of fluff pulp with different AQAS

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