

Effect of Dicarboxylic Acid Chain Length on the Self-Cleaning Property of Nano-TiO₂-Coated Cotton Fabrics

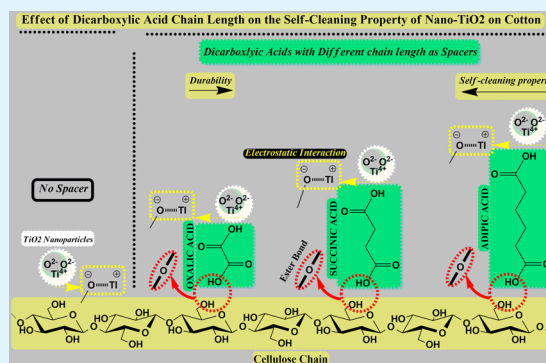
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ABSTRACT: In this study, the effect of dicarboxylic acid chain length on the amount of TiO₂ nanoparticles (TiO₂NPs) adsorption-produced self-cleaning property and washing durability on cotton fabrics were investigated. First, cotton fabric samples were treated with three kinds of dicarboxylic acids—oxalic, succinic, and adipic acids—and then dipped in TiO₂NP solution with a certain concentration. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to investigate bonds formation between dicarboxylic acid groups and hydroxyl groups of cellulose, and a scanning electron microscope (SEM) was applied for the analysis of surface morphology in specimens. Drop absorbency time was determined for samples using the AATCC TM 79:2000. Washing stability and the amount absorption of TiO₂NPs were determined by weighing and absorption spectrophotometry procedures, and the stain removal evaluation was conducted to assess the self-cleaning property. Results showed that all of the dicarboxylic acids used in this experiment improved the amount of TiO₂NPs absorbed onto cotton samples and their durability to washing. In addition, color variation of samples treated with oxalic acid after 180 min of UV irradiation and drop absorbency time for samples treated with succinic acid were significantly increased by about 126 and 600%, respectively. The best durability was obtained from adipic acid, while a better self-cleaning property was obtained from oxalic acid.

KEYWORDS: cotton, dicarboxylic acid, TiO₂, absorbance, self-cleaning, washing durability



INTRODUCTION

Today, self-cleaning textiles have become increasingly important due to market demand, and extensive research has been conducted in this area. Nanoscale TiO₂ is one of the most widely used materials to make self-cleaning textiles.^{1–5} Because of their unique photocatalytic activity and other benefits such as being nontoxic and cost-effective, TiO₂ nanoparticles (TiO₂NPs) have a wide range of applications in water and air purification sectors, wastewater treatment, chemical synthesis, and electro-fabrication.^{6–13}

However, applying TiO₂NPs to natural textile fibers has some disadvantages. On cotton fibers, for example, relatively weak electrostatic interaction between the TiO₂ and hydroxyl groups of cellulose results in a low durability. Because most fabrics are made from natural fibers (especially cotton), alternative approaches have been developed to solve this problem, such as in situ coating of nanoparticles on textile fibers, using adhesives and resins, improving surface tendency by surface modification techniques (plasma treatment), and cross-linking between TiO₂ particles and cotton fabrics.^{14,15}

Ester linking of cotton by poly(carboxylic acid)s (using sodium carbonate or triethylamine as catalysts) was first reported by Rowland et al. in 1967.¹⁶ Carboxyl groups of these compounds can form strong electrostatic bonds to TiO₂NPs while producing covalent ester bonds with the

hydroxyl groups of cotton fabrics via esterification.¹⁷ These are referred as spacers.¹⁸

Some studies have reported the use of carboxylic acids as spacers for attaching TiO₂ on cotton cellulose.^{15,19–22} Meilert et al. used three poly(carboxylic acids) (succinic acid, 1,2,3-propanetricarboxylic acid, and 1,2,3,4-butanetetracarboxylic acid) to attach TiO₂ to the cotton. It was reported that a significant increase in the rate of TiO₂NP absorption and washing durability (about 25 times greater) is achieved by using poly(carboxylic acid)s.¹⁵ Karimi et al. showed that stability of nano TiO₂ attached onto cotton surfaces using succinic acid, and the self-cleaning degree of the fabric was much higher than that of non cross-linked cotton fabrics.¹⁹ Nazari et al. reported an enhanced cross-linking property of TiO₂-coated cationized cotton fabric cross-linked with butanetetracarboxylic and citric acids.²⁰ Improved UV protection properties of protease pretreated wool fabrics coated with TiO₂NPs using butanetetracarboxylic and citric acids as spacers has been reported by Nazari.²¹ Montazer et al. produced a cotton fabric with hydrophobicity and photoactivity properties using nano titanium dioxide as a photocatalyst and 1,2,3,4-butanetetracarboxylic acid as a cross-linking agent, and in that study, fabric

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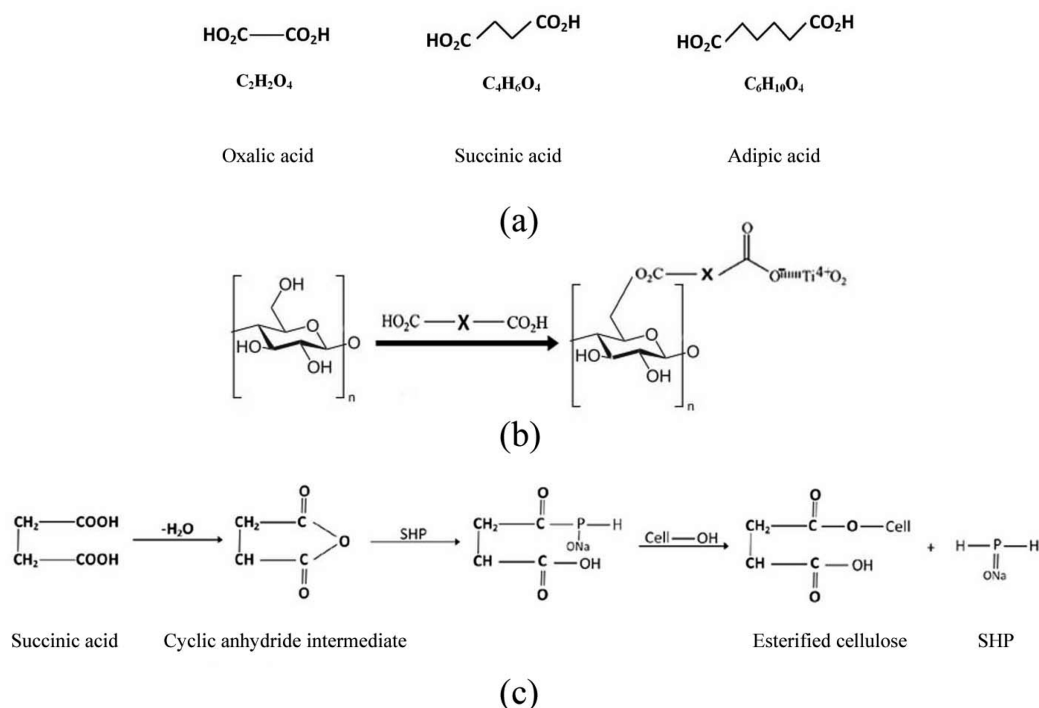


Figure 1. (a) Structure of dicarboxylic acids; (b) ester covalent and electrostatic bonds between dicarboxylic acids, cellulose, and TiO_2 NPs; and (c) formation of cyclic anhydride intermediates during esterification of cellulose with succinic acid.

wrinkling was also reduced as the result of cross-linking between cellulosic chains.²²

Literature summary shows that there is no report on investigating the impact of dicarboxylic acid chain length on cross-linking of cotton, its self-cleaning property, or the amount of TiO_2 adsorption. In the present study, cotton fabric was treated with three different poly(carboxylic acids): succinic, oxalic, and adipic acids. The effect of dicarboxylic acid chain length on TiO_2 NP adsorption, self-cleaning property of cotton, and washing durability were assessed and compared by weighing, absorption spectrophotometry, stain removal evaluation, and drop absorbency techniques.

EXPERIMENTAL SECTION

Chemicals. Adipic, oxalic and succinic acids; sulfuric acid (98%); nitric acid (65%); sodium hypophosphite (SHP); hydrogen peroxide (30%); and methylene blue dye (C.I.BLUE 9) were purchased from Merck KGaA (Darmstadt, Germany). TiO_2 nanocolloid (5% w/w) with the anatase crystalline structure and average particle size of 4–8 nm was purchased from PlasmaChem GmbH (Berlin, Germany). The bleached plain weaved 100% cotton fabric was used with fabric weight of 161.13 g/m².

Cotton Treatment with Carboxylic Acids and TiO_2 Nanoparticles. Prepared cotton fabrics (washed with 1% on weight of fabric (owf) nonionic detergent, 0.5% owf sodium hydroxide, L:R = 8:1, 60 min at 100 °C) were cut into 9 cm diameter circles and immersed in solutions (two different concentrations, 0.2 and 0.6 mol/L with 4% w/w SHP, were chosen for each dicarboxylic acid) for 1 h at 30 °C, dried for 3 min at 80 °C, and finally cured at 120 °C for 5 min. Pristine and cross-linked samples were immersed in solutions containing 0.5% owf TiO_2 NPs for 60 min at 75 °C and were cured for 60 min at 100 °C. Finally, all samples were washed with deionized (DI) water for 5 min at 30 °C.

Characterizations. To investigate bond formation between carboxylic groups of dicarboxylic acids and hydroxyl groups of cellulose chains, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded using a Thermo Nicolet Nexus

870 (Waltham, MA) in the range of 4000–600 cm^{-1} and a resolution of 2 cm^{-1} . Surface morphology of samples was examined using a scanning electron microscope (SEM; LEO 440i, England). Prior to imaging, samples were sputter coated with gold (Quorum Technologies, Ltd., Q150T, East Sussex, England) in order to get good electrical contact. To determine the amount of TiO_2 adsorption on cotton fabric, burning and spectrophotometric techniques were applied. At the process of burning, the samples were first dried and weighed at 105 °C, then placed into a furnace at 900 °C for 15 min. Finally the remainder ash weight was determined and subtracted from the ash weight of the pristine fabric. In the spectrophotometric measurement, the ash of the burned samples was added into a mixture of nitric and sulfuric acids (1:1.5 molar ratio) and 0.3 mL of H_2O_2 . With a UV–vis spectrophotometer (Cary 300, Agilent, Victoria, Australia), the absorbance value of each solution was measured and compared with the absorbance value of nano- TiO_2 standard solution with a given weight percentage. To determine washing durability of TiO_2 NPs, we washed the samples at 50 °C for 15 min with 2 g/L of a nonionic detergent. Weight percent of TiO_2 NPs after consecutive washing cycles was determined using spectrophotometric measurement. Water drop absorption time was determined according to the AATCC79–2000. The average time for complete water absorption (water droplet dropped from 1 cm above sample surface) was reported. To study the self-cleaning property, we stained the samples with a solution of C.I.BLUE 9 (0.1 g/L) and black tea extract (0.4 mL) and then exposed it to UV light irradiation (UV-A lamp, 400 W, Philips, The Netherlands) for 180 min. The color variations (ΔE) were calculated before and after UV exposure at 30 min intervals.

RESULTS AND DISCUSSION

Esterification with Carboxylic Acids. The structures of three dicarboxylic acids are depicted in Figure 1a. It has been shown that dicarboxylic acids can form an ester bond between carboxylic group of dicarboxylic and hydroxyl group of cellulose polymer chains (Figure 1b). It has also been reported that sodium hypophosphite (SHP) can accelerate ester formation reactions. It reacts with cyclic anhydride intermediate and then with cellulose (Figure 1c). The formation of the cyclic

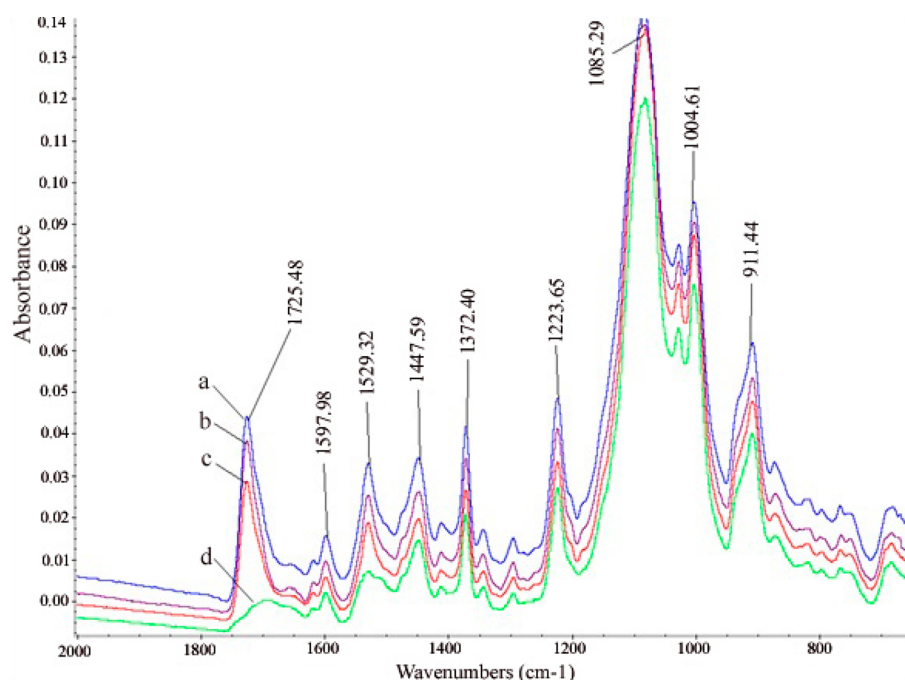


Figure 2. ATR-FTIR spectra of samples prepared from (a) oxalic acid, (b) succinic acid, (c) adipic acid, and (d) pristine fabric.

anhydride form of carboxylic acid is expectable for BTCA or succinic acid, but its formation is not possible for carboxylic with short molecular length such as oxalic acid.

Recorded ATR-FTIR spectra for samples treated with different dicarboxylic acids and the same concentration of TiO_2 NPs are shown in Figure 2. For esters, the absorbance peak of the carbonyl group ($\text{C}=\text{O}$) appears in the range of $1700\text{--}1750\text{ cm}^{-1}$. The absorption band at 1725 cm^{-1} is due to the antisymmetric stretching vibrations of ester carbonyl in carboxyl groups.¹³ This band is observable for all samples treated with carboxylic acids. This indicates that all three dicarboxylic acids have formed ester bonds with cotton fabric. Also, the peak at 1529 cm^{-1} is assigned to COO^- groups (Figure 2a–c).²³ The peak height and area under the curve are proportional to the level of esterification by dicarboxylic acids. Compared with that of other dicarboxylic acids, the intensity of oxalic acid 1725 cm^{-1} peak is stronger, meaning that it has formed more ester bonds with hydroxyl groups of cellulose (Figure 2a).

Surface Morphology. All SEM micrographs of dipped cotton samples in TiO_2 solution showed the settlement of TiO_2 NPs on cotton fibers and as there were no observable difference for all carboxylic pretreated samples, just The SEM micrograph of untreated, pristine and treated with oxalic acid cotton samples are presented in this paper (Figure 3).

Amount of TiO_2 Adsorption. The amounts of adsorbed TiO_2 NPs for both burning and spectrophotometric methods

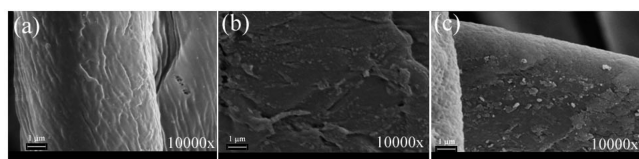


Figure 3. SEM micrographs of (a) untreated, (b) TiO_2 -coated, and (c) oxalic-acid-treated cotton samples.

were in agreement, and they were between 0.9 and less than 2 wt % (Figure 4). The amount of TiO_2 NP adsorption for cotton

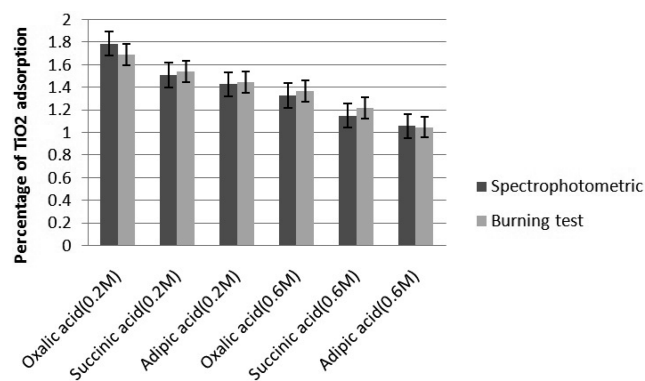


Figure 4. Amount of TiO_2 adsorption by spectrophotometric and burning tests.

treated with longer molecular length acids leads to a decrease in TiO_2 adsorption of about 20% (Figure 3; compared to samples treated with oxalic and adipic acids). It can be attributed to the more acidic potential and greater pKa of oxalic acid (1.27) compared to that of two other dicarboxylic acids (pKa succinic acid = 4.21, pKa adipic acid = 4.41).²⁴ So, the release of H protons is more facilitated, and hence, the trend for adsorption of TiO_2 NPs would be increased. Moreover, increasing the acid concentration to 0.6 M decreases the amount of TiO_2 adsorption. When there are more than two carboxyl groups, internal anhydrides are likely to form inside acid molecule itself; so, in terms of using poly(carboxylic acids), it is possible that not all of the carboxyl groups interact with cellulose hydroxyl groups.¹⁵

Drop Adsorption Time and Washing Durability.

Dicarboxylic-acid-containing samples showed better washing durability than the pristine fabric (Table 1). In spite of carboxylic groups, there is poor linkage between TiO_2 NPs and

Table 1. Washing Durability of Pristine and Treated Samples with Dicarboxylic Acids

treated sample	TiO ₂ % (w/w)					reduction percentage
	before washing	after 5 cycles of washing	after 10 cycles of washing	after 15 cycles of washing	after 20 cycles of washing	
oxalic acid (0.2 M)	1.79 ± 0.12	1.64	1.53	1.41	1.15	35.7 ± 0.17
succinic acid (0.2 M)	1.51 ± 0.08	1.48	1.42	1.37	1.28	15.2 ± 0.07
adipic acid (0.2 M)	1.43 ± 0.02	1.41	1.38	1.34	1.30	9 ± 0.04
oxalic acid (0.6 M)	1.33 ± 0.03	1.24	1.18	1.11	0.91	31.5 ± 0.12
succinic acid (0.6 M)	1.15 ± 0.04	1.11	1.09	1.06	0.96	16.5 ± 0.05
adipic acid (0.6 M)	1.06 ± 0.05	0.99	0.95	0.89	0.83	10.6 ± 0.06
pristine	1.05 ± 0.10	0.89	0.79	0.66	0.46	56.1 ± 0.16

hydroxyl groups of cotton. For all samples, the highest reduction in the amount of TiO₂ occurred after 20 washing cycles. However, for samples treated with adipic acid, the weight of reduction was less than 10%. As mentioned before, the amount of TiO₂NP absorption and the formation of ester bonds are greater for samples treated with oxalic acid. However, due to the lack of valence bonds between oxalic acid and TiO₂NPs and the hydrophilicity of oxalic acid (tendency of the acid to absorb water because of higher acidic dissociation constant and surface free energy), washing durability of cotton samples treated with it decreased significantly (about 35%) after 20 washing cycles. Additionally, the wettability of the textile substrate was increased by the added amount of TiO₂NPs. As a result, during washing, removal of the nanoparticles was being facilitated. For samples treated with dicarboxylic acids containing longer chain length, an increase in hydrocarbon chain length of acid decreases surface free energy and reduces TiO₂NPs removal during washing.

Results of drop absorption time were also in agreement with washing durability (Table 2). As there are large numbers of

Table 2. Drop Absorption Time for Pristine and Treated with Dicarboxylic Acid Samples

treated sample	drop absorption time (s)
oxalic acid (0.2 M)	3 ± 1
succinic acid (0.2 M)	21 ± 3
adipic acid (0.2 M)	16 ± 2
untreated and pristine	0

hydroxyl groups on the cotton and TiO₂ surfaces, untreated and TiO₂-coated samples absorbed water droplets immediately. The time of drop absorption increased for samples treated with carboxylic acids (about 200% compared to that of TiO₂-coated samples without using carboxylic acids). Formation of ester bonds between hydroxyl and carboxyl groups led to block the hydroxyl groups of cellulose and prevented their participation in water absorption. Despite more ester bonds formed between carboxyl groups of oxalic acid and hydroxyl groups of cotton, due to greater amounts of TiO₂NP absorption and higher surface free energy of oxalic acid the time of drop absorption decreased compared to that of samples treated with two other acids.

Self-Cleaning Property. According to Figure 5, treating cotton fabric with carboxylic acids increased self-cleaning property. Samples treated with oxalic acid, which had absorbed greater amounts of TiO₂NPs, showed better self-cleaning property (about 30% more color variation than samples treated with adipic acid after 180 min of UV irradiation). Additionally, compared with that of pristine and untreated samples, color

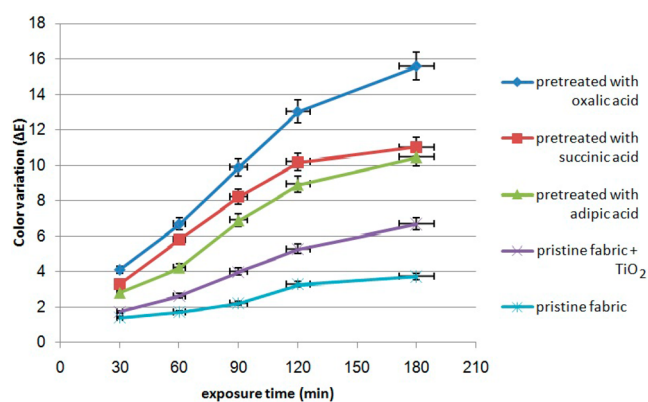


Figure 5. Color variation as a function of exposure time for pristine and cotton samples treated with dicarboxylic acids.

variation for cotton cross-linked with oxalic acid increased significantly, about 58% and 75%, respectively. Samples that had absorbed greater amounts of TiO₂NPs showed better self-cleaning properties as well (Figures 4 and 5).

CONCLUSIONS

The effect of dicarboxylic acid chain length on the self-cleaning property of nano-TiO₂-coated cotton samples was studied. Results showed that formation of cyclic anhydrides would not be necessary for establishing ester bonds between carboxyl groups of dicarboxylic acid and hydroxyl groups of cellulose polymer chains. On the basis of the ATR-FTIR spectra, oxalic acid without the capability of forming cyclic anhydrides showed more esterification of cellulose than two other acids. Moreover, due to a higher acid dissociation constant and more electrostatic reactions between oxalic acid and TiO₂NPs, samples treated with oxalic acid absorbed greater amounts of TiO₂NPs and showed better self-cleaning properties, about 25 and 30% more, respectively, than samples treated with adipic acid. However, due to lack of valence bonds and higher surface free energy of oxalic acid, treated samples exposed to 20 successive washing cycles experienced a 64% decrease in washing durability. Our findings showed that compared with succinic acid, which has been widely used as a cross-linking agent for cotton fibers, using oxalic acid has some advantages such as increasing the amount of TiO₂NP absorption and self-cleaning property.

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Notes

The authors declare no competing financial interest.

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