



# Chitosan as a potential stabilizing agent for titania nanoparticle dispersions for preparation of multifunctional cotton fabric



Nidhi Goyal<sup>a</sup>, Deepali Rastogi<sup>a</sup>, Manjeet Jassal<sup>b,\*</sup>, Ashwini K. Agrawal<sup>b,\*</sup>

<sup>a</sup> Department of Fabric and Apparel Science, Lady Irwin College, University of Delhi, New Delhi 110001, India

<sup>b</sup> SMITA Research Lab, Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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## ABSTRACT

Titania (TiO<sub>2</sub>) nanoparticle dispersions in water were prepared using chitosan (CS) as the stabilizing agent. The dispersion stability was evaluated with respect to storage time, hydrodynamic particle size, and zeta potential. The effect of the molecular weight of CS and presence of non-ionic polymers (poly(vinyl alcohol) and poly(ethylene glycol)) as co-dispersants was investigated. Despite the increase in size of dispersed particles, the long-term storage stability of the dispersions improved with increasing concentration and molecular weight of CS. The TiO<sub>2</sub>/CS dispersions were applied on cotton fabric and characterized. The presence of CS did not seriously affect the photocatalytic self-cleaning activity (SCA) of TiO<sub>2</sub>; with CS, a SCA of 89% was achieved compared with a value of 96% without CS. In addition, the TiO<sub>2</sub>/CS-treated cotton fabrics provided UV protection and significant antimicrobial activity.

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## 1. Introduction

Titania (TiO<sub>2</sub>) nanoparticle (NP)-based self-cleaning finishes have received significant attention because of their efficient activity and non-toxicity (Benedix, Dehn, Quaas, & Orgass, 2000; Mellott, Durucan, Pantano, & Guglielmi, 2006; Mills & Hunte, 1997; Pasqui & Barbucci, 2014; Uddin et al., 2007). However, NPs in dispersed form have a high tendency to agglomerate because of their high surface energy and van der Waals attraction, which adversely affects their application. Agglomerated TiO<sub>2</sub> exhibits comparatively much lower activity as the active surface area decreases. For commercial applications in self-cleaning surfaces on glass, plastics, and textiles, TiO<sub>2</sub> dispersions must be highly stable to enable their transport, storage, and application without loss of activity. In addition, agglomerated NPs are expected to result in poor adhesion to and durability on applied surfaces. Therefore, repulsive forces and/or steric hindrance between the particles are required to counteract these attractive interactions and improve the stability. Several studies have been performed to stabilize NP dispersions in aqueous media. It has been demonstrated that the pH may be altered to create a surface charge on TiO<sub>2</sub> NPs and that polymeric dispersants can be added to keep the NPs separate from each other.

The use of dispersants has been observed to be the most effective approach. (Bing et al., 2007; Veronovski, Andreozzi, Mesa, Smole, & Ribitsch, 2010).

In our previous study (Goyal, Rastogi, Jassal, & Agrawal, 2013), a comparison was made between different types of low-molecular-weight (LMW) dispersants. Cationic dispersants were shown to impart improved stability to a TiO<sub>2</sub> NP dispersion compared with anionic and non-ionic dispersants. A very high positive surface charge of >50 mV was observed on TiO<sub>2</sub> NPs prepared using the cationic dispersant. This high surface charge yielded a NP dispersion with higher stability. Chitosan (CS) is a polysaccharide with primary amine groups that can consequently develop positive charge on the chain in an acidic environment (Nicu, Bobu, & Desbrieres, 2011) and may thus be useful in dispersing and stabilizing TiO<sub>2</sub> NPs in aqueous media.

CS has been used for various textile applications such as antimicrobial finishes, dyeing of cotton, durable press finishes, antistatic finishes, and textile printing (Gupta & Haile, 2007; Houshyar & Amirshahi, 2002; Rippon, 1984). Recently, researchers in the area of NPs have started investigating the possible application of CS as a stabilizer. Dispersions prepared using CS have resulted in improved stability of NPs in water (Castro & Gouvêa, 2003; Ozarkar, Jassal, & Agrawal, 2008; Yang, Ge, Hu, Jiang, & Yang, 2000; Zhua, Yuan, & Liao, 2008). However, no systematic studies have been performed on the effect of CS on the stability of TiO<sub>2</sub> NP dispersions or its self-cleaning activity (SCA) on textiles.

\* Corresponding authors.

E-mail addresses: [manjeet.jassal@smita-iitd.com](mailto:manjeet.jassal@smita-iitd.com) (M. Jassal), [ashwini@smita-iitd.com](mailto:ashwini@smita-iitd.com) (A.K. Agrawal).

**Table 1**  
Preparation of TiO<sub>2</sub>/LMW CS dispersion in the presence of non-ionic polymers.

Dispersion	HMW CS g	TiO <sub>2</sub> NP g	PVA g	PEG g	0.1 M acetic acid solution
TiO <sub>2</sub> /CS	0.1	0.5	–	–	To make 100 ml
TiO <sub>2</sub> /LMW-600 CS/PVA	0.1	0.5	3.15	–	To make 100 ml
TiO <sub>2</sub> /LMW-250 CS/PVA	0.1	0.5	3.15	–	To make 100 ml
TiO <sub>2</sub> /LMW-600 CS/PEG	0.1	0.5	–	8.5	To make 100 ml
TiO <sub>2</sub> /LMW-250 CS/PEG	0.1	0.5	–	8.5	To make 100 ml

This study aims to investigate the use of CS as a stabilizer for TiO<sub>2</sub> NP dispersions and the effect of the molecular weight (M<sub>w</sub>) of CS on the dispersion behavior with respect to long-term storage stability and particle size. The TiO<sub>2</sub>/CS coatings on cotton fabric were also tested for multifunctional applications, i.e., self-cleaning, ultraviolet protection, and antimicrobial properties.

## 2. Experimental

### 2.1. Materials

TiO<sub>2</sub> NPs, namely, P25, were procured from Evonik India (P) Ltd. CS high molecular weight (HMW CS) polymer, M<sub>w</sub> ~12,000; degree of deacetylation ~75% was obtained from India Sea Foods, India. Acetic acid (Merck, India), sodium chloride (Merck, India), sodium nitrite (Merck, India), sodium hydroxide (Rankem, India), poly(vinyl alcohol) (PVA, cold, M<sub>w</sub> ~1,25,000, CDH, India), and poly(ethylene glycol) (PEG, M<sub>w</sub> ~35,000, Merck, Germany) of analytical grade were also used. Direct dye, C.I. Direct Green 26 (Solophenyl Green BLE, Huntsman International) with a light fastness rating of 4 was used as the standard dye for staining. Finally, 100% cotton, plain weave, scoured, and bleached fabric was used.

### 2.2. Methods

#### 2.2.1. Depolymerization of CS

An oxidative degradation approach was used to depolymerize HMW CS. Low molecular weight CSs (LMW-CSs) with M<sub>w</sub>s of 600 and 250 were prepared using different amounts of 0.1 M sodium nitrite (NaNO<sub>2</sub>), as described in the literature (Maoa et al., 2004). First, a HMW CS solution (1% w/v) was prepared by dissolving 1 g CS in 100 ml of 1% acetic acid under vigorous stirring. Then, 2.5 or 5 ml of 0.1 M NaNO<sub>2</sub> solution was gradually added to the CS solution followed by stirring for 3 h. The depolymerized CS solution obtained was neutralized and precipitated by adding a sufficient amount of 1 N aqueous sodium hydroxide solution. The precipitated CS was recovered by centrifugation, washed several times with deionized (DI) water, and freeze-dried (Lyophilizer, Labconco). The products obtained were coded as LMW-600 and LMW-250 as per the volume of NaNO<sub>2</sub> used in the reaction, i.e., 2.5 and 5 ml, respectively.

#### 2.2.2. Determination of intrinsic viscosity and viscosity-average molecular weight

The intrinsic viscosity of CS was determined using a Ubbelohde-type capillary viscometer (Schott) in 0.1 M acetic acid with 0.2 M NaCl in a constant-temperature water bath at 25 °C. The viscosity-average molecular weight (M<sub>v</sub>) of the CS was calculated using the Mark–Houwink equation:

$$[\eta] = K(M_v)^\alpha \quad (1)$$

where  $K = 1.81 \times 10^{-3}$  and  $\alpha = 0.93$  (Roberts & Domszy, 1982; Wang, Bo, Li, & Qin, 1991).

#### 2.2.3. Characterization

##### (a) X-ray diffraction

Powder X-ray diffraction (XRD) of HMW, LMW-600, LMW-250 CS was performed using a PANalytical XRD system (Netherlands). The X-ray source was Cu K $\alpha$  radiation (40 kV, 80 mA), and the samples were scanned at 4° min<sup>-1</sup>.

##### (b) Fourier-transform infrared spectroscopy

Fourier-transform infrared (FTIR) spectra of HMW, LMW-600, LMW-250 CS were recorded using KBr pellets and a PerkinElmer BX II FTIR spectrometer (USA).

#### 2.2.4. Preparation of TiO<sub>2</sub>/CS dispersion

To prepare the TiO<sub>2</sub>/CS dispersion containing 0.5% (w/v) TiO<sub>2</sub> and 0.1% (w/v) CS, the CS solution and TiO<sub>2</sub> NP dispersion were first prepared separately. The CS solution was prepared by dissolving 0.1 g of CS flakes in 50 ml of 0.1 M acetic acid solution with constant magnetic stirring. The TiO<sub>2</sub> NP dispersion was prepared separately by sonicating 0.5 g TiO<sub>2</sub> NP in 50 ml of 0.1 M acetic acid solution in a sonicating bath (Elma, at 100% power) at a frequency of 35 kHz. Thereafter, the TiO<sub>2</sub> NP dispersion was slowly added to the CS solution and magnetically stirred at 1000 rpm for 1 h. The prepared TiO<sub>2</sub>/CS dispersion was then sonicated for 1 h at 35 kHz at 30 °C.

For comparison, a TiO<sub>2</sub> NP dispersion was also prepared without CS in 0.1 M acetic acid solution using the above method.

#### 2.2.5. Preparation of TiO<sub>2</sub>/LMW CS dispersion in the presence of non-ionic polymers

TiO<sub>2</sub>/LMW CS dispersions in the presence of non-ionic polymers were prepared to obtain dispersions of similar viscosity to that obtained with the 0.1% HMW CS. The non-ionic polymers PVA and PEG were added to the TiO<sub>2</sub>/LMW CS dispersions (both LMW-600 and LMW-250). The concentrations of PVA and PEG needed to achieve the same viscosity as that of the 0.1% HMW CS dispersion were 3.15% and 8.5% (w/v), respectively. All the materials, PVA and PEG, LMW-600 and LMW-250, and 0.5% (w/v) TiO<sub>2</sub> NPs were dispersed in 0.1 M acetic acid solution separately using the method discussed above. Then, the TiO<sub>2</sub> NP dispersion was slowly added to the LMW CS solution and mixed by magnetic stirring. Thereafter, the obtained TiO<sub>2</sub>/LMW CS dispersion was added to the PVA or PEG solution and magnetically stirred. The amounts of materials used to prepare the different dispersions are listed in Table 1.

#### 2.2.6. Characterization of TiO<sub>2</sub>/CS dispersion

The particle size distribution and zeta ( $\xi$ ) potential of the dispersions were determined using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). For the  $\xi$  potential measurements, the dispersions were diluted to 0.1% (w/v) of TiO<sub>2</sub>. Raman spectroscopy

**Table 2**  
Particle size of TiO<sub>2</sub> dispersion prepared using CS with varying M<sub>w</sub>.

Sample	Particle size: Z avg (nm)	
	1 h	1 day
TiO <sub>2</sub> /CS-0	187	201
TiO <sub>2</sub> /HMW	663	664
TiO <sub>2</sub> /LMW-600 CS	210	210
TiO <sub>2</sub> /LMW-250 CS	210	209

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