ELSEVIER

Ceramics International 32 (2006) 637–646

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Surface chemical studies on SiC suspension in the presence of chitosan

L. Saravanan [a], S. Subramanian [a,*], A.B. Vishu Kumar [b], R.N. Tharanathan [b]

[a] *Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India*
[b] *Department of Biochemistry and Nutrition, Central Food Technological Research Institute, Mysore 570013, India*

Received 20 December 2004; received in revised form 7 March 2005; accepted 20 April 2005

Abstract

The surface chemical characteristics of SiC suspension were examined in the presence of chitosan, a cationic polymer. The adsorption density of chitosan onto SiC showed a distinct maximum around pH 7, and the isotherms exhibited Langmuirian behaviour. The isoelectric point (i.e.p.) of SiC was located at pH 3 and the presence of chitosan shifted the i.e.p. values towards the alkaline pH region in proportion with the amount of polymer added. Consequent to the addition of chitosan, the zeta potential value of SiC surface was increased to +30 mV in the pH range of 2–5, while it was >-40 mV between pH 9.5 and 11.5. The favourable pH regimes for the stability of SiC dispersions were found to be between pH 2–6 and 9–11, with the optimum concentration of chitosan. The FTIR spectral measurements provided evidence in support of hydrogen bonding forces between chitosan and SiC surface.

Keywords: A. Suspensions; B. Spectroscopy; C. Chemical properties; D. SiC

1. Introduction

Silicon carbide (SiC) is a non-oxide covalent ceramic material that has gained importance in a wide range of industrial applications. The superior mechanical, chemical and thermal properties of SiC, have increased its usage in applications such as abrasives, refractories, sand blast nozzles, mechanical seal valve, friction and wear resistance components, heat engine parts, diesel and gas turbines and high temperature energy conversion systems [1–8]. Apart from these applications, SiC is finding its place increasingly in electronic industries [9]. The quality of the ceramic materials is of great concern when they are used in these types of extreme conditions. There are many novel colloidal ceramic processing methods that have been developed to obtain high quality, defectless products [10,11]. The preparation of stable and homogeneous colloidal slurry is the first important step to get ceramic products with a high degree of quality through these processes. There are two ways to stabilize the slurry; one is through increasing the surface charge by adjusting the pH (electrostatic), and the other is through the addition of polymers (steric). Polyelectrolytes are widely used in ceramic processing to electrosterically stabilize the slurries [12]. Polyacrylic acids and their derivatives are commonly used polyelectrolytes for the stabilization process of both oxide [13–17] and non-oxide [18–20] ceramic slurries.

Poly(ethylene imine), a cationic polyelectrolyte has been used to stabilize SiC suspensions [21]. Chitosan, a cationic bio-polymer, is a biodegradable, non-toxic, copolymer of poly [β(1-4)-2-acetamido-2-deoxy-D-glucopyranose] and poly [β(1-4)-2-amino-2-deoxy-D-glucopyranose], derived from partial deacetylation of chitin [22]. There has been an increased research interest on chitosan properties in the application areas such as pharmaceuticals, biomaterials, cosmetics, food processing and chelation of heavy metals [23]. Recently, it has been tried as a dispersant for tin oxide (SnO_2) ceramic suspensions [24], while many of the earlier research findings were concentrated on the flocculation of particles and cells using chitosan [25,26]. Needless to emphasize, surface chemical studies at the solid/liquid interface have an important role in understanding the nature of the suspension. In the present investigation, with the

---

[*] Corresponding author. Tel.: +91 80 2293 2261; fax: +91 80 2360 0472.
E-mail address: ssmani@metalrg.iisc.ernet.in (S. Subramanian).

0272-8842/$30.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.04.023

above objectives in mind, surface chemical studies have been carried out on SiC suspensions using chitosan. Detailed adsorption, desorption, electrokinetic and dispersion tests have been performed to delineate the mechanisms of interaction between chitosan and SiC. FT-IR spectral studies have been carried out to characterize the adsorbed species.

2. Experimental materials

Silicon carbide (α-SiC) was obtained from Aldrich, USA. The mean particle size (d_{50}) of the sample was determined to be 8.43 μm, using a Malvern Mastersizer S, UK. The BET nitrogen surface area of the sample was found to be 0.26 m^2/g using a Quantasorb Analyzer, USA.

The cationic polysaccharide used in this study was chitosan, which was derived through the following procedure. Shrimp chitin, procured from CFTRI regional center at Mangalore, India was subjected to heterogeneous N-deacylation to produce native chitosan. Then the depolymerization of the native chitosan was carried out by incubating it with pronase for a specified time. Low molecular weight chitosan (LMWC) was one of the fractions obtained from the depolymerization reaction and was used in this study. The molecular weight of the LMWC was deduced as 8.5 KDa, by viscosimetric measurements and the degree of deacetylation was determined to be 14% by IR and solid state ^{13}C NMR. The detailed procedures for synthesis and characterization are reported elsewhere [27]. The chitosan mentioned throughout this paper is the LMWC obtained as described above. The chitosan stock solutions were prepared using 1 M acetic acid solutions. Cibacron brilliant red 3B-A (also named as Reactive Red 4, C.I. 18105) was procured from Aldrich, USA and used for the analysis of chitosan in solution. Potassium nitrate was used as a background electrolyte. Nitric acid and potassium hydroxide were used as pH modifiers. All the reagents were of analytical grade. Deionised, double distilled water of conductivity $<1.5\ \mu\Omega^{-1}$ was used for all the experiments.

3. Experimental methods

3.1. Adsorption studies

For each experiment, 1 g of SiC was taken in a 250 ml Erlenmeyer flask and mixed with 50 ml of 10^{-3} M KNO_3 electrolyte solution. The pH of the prepared suspension was adjusted to a desired value, using either nitric acid or potassium hydroxide. The suspension was then equilibrated in a Remi orbital shaking incubator at 180 rpm for 3 h at 28 °C. Fifty milliliters polymer solution of desired concentration and pH, equivalent to the corresponding suspension pH value, was prepared and mixed with the suspension. The background electrolyte concentration was kept at 10^{-3} M KNO_3. The SiC suspension containing the polymer solution was equilibrated in the orbital shaking incubator for a specified time. It was then centrifuged in a Remi centrifuge at 5000 rpm for 45 min. The supernatant was then analysed for the chitosan polymer concentration following the colorimetric method of Muzzarelli [28]. Cibacron brilliant red 3B-A dye solution was prepared as per the specified procedure [28]. For each test, 5 ml of the polymer sample was vigorously mixed with 3 ml dye solution, using a Remi vortex mixer. The absorbance was measured in a Shimadzu UV-260 spectrophotometer at a wavelength of 575 nm, against a reagent blank. The residual concentration of the polymer was determined from the calibration curve. From the supernatant concentration, the adsorbed amount was arrived at by difference between the initial and final polymer concentrations and expressed in mg/m^2.

3.2. Desorption tests

Desorption of the adsorbed chitosan from SiC, has been assessed at different pH values to evaluate the reversibility of the adsorption process. Each of the residues obtained after centrifuging the suspension of different pH values, containing the adsorbed chitosan, was mixed with 20 ml of distilled water of corresponding pH and reagitated in the orbital shaker for 1 h at 180 rpm and 28 °C. Subsequently, the suspension was centrifuged and the supernatant was analysed for the desorbed chitosan concentration. The percentage desorption was calculated.

3.3. Electrokinetic measurements

Electrokinetic experiments were carried out using a Malvern 3000 model zetasizer, UK. The zeta potential values of dilute SiC suspensions (10 mg in 100 ml) with the background electrolyte concentration kept constant at 10^{-3} M KNO_3, were measured at different pH values. To find out the effect of chitosan on the electrokinetic behaviour of SiC suspension, initially 10 mg of SiC in 50 ml deionised, double distilled water was prepared and the pH was adjusted to a desired value. Then 50 ml of chitosan solution of desired concentration, whose pH was preadjusted to the suspension pH value, was added to the SiC suspension and allowed to equilibrate for 5 h in a Remi orbital shaker at 180 rpm and 28 °C. The zeta potential values were measured as a function of pH and polymer concentration.

3.4. Dispersion studies

For these tests, 100 mg of SiC powder was taken in a 100 ml measuring cylinder and mixed with deionised, double distilled water and the pH of the suspension was adjusted to a desired value. The required amount of polymer solution, with the pH preadjusted to the corresponding value, was mixed with the suspension such that the total suspension volume was 100 ml. Then the measuring cylinder was tumbled 30 times by gentle inversion and allowed to equilibrate for 1 h. The suspension was again tumbled 30 times by gentle inversion and left without disturbance for 1 h. At the end of the period, the top 25 ml of the suspension was siphoned out and made upto 50 ml. The turbidity of the diluted suspension was directly measured in a Systronics Nephelo Turbidity Meter 132, which was calibrated with Formazine standard and expressed in Nephelometric Turbidity Units (NTU).

3.5. FT-IR studies

FT-IR spectra of SiC before and after interaction with chitosan were recorded using a JASCO-410 FT-IR spectrometer, UK, in the wavenumber range 4000–400 cm^{-1}, adopting the KBr pellet technique.

4. Results and discussion

4.1. Adsorption studies

4.1.1. Effect of time

The kinetics of adsorption of chitosan onto SiC is shown in Fig. 1, for two different concentrations, namely 50 and 100 ppm. In both the cases, the adsorption density steeply increases with increase in time upto 5 h and thereafter saturation coverage is attained. The maximum adsorption density for 100 ppm chitosan concentration is about two times that for the 50 ppm concentration. In all subsequent experiments, the equilibration time was maintained at 5 h.

4.1.2. Effect of pH

Fig. 2 portrays the adsorption density of chitosan onto SiC as a function of pH for three different concentrations namely 25, 50 and 100 ppm of chitosan. In all cases, a gradual increase in the adsorption density is observed upto pH 6, followed by a rapid increase upto pH 7–7.2, wherein a maximum is reached. The adsorption density drastically decreases in the pH range from 7.5 to 11.3. It has been reported that the dissociation constant of the glucosamine monomer present in the cationic chitosan polymer is between pH 6.3 and 7.5 [24,29]. Thus, below pH 7.5 chitosan is positively charged due to ionization of the amino group. It is well documented that the surface of SiC has a layer of silica due to natural oxidation [20,30–32], which results in the formation of surface silanol (Si–OH) groups. Electrokinetic studies have indicated that the isoelectric point of SiC is located at pH 3 (Fig. 5). The electrostatic interaction between the positively charged chitosan and negatively charged SiC surface in the pH range 3–7, results in the higher adsorption density of chitosan onto SiC. Additionally, hydrogen bonding between the surface Si–OH groups of SiC and the –OH and –NH$_2$ groups of chitosan enhances the adsorption density, in this pH range. Furthermore, in the areas where the silica surface is hydrophobic, there is a possibility of hydrophobic bonding with the glucopyranose ring of chitosan. It has been reported that the pK_a value of surface Si–OH groups varies from 6.5 at 0% neutralization to about 9.2 at 50% neutralization [33]. The ionization of the Si–OH groups to siloxane (Si–O–Si) in the alkaline pH range reduces the affinity of SiC with chitosan.

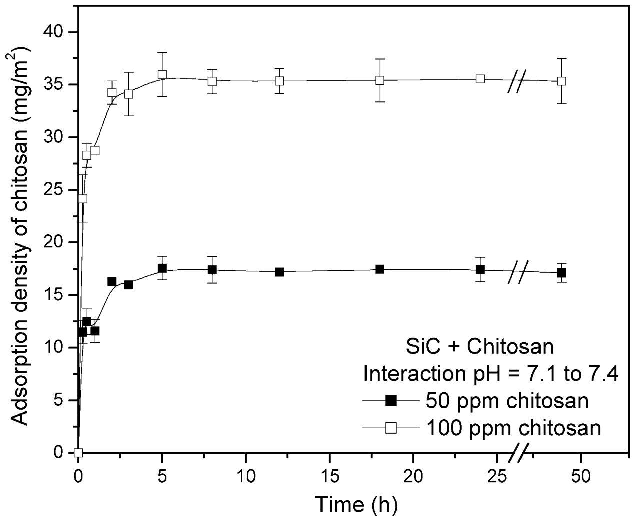


Fig. 1. Adsorption density of chitosan for SiC as a function of time.

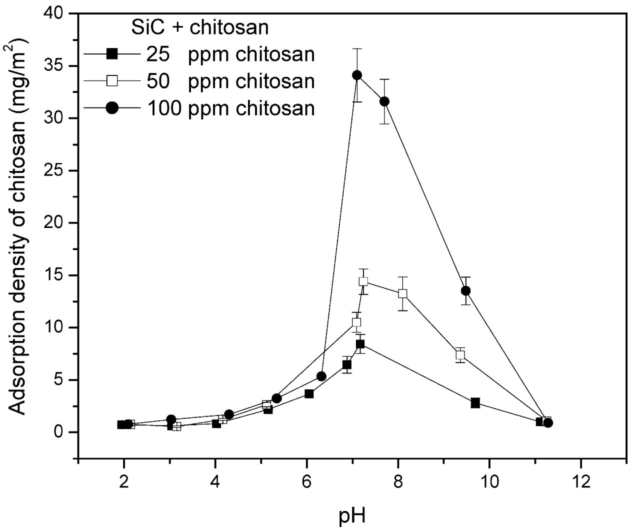


Fig. 2. Adsorption density of chitosan for SiC as a function of pH.

Taking into consideration the cumulative effect of the interaction forces namely, hydrogen bonding, electrostatic attraction and hydrophobic bonding, the observed maximum in the adsorption density of chitosan onto SiC, around pH 7 is expected. The role of electrostatic forces as the major interaction mechanism for the adsorption of other cationic polymers with silica and SiC has been widely implicated [5,21,34,35]. Domard et al. [36] have postulated electrostatic attraction as the dominant interaction mechanism between chitosan and kaolin surfaces. On the other hand, the

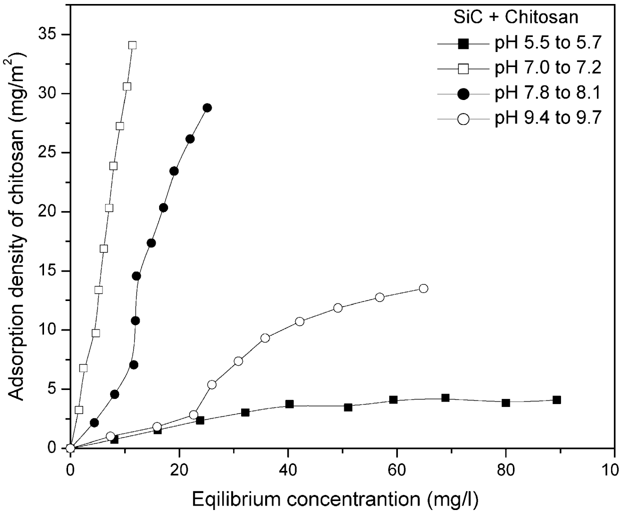


Fig. 3. Adsorption isotherms of chitosan for SiC.

interaction between SiC and poly(ethylene imine) has been explained in terms of hydrogen bonding with free surface Si–OH groups [21].

4.1.3. Effect of polymer concentration

The adsorption isotherms of chitosan onto SiC, at four different pH values are depicted in Fig. 3. The adsorption densities as a function of equilibrium concentration are comparatively higher for the pH values around 7 and 8 and are lower for the pH values around 5.5 and 9.5. These results are in agreement with the pH trends of adsorption observed earlier (Fig. 2). The isotherms at the pH values around 5.5 and 9.5, follow the low affinity type Langmuirian behaviour. The isotherm at pH 5.5 attains a saturation level of adsorption beyond 40 mg/l equilibrium concentration, while that at pH 9.5 tends towards a plateau region of adsorption beyond 50 mg/l concentration. On the other hand, the isotherms obtained for the pH values around 7 and 8, exhibit a steep continuous rise in the adsorption density. The saturation level in adsorption density is not observed for these two isotherms in the concentration range investigated. The adsorption isotherms for chitosan onto kaolin, showed a similar trend [36]. Domard et al. [36], found that there was no adsorption plateau for the isotherm at pH 6, but at pH 4, the adsorption density reached a saturation value beyond a certain concentration of the polymer. More importantly, from the trends of the adsorption isotherms of chitosan onto SiC, it is evident that the amount of unadsorbed free polymer concentration is higher for the isotherms at pH values around 5.5 and 9.5, when compared to those for the pH values around 7 and 8, which presumably results in the enhanced stability of the suspension.

4.2. Desorption studies

The adsorption density of chitosan for 100 ppm initial concentration onto SiC and the corresponding percentage desorption as a function of pH are shown in Fig. 4. The percentage desorption is higher in the pH regions of 2–6 and 9–11 (~90–97%). Interestingly, the percentage desorption attains a minimum value of about 60% at pH ~ 7. It is readily apparent that the reversibility of chitosan adsorption is higher, when the adsorption density is low, whereas in the pH range of higher adsorption density, the amount desorbed is comparatively low. This can be attributed to differences in the adsorption mechanisms operating at different pH values. At around pH 7, the combination of electrostatic attraction, hydrophobic and hydrogen bonding results in enhanced adsorption density, and in turn the observed lower reversibility of adsorption. On the other hand, in pH region of 2–6 and 9–11, wherein there is a reduction in the number of favourable sites for hydrogen bonding, a higher percentage of desorption is facilitated.

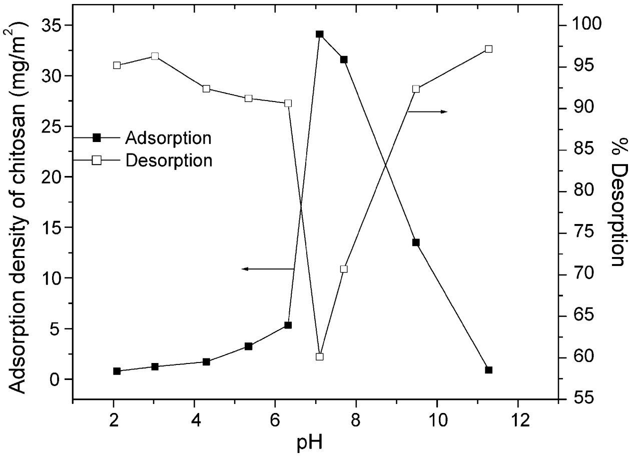


Fig. 4. Percentage desorption of chitosan from SiC as a function of pH.

4.3. Electrokinetic studies

The electrokinetic behaviour of the SiC suspension in the absence and presence of different concentrations of chitosan is shown in Fig. 5. In the absence of the polymer, the negative zeta potential values of the SiC surface increase as the pH is increased from 3 to 10. Below pH 3, the surface becomes positively charged. The isoelectric point (i.e.p.) of SiC suspension is observed to be located at pH 3. This is in good agreement with the values reported in the literature, which vary from pH 2 to 3.5 [5,14,21,37–43]. Addition of different concentrations of cationic chitosan polymer shifts the i.e.p. of the system towards the alkaline pH region, in proportion with the added concentration of chitosan. For example, the i.e.p. is shifted from pH 3 in the absence of chitosan to pH 7.5 after 100 ppm chitosan addition. It is noteworthy that the negative SiC surface becomes increasingly positively charged (or less electronegative) as the chitosan concentration is increased. Even at pH 3, SiC surface acquires a positive charge, consequent to the addition of chitosan. The zeta potential attains a value of about +30 mV, between pH 2 and 4.5, and in the chitosan

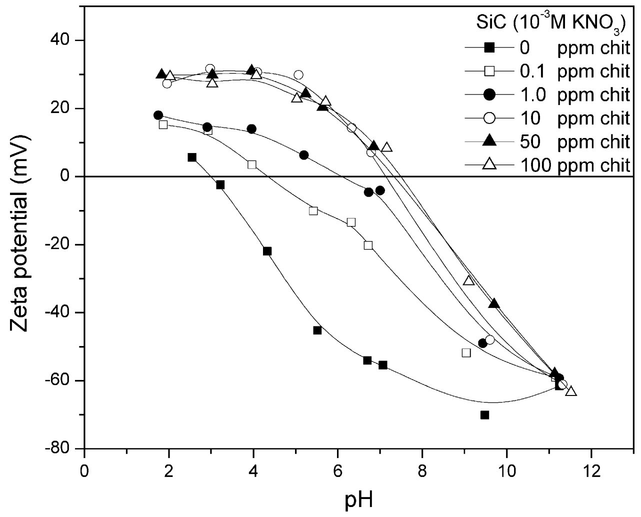


Fig. 5. Zeta potential values of SiC suspension as a function of pH, before and after interaction with chitosan.

concentration range of 10–100 ppm. In an analogous manner, the zeta potential values are highly electronegative (>−40 mV), in the pH range of 9.5–11.5 for the different concentrations of chitosan. Shifts in the i.e.p. of SiC have been similarly reported after addition of cationic polyethylene imine and dodecyl amine [5,21].

4.4. Dispersion studies

Fig. 6 illustrates the dispersion behaviour of SiC suspension in the absence and presence of different concentrations of chitosan as a function of pH. In the absence of chitosan, the turbidity of the suspension increases steeply from 190 NTU at pH 2 to 300 NTU at pH 4. Beyond pH 4, the turbidity gradually increases and attains a value of 350 NTU around pH 11. A comparison of Figs. 5 and 6 reveals that the dispersion behaviour of SiC in the absence of chitosan complements its electrokinetic characteristics. As can be expected, the turbidity of the dispersion is lower at the i.e.p. of SiC namely pH 3, while in the alkaline pH region, the turbidity is significantly higher, as also the zeta potential values. The results obtained consequent to the addition of different concentrations of chitosan to the SiC suspension, are also depicted in Fig. 6. The following observations are noteworthy from this figure:

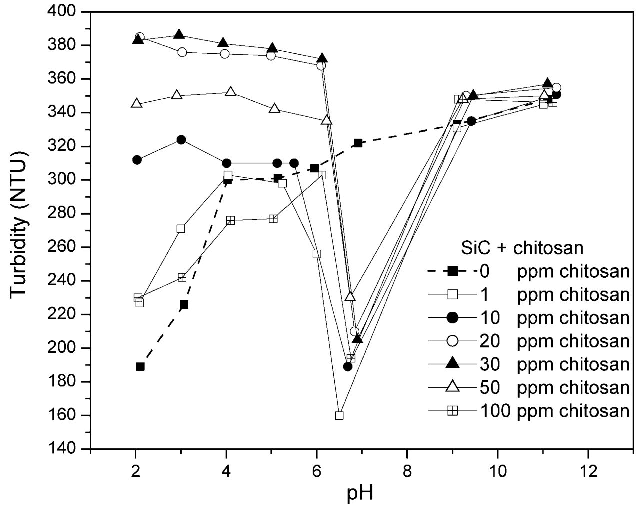


Fig. 6. Turbidity of SiC suspension as a function of pH, before and after interaction with chitosan.

(1) In the pH range of 2–6, a steady increase in the turbidity values is observed, when the chitosan concentration is increased from 1 to 30 ppm. This is indicative of enhanced stability of SiC dispersion in this pH range. It is pertinent to recall that the zeta potentials are about +30 mV in this pH range in the presence of different concentrations of chitosan, corroborating the higher turbidity values (Fig. 5). Domard et al. [36] also observed stabilization of kaolin suspension at pH 4 to be due to an increase in the zeta potential value with the addition of chitosan. Further, it may be recalled that less than pH 5.5, the adsorption density of chitosan onto SiC was relatively very low (Fig. 3). Thus the amount of free polymer in the bulk solution is comparatively higher. The free chitosan present in the bulk solution would be ionized at this pH region. Plausibly, this also can be attributed to the enhancement of suspension stability through "depletion stabilization" in this pH region. It can be expected that the depletion stabilization effect would get enhanced, when the free polymer present in the bulk solution is completely ionized, due to the increased inter-polymer repulsion. The theory of depletion effects on the suspension stability has been well explained [44–46]. Sato and Kohnosu [47], have found that the increase in the amount of unadsorbed free PVP, increased the titanium dioxide suspension stability. In another study, the enhanced suspension stability of Si_3N_4, in the presence of completely ionized, unadsorbed, polyacrylic acid (PAA), through depletion stabilization has been reported [19].

(2) A decrease in the turbidity values is observed in the pH range of 2–6, when the chitosan concentration is increased from 30 to 50 ppm and 100 ppm. These findings attest to the fact that the addition of excess concentration of the polymer beyond the optimum, results in the flocculation of the suspension leading to reduced turbidity values.

(3) A characteristic minimum in the turbidity values is apparent around pH 6.5–7 in the presence of different concentrations of chitosan. It may be recalled that the adsorption density of chitosan onto SiC was found to exhibit a maximum around pH 7 (Fig. 2), when the chitosan concentration was varied from 25 to 100 ppm. Additionally, shifts in the i.e.p. of the SiC-chitosan system to about pH 7–7.5 were observed to take place in the presence of 10–100 ppm chitosan concentration,

compared to its original i.e.p. of pH 3 (Fig. 3). These results indicate that at pH 7, the maximum adsorption of chitosan results in the flocculation of the suspension. Domard et al. [36] also found that the maximum flocculation of kaolin occurred at pH 6, where the maximum adsorption of chitosan was observed.

(4) In the pH range of 9–11, the turbidity of the suspension is higher, which is in agreement with the enhanced negative zeta potential values of the SiC suspension (Fig. 5). Thus, the favourable pH regimes for the stability of the SiC dispersion are between 2–6 and 9.5–11.5, with the optimum addition of chitosan.

4.5. FT-IR studies

The FT-IR spectra of SiC, chitosan and SiC interacted with chitosan are portrayed in Fig. 7(a–c). The spectral assignments have been made based on reported data [9,48–51].

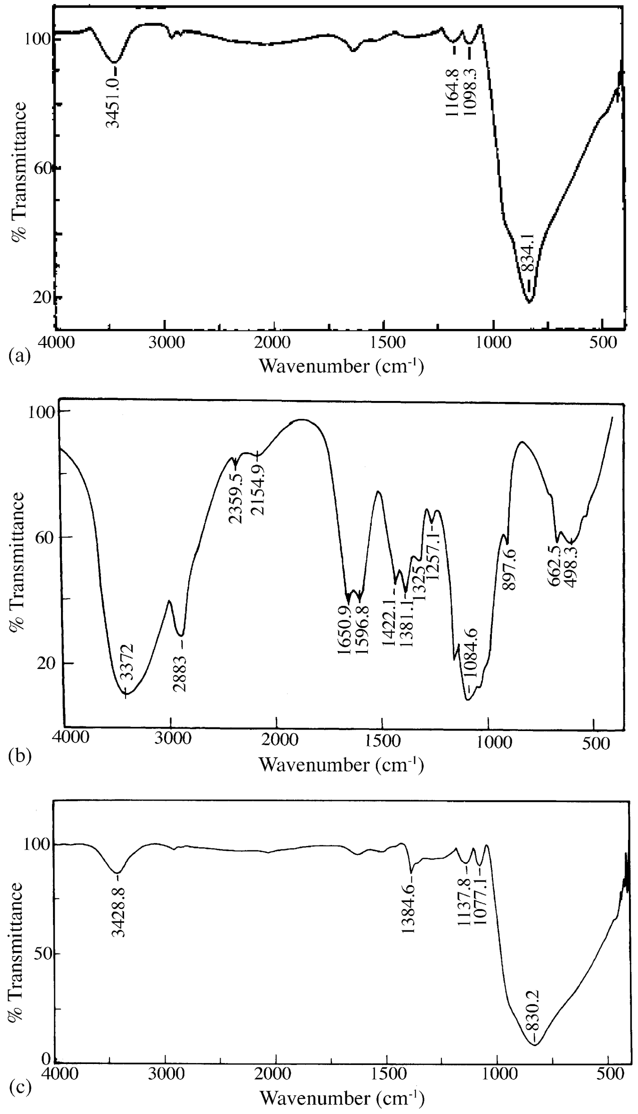


Fig. 7. FTIR spectrum of SiC (a) surface; (b) chitosan; and (c) surface interacted with chitosan.

4.5.1. Silicon carbide

The FT-IR spectrum of SiC is portrayed in Fig. 7(a). The broad band centered at 3451 cm^{-1} can be attributed to the surface silanol groups from the SiO_2 layer present on the SiC surface. The peak that appears at 1165 cm^{-1} is due to the stretching vibrations of Si–O–C–O and the next band at 1098 cm^{-1} can be attributed to the stretching vibrations of Si–O–C and Si–O–Si, present on the surface of SiC. The intense peak at 834 cm^{-1} arises from the Si–C stretching vibrations of the SiC matrix.

4.5.2. Chitosan

The FT-IR spectrum of the chitosan polymer is presented in Fig. 7(b). The presence of the intense peak at 3372 cm^{-1} is due to the stretching vibrations of hydroxyl groups present in the polymer. The band that appears at 2883 cm^{-1}, is attributable to the $-CH_3$ assymmetric deformation vibrations. The band at 1651 and 1597 cm^{-1} are assignable to N–H deformation vibrations of amide groups. The bands at 1420 and 1381 cm^{-1} can be attributed to the CH_2 bending and C–N stretching vibrations, respectively. The small peak at 1325 cm^{-1} corresponds to the GlcNAc residues [52]. The intense broad band centered at 1085 cm^{-1} is assignable to primary alcoholic group ($-CH_2OH$) vibrations.

4.5.3. SiC–chitosan

Fig. 7(c) illustrates the FT-IR spectrum of SiC after interaction with chitosan. The broad band centered at 3451 cm^{-1} corresponding to the surface Si–OH groups, present in SiC is shifted to a lower wave number namely 3429 cm^{-1} after interaction with chitosan due to hydrogen bonding between the Si–OH groups of SiC and the hydroxyl groups of chitosan. The band at 1381 cm^{-1} corresponding to C–N stretching vibrations of chitosan is slightly shifted to 1385 cm^{-1} after interaction with SiC. The small peak that appeared at 1165 cm^{-1}, assigned to the Si–O–C–O stretching vibrations of SiC, after the interaction with chitosan, has shifted to 1138 cm^{-1}. Similarly, the next small band at 1098 cm^{-1}, corresponding to the Si–O–C and Si–O–Si stretching vibrations of SiC surface, has shifted to 1077 cm^{-1}, after interaction with chitosan. These two shifts can be attributed to the possibility of hydrogen bonding between the oxygen present on the surface of SiC and the hydrogen of chitosan. The intense band that appeared at 834 cm^{-1} corresponding to the Si–C stretching vibrations of SiC matrix, after interaction with chitosan, appears at 830 cm^{-1}.

4.6. Interaction mechanisms

Before discussing the interaction mechanisms, it becomes pertinent to highlight the surface characteristics of SiC as well as the structural aspects of chitosan.

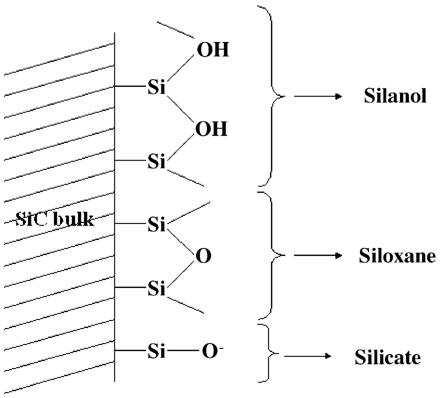


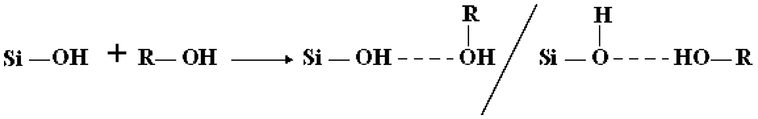
Fig. 8. Schematic diagram of SiC surface functional groups.

The surface of SiC has a mixture of silica and free unreacted carbon [31]. Hence, the surface chemistry of SiC can be considered as akin to the surface chemistry of silica. Among mineral oxides, the surface chemistry of silica has been extensively studied [33]. Silica forms silanol groups on the surface when it interacts with moisture or with water in suspensions. Crimp et al. [53] have explained that the silanol groups are the major functional groups available on the surface of SiC. The hydroxyl moieties of the silanol groups can be considered as both proton donating and proton accepting centers [54]. The density of silanol groups of SiC at an aqueous interface varies with respect to the pH of the suspension. Silanol density decreases as the pH increases [55] and it forms siloxane and silicate groups on the surface. The surface active groups present on the surface of SiC (silica layer), at different pH values are schematically portrayed in Fig. 8.

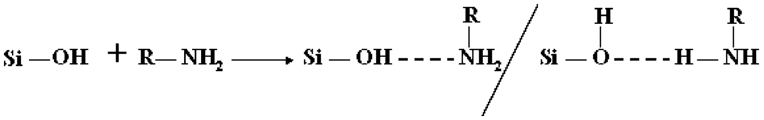
Hydroxyl and amine groups are the two active functional groups present in the repeating unit of the chitosan polymeric chain. Fig. 9 shows the structure of chitosan. Both the hydroxyl and amine functional groups of chitosan can act as proton donating and accepting centers. In general the hydroxyl functional group can donate proton and act as an acidic center as well as can accept proton through oxygen and act as a basic center [56]. Similarly, the amine functional group can donate proton and act as an acidic center and N can act as a basic center due to the presence of free electron pair [57].

The interaction mechanisms between chitosan and SiC in suspension can be explained based on their acid–base properties. Hydrogen bonding is considered to be the special case of acid-base interaction mechanisms, when protons are involved in the interaction between the surface and the polymer molecule [56]. Based on the surface chemical characteristics of SiC and the structural functional groups of chitosan, the interaction between them can be considered to be predominantly governed by hydrogen bonding forces. The possible schemes of interaction by hydrogen bonding have been illustrated in Eqs. (1)–(4), where R–NH_2 represents the primary amine functional group of chitosan, while R–OH denotes the hydroxyl functional group of chitosan. All possible combinations of proton accepting and donating abilities of both SiC and chitosan are considered for the representation of the hydrogen bonding interactions. Apart from the hydrogen bonding forces, the electrostatic interaction between the positively charged chitosan (ionized) and the negatively charged SiC can also take place, in the appropriate pH ranges of the suspension.

Representation of hydrogen bonding between silanol of SiC and hydroxyl/amine groups of chitosan is given in Eq. (1) and (2):



$$\mathrm{Si{-}OH} + \mathrm{R{-}OH} \longrightarrow \mathrm{Si{-}OH}{-}{-}{-}{-}\overset{\mathrm{R}}{\overset{|}{\mathrm{OH}}} \;\Big/\; \mathrm{Si{-}}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}{-}{-}{-}{-}\mathrm{HO{-}R} \quad (1)$$



$$\mathrm{Si{-}OH} + \mathrm{R{-}NH_2} \longrightarrow \mathrm{Si{-}OH}{-}{-}{-}{-}\overset{\mathrm{R}}{\overset{|}{\mathrm{NH_2}}} \;\Big/\; \mathrm{Si{-}}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}{-}{-}{-}{-}\mathrm{H{-}}\overset{\mathrm{R}}{\overset{|}{\mathrm{NH}}} \quad (2)$$

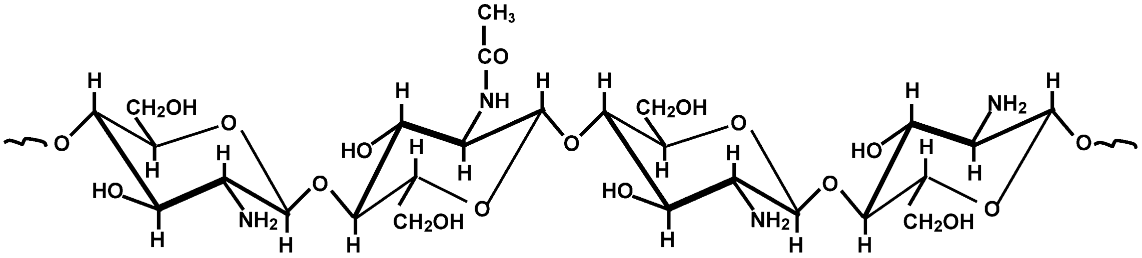
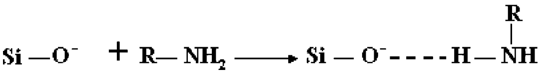


Fig. 9. Structure of chitosan polymer.

Representation of hydrogen bonding between silicates of SiC and hydroxyl/amine groups of chitosan is given in Eq. (3) and (4):

$$\mathrm{Si{-}O^- + R{-}OH \rightarrow Si{-}O^-{-}{-}{-}{-}HO{-}R} \qquad (3)$$



$$\mathrm{Si{-}O^- + R{-}NH_2 \longrightarrow Si{-}O^-{-}{-}{-}{-}H{-}\overset{\displaystyle R \atop |}{N}H} \qquad (4)$$

The different types and the densities of the hydrogen bonded and isolated silanol groups on the surface of silica have been studied in detail using FTIR–ATR spectroscopy [58]. A higher surface silanol density at the silica layer/water interface results in greater interaction between the hydroxyl groups of same surface. As mentioned earlier, since the number of hydroxyl groups on the surface of silica decreases as the pH increases, more of hydrogen bonded silanol groups in the acidic region and more of isolated silanol groups in the neutral pH region can be expected. The isolated silanol groups are more favourable for the hydrogen bonding interaction with the molecules in solution rather than the hydrogen bonded silanol groups. Further increase in pH leads to the formation of $\mathrm{SiO^-}$ groups from isolated silanol, in the alkaline region. An other important factor to be kept in mind is that the surface of SiC, becomes more negatively charged, which has all possibilities to interact electrostatically with the positively charged molecules in neutral and weakly alkaline pH region. With respect to chitosan, the polymer is in the associated form beyond pH 7, where the inter- and intra-molecular attraction is more favourable through hydrogen bonding between the amine and hydroxyl functional groups of chitosan. As a result, the functional groups of the polymer would not be available for interaction with the SiC surfaces. On the other hand at and above the $\mathrm{p}K_\mathrm{a}$ value, namely $\mathrm{pH} \geq 7$, the ionization of the amine functional groups of chitosan lead to the increased repulsion between the polymer molecules, which in turn favours the enhanced availability of polymer functional groups to interact with the solid surfaces. Moreover, the formation of $-\mathrm{NH_3}^+$ at and below $\mathrm{pH} \sim 7$, increases the positive charge of chitosan, which can electrostatically associate with negatively charged SiC surfaces.

On consideration of all the above factors, it is evident that in the neutral pH region ($\mathrm{pH} \sim 7$), enhanced interaction of SiC and chitosan polymer, through the cumulative effect of hydrogen bonding and electrostatic interaction takes place (see Section 4.1.2), which corresponds to the characteristic maximum adsorption region observed in our experimental results (Fig. 2).

5. Conclusions

The following conclusions can be drawn, based on the investigations carried out:

(1) The adsorption density shows a gradual increase from pH 2 to 6 and then rapidly increases exhibiting a characteristic maximum at pH 7–7.5, followed by a steep decrease upto pH 11.5.

(2) The adsorption isotherms at pH 5.5 and 9.5 attain saturation values beyond 40 and 50 mg/l of chitosan equilibrium concentrations, respectively. On the other hand, saturation is not observed for the isotherms corresponding to the pH values of around 7 and 8, which show a continuous increase in the adsorption density.

(3) A higher percentage of desorption is observed in the pH range of 2–6 and 9–11 (90–97%), whereas the desorption is only 60% around pH 7.

(4) The isoelectric point of SiC is observed to be located at pH 3. The addition of chitosan shifts the i.e.p. values of SiC surface towards the alkaline region, in proportion with the concentration of the polymer added. In the pH range of 2–5, the zeta potential values become positive ($\sim$+30 mV) consequent to the addition of the cationic chitosan, while the zeta potentials are >-40 mV in the pH range of 9.5–11.5.

(5) The favourable pH regimes for the stability of SiC dispersions are found to be between pH 2–6 and 9–11, with the optimum concentration of chitosan.

(6) FTIR spectral data provide evidence in support of the hydrogen bonding forces of interaction between chitosan and SiC.

References

[1] K. Niihara, New concepts of structural ceramics-ceramic nanocomposites, J. Ceram. Soc. Jpn. 99 (10) (1991) 974.

[2] T. Sakka, D.D. Bidinger, I.A. Aksay, Processing of silicon carbide–mullite–alumina nanocomposites, J. Am. Ceram. Soc. 78 (2) (1995) 479.

[3] R.N. Katz, Opportunities and prospects for the application of structural ceramic, in: J.B. Wachtman, Jr. (Ed.), Structural ceramics, Treatise on Materials Science and Technology, 29, Academic Press Inc., New York, 1989, pp. 1–26.

[4] K. Komeya, M. Matsui, High temperature engineering caramics, in: M.V. Swain (Ed.), Materials Science and Technology. A Comprehensive Treatment, Structure and Properties of ceramics, 11, VCH Publishers Inc., New York, NY, USA, 1994, pp. 517–565.

[5] J. Iskra, Flotation properties of silicon carbide. I. Flotation of silicon carbide with anionic and cationic collector, Ceram. Int. 23 (1997) 337–342.

[6] W. Boecker, H. Kruener, Silicon carbide and silicon nitride ceramics for high performance structural applications, in: S. Somiya (Ed.), Transactions of the Materials Research Society of Japan, vol. 19B, Development Status and Potential, Advanced Materials ’93, VI/Frontiers in Materials Science and Engineering, Elsevier Science B.V., 1994, pp. 865–872.

[7] I. Moon, G. Cho, Transperant SiC thin films by PEG-SDS-assisted self assembly of SiC nanoparticles, Mat. Sci. Eng. C 24 (2004) 301–305.

[8] S.Y. Lee, C.T. Fu, The effect of rheological behaviour of tape casting on the green sheet and sintered silicon carbide, Ceram. Int. 30 (2004) 151–156.

[9] S.P. Lau, J.M. Marshall, T.E. Dyer, Structural and electrical transport properties of excimer (ArF)-laser-crystallized silicon carbide, Phil. Mag. B 72 (3) (1995) 323–333.

[10] W.M. Sigmund, N.S. Bell, L. Bergstrom, Novel powder-processing methods for advanced ceramics, J. Am. Ceram. Soc. 83 (7) (2000) 1557–1574.

[11] J.A. Lewis, Colloidal processing of ceramics, J. Am. Ceram. Soc. 83 (10) (2000) 2341–2359.

[12] J.S. Reed, Introduction to the Principles of Ceramic Processing, Wiley, New York, 1988.

[13] J. Cesarano III, I.A. Aksay, Processing of highly concentrated aqueous α-alumina suspensions stabilized with polyelectrolytes, J. Am. Ceram. Soc. 71 (12) (1988) 1062–1067.

[14] S. Baklouti, C. Pagnoux, T. Chartier, J.F. Baumard, Processing of aqueous α-Al_2O_3, α-SiO_2 and α-SiC suspensions with polyelectrolytes, J. Eur. Ceram. Soc. 17 (1997) 1387–1392.

[15] J. Davies, J.G.P. Binner, The role of ammonium polyacrylate in dispersing concentrated alumina suspensions, J. Eur. Ceram. Soc. 20 (2000) 1539–1553.

[16] F. Shojai, A.B.A. Pettersson, T. Mantyla, J.B. Rosenholm, Electrostatic and electrosteric stabilization of aqueous slips of 3Y-ZrO_2 powder, J. Eur. Ceram. Soc. 20 (2000) 277–283.

[17] M.C.B. Lopez, B. Rand, F.L. Riley, Polymeric stabilisation of aqueous suspensions of barium titanate. Part I: Effect of pH, J. Eur. Ceram. Soc. 20 (2000) 1579–1586.

[18] C. Shih, B. Lung, M. Hon, Colloidal processing of titanium nitride with poly(methacrylic acid) polyelectrolyte, Mater. Chem. Phys. 60 (1999) 150–157.

[19] V.A. Hackley, Colloidal processing of silicon nitride with poly(acrylic acid). I. Adsorption and electrostatic interactions, J. Am. Ceram. Soc. 80 (9) (1997) 2315–2325.

[20] R. Zhou, Y. Jiang, Y. Liang, F. Zheng, Y. Chen, Dispersion behaviour of laser-synthesized nanometric SiC powders in aqueous medium with ammonium polyacrylate, Ceram. Int. 28 (2002) 847–853.

[21] J. Sun, L. Gao, Dispersing SiC powder and improving its rheological behaviour, J. Eur. Ceram. Soc. 21 (2001) 2447–2451.

[22] K.M. Varum, M.W. Anthonsen, H. Grasdalen, O. Smidsrod, Determination of the degree of N-acetylation and the distribution of N-acetyl groups in partially N-deacetylated chitins (chitosan) by high-field n.m.r. spectroscopy, Carb. Res. 211 (1991) 17–23.

[23] O. Smidsrød, M.H. Ottøy, M.W. Anthonsen, K.M. Vårum, Solution properties of chitosan, in: A. Domard, G.A.F. Roberts, K.M. Vårum (Eds.), Advances in Chitin Science 7th ICCC, 2, 1998, p. 402.

[24] R.H.R. Castro, D. Gouvea, The influence of the chitosan adsorption on the stability of SnO_2 suspensions, J. Eur. Ceram. Soc. 23 (6) (2003) 897–903.

[25] M. Ashmore, J. Hearn, Flocculation of model latex particles by chitosans of varying degrees of acetylation, Langmuir 16 (2000) 4906–4911.

[26] S.P. Strand, K.M. Varum, K. Ostgaard, Interactions between chitosans and bacterial suspensions: adsorption and flocculation, Colloids Surf. B. 27 (2003) 71–81.

[27] A.B.V. Kumar, L.R. Gowda, R.N. Tharanathan, Non-specific depolymerization by pronase and characterization of the restultant products, Eur. J. Biochem. 271 (4) (2004) 713–723.

[28] R.A.A. Muzzarelli, Colorimetric determination of chitosan, Anal. Biochem. 260 (1998) 255–257.

[29] P.M. Claesson, B.W. Ninham, pH-dependent interactions between adsorbed chitosan layers, Langmuir 8 (5) (1992) 1406–1412.

[30] K. Heinz, U. Starke, J. Bernhardt, J. Schardt, Surface structure of hexagonal SiC surfaces: key to crystal growth and interface formation, Appl. Surf. Sci. 162–163 (2000) 9–18.

[31] M.N. Rahaman, L.C. De Jonghe, Angle-resolved XPS analysis of oxidized polycrystalline SiC surfaces, Ceram. Bull. 66 (5) (1987) 782–785.

[32] A. Tsuge, Y. Uwamino, T. Ishizuka, Determination of silicon dioxide in silicon carbide by diffuse reflectance infrared fourier transform spectrometry, Appl. Spect. 40 (3) (1986) 310–313.

[33] R.K. Iler, The Chemistry of Silica: Solubility, Polymerisation, Colloid and Surface Properties and Biochemistry, John Wiley and Sons Inc., New York, 1979.

[34] A. Dietrich, A. Neubrand, Effects of particle size and molecular weight of polyethyleneimine on properties of nanoparticulate silicon dispersions, J. Am. Ceram. Soc. 84 (4) (2001) 806–812.

[35] G.M. Lindquist, R.A. Stratton, The role of polyelectrolyte charge density and molecular weight on the adsorption and flocculation of colloidal silica with polyethyleneimine, J. Colloid Interface Sci. 55 (1) (1976) 45–59.

[36] A. Domard, M. Rinaudo, C. Terrassin, Adsorption of chitosan and a quaternized derivative on kaolin, J. Appl. Pol. Sci. 38 (1989) 1799–1806.

[37] S. Wang, W.J. Wei, Electrokinetic properties of nanosized SiC particles in highly concentrated electrolyte solutions, J. Am. Ceram. Soc. 84 (7) (2001) 1411–1414.

[38] Y. Hirata, S. Tabata, J. Ideue, Interactions in the silicon carbide-polyacrylic acid-yittrium ion system, J. Am. Ceram. Soc. 86 (1) (2003) 5–11.

[39] E.M.M. Ewais, Y.M.Z. Ahmed, Consolidation of silicon carbide in aqueous medium based on gelation of agarose, Br. Ceram. Trans. 101 (6) (2002) 255–258.

[40] R.R. Rao, H.N. Roopa, T.S. Kannan, Effect of pH on the dispersability of silicon carbide powders in aqueous media, Ceram. Int. 25 (1999) 223–230.

[41] P. Tartaj, M. Reece, J.S. Moya, Electrokinetic behaviour and stability of silicon carbide nanoparticulate dispersions, J. Am. Ceram. Soc. 81 (2) (1998) 389–394.

[42] Q. Huang, M. Gu, K. Sun, Y. Jin, Effect of pretreatment on rheological properties of silicon carbide aqueous suspension, Ceram. Int. 28 (2002) 747–754.

[43] R.J. Pugh, L. Bergstrom, The uptake of Mg(II) on ultrafine α-silicon carbide and α-alumina, J. Colloid Interface Sci. 124 (2) (1988) 570–580.

[44] R.I. Feigen, D.H. Napper, Stabilization of colloids by free polymer, J. Colloid Interface Sci. 74 (1980) 567–571.

[45] R.I. Feigen, D.H. Napper, Depletion stabilization and depletion flocculation, J. Colloid Interface Sci. 75 (1980) 525–541.

[46] J.M.H.M. Scheutjens, G.J. Fleer, Effect of polymer adsorption and depletion on the interaction between two parallel surfaces, Adv. Colloid Interface Sci. 16 (1982) 361–380.

[47] T. Sato, S. Kohnosu, Effect of polyvinylpyrrolidone on the physical properties of titanium dioxide suspensions, Colloids Surf. A 88 (1994) 197–205.

[48] G. Ramis, P. Quintard, M. Cauchetier, G. Busca, V. Lorenzelli, Surface chemistry and structure of ultrafine silicon carbide: an FT-IR study, J. Am. Ceram. Soc. 72 (9) (1989) 1692–1697.

[49] T. Sannan, K. Kurita, K. Ogura, Y. Iwakura, Studies on chitin: 7. IR spectroscopic determination of degree of deacetylation, Polymer 19 (1978) 458–459.

[50] P. Park, J. Je, S. Kim, Free radical scavenging activities of differently deacetylated chitosans using an ESR spectrometer, Carb. Polym. 55 (2004) 17–22.

[51] R.A. Nyquist, C.L. Putzig, A.M. Lengers, Hand Book of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts (4-volume set), Academic Press, London, UK, 1997.

[52] J. Brugnerotto, J. Lizardi, F.M. Goycoolea, M.W. Argiielles, J. Desbrieres, M. Rinaudo, An infrared investigation relation with chitin and chitosan characterization, Polymer 42 (2001) 3569–3580.

[53] M.J. Crimp, R.E. Johnson Jr., J.W. Halloan, D.L. Feke, Colloidal behavior of silicon carbide and silicon nitride, in: L.L. Hench, D.R. Ulrich (Eds.), Science of Ceramic Chemical Processing, Wiley, New York, 1986, pp. 539–549.

[54] E. Garrone, P. Ugliengo, Two-fold adsorption of a molecule at the same site: the case of the isolated hydroxyl at the silica surface, Langmuir 7 (1991) 1409–1412.

[55] S.A. Carroll, R.S. Maxwell, W. Bourcier, S. Martin, S. Hulsey, Evaluation of silica-water surface chemistry using NMR spectroscopy, Geochim. Cosmochim. Acta 66 (6) (2002) 913–926.

[56] P. Schuster, G. Zundel, C. Sandorfy, The Hydrogen Bond, Recent developments in theory and experiments, Dynamics, Thermodynamics and Special Systems, III, North-Holland Publishing Company, Amsterdam, 1976.

[57] E. Taboda, G. Cabrera, G. Cardenas, Retention capacity of chitosan for copper and mercury ions, J. Chil. Chem. Soc. 48 (1) (2003) 7–12.

[58] V. Dugas, Y. Chevalier, Surface hydroxylation and silane grafting on fumed and thermal silica, J. Colloid Interface Sci. 264 (2003) 354–361.