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Surface Chemical Studies on Silicon Carbide Suspensions in the Presence of Poly (Ethylene Glycol) and Chitosan

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Abstract: The changes in the surface chemical properties of SiC suspensions consequent to the addition of polyethylene glycol (PEG) and chitosan, both individually and in the presence of each other were studied. The adsorption densities of PEG and chitosan for SiCwere found to be higher at pH 2-3 and 7-7.5 respectively. The adsorption behaviour in the combined presence of PEG and chitosan was akin to those observed for the individual systems. The isoelectric point (i.e.p.) of SiC was found to be located at pH 3. The addition of chitosan shifted the i.e.p. towards more alkaline pH values, in proportion with the concentration of chitosan added, with a concomitant change in the zeta potentials to less electronegative or more electropositive values. On the contrary, only a marginal change in the electrokineticbehaviour of SiC suspension was found after PEG addition. The favourable pH regimes were established to be 2-6 and 9-11, for the enhanced stability of SiC suspension with the optimum dosage of chitosan. The electrokinetic and dispersion characteristics of the SiC-chitosan system were only slightly altered by the addition of PEG. FTIR spectral investigations provided evidence in support of the proposed hydrogen bonding forces of interaction between SiC and PEG or chitosan.

Keywords: Silicon Carbide, Chitosan, Poly (Ethylene Glycol), Adsorption, Electrokinetics, Dispersion

1. Introduction

Colloidal processing techniques have gained attention for the manufacture of complex shaped, high quality ceramic products, by facilitating the proper control of the surface forces, which governs the stability of the suspension [1-3]. Polymeric reagents of diverse chemical structures and charge characteristics have been extensively used as dispersants, binders, plasticizers, lubricants or defoaming agents in ceramic formulations, in order to produce defect-free products with a high degree of reliability [4-6]. Polyacrylic acid and its derivatives, which are anionic in nature, have found wide applications in the processing of several oxide and non-oxide ceramic suspensions [7-11]. Polyethylene glycol (PEG) is a common, non-ionic polymeric additive used as a binder or plasticizer [12, 13]. There are limited reports on the utility of chitosan, a positively charged, non-toxic, biodegradable polymer as a dispersant [14]. The favourable thermal, mechanical and chemical properties of silicon carbide (SiC) have facilitated its use in certain critical components in a cost effective and reliable manner [15-20].

In colloidal ceramic processing, it often becomes necessary to understand the surface chemical characteristics of particulate suspensions in the simultaneous presence of more than one reagent [21-26]. Motivated by this, the present investigation has been directed to the study of the competitive adsorption of polyethylene glycol, a typical binder and chitosan, a cationic polymeric dispersant onto silicon carbide. Detailed adsorption, electrokinetic and turbidity tests have been carried out to arrive at the optimum conditions for stability. The mechanisms of interaction of the binder and dispersant with SiC have been delineated.

2. Experimental Materials

Silicon carbide (α-SiC) has been procured from Aldrich, USA. The mean average particle size of the sample was found to be 8.43 µm, using a Malvern Mastersizer S, UK. The BET nitrogen absorption surface area was determined to be 0.26 m^2/g, using a Quantasorb Analyzer supplied by Quantachrome Instruments, USA.

Poly (ethylene glycol) (PEG) of molecular weight $\approx$ 10 000, was obtained from Polysciences Incorporated, USA.

Chitosan**,** acationic biopolymer was derived through the following procedure. Shrimp chitin, procured from CFTRI regional centre at Mangalore, India was subjected to heterogeneous N-deacetylation to produce native chitosan. Then the depolymerization of the native chitosan was carried out by incubating it with pronase for a particular 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 calculated as 8.5 KDa, by viscosimetric measurements. The viscosity of LMWC dissolved in sodium acetate buffer (0.5 M acetic acid + 0.2 M sodium acetate, pH 4.5) was measured using an Ostwald viscometer [27]. The average molecular mass was deduced using the Mark-Houwink's equation η = K $\times$ (molecular mass)^a where, η is the intrinsic viscosity, K = 3.5×10^4 and a = 0.76. The degree of deacetylation was determined to be 14% by IR (Perkin Elmer 2000 spectrometer) and solid state ^{13}C-NMR (Bruker DSX-300 spectrometer at 75 KHz). The detailed synthesis and characterization procedures are reported elsewhere [28]. The chitosan mentioned throughout this work is LMWC, obtained as described above.

Nitric acid and potassium hydroxide were utilized as pH modifiers. All other reagents were of analytical grade. Deionised double distilled water of conductivity < 1.5 μohm$^-$^{1} was used for all the experiments.

3. Experimental Methods

3.1. Polymer Analysis

Polyethylene glycol (PEG) in solution was analysed as per the procedure given by Ingham and Ling [29]. Nessler's assay was prepared by mixing Nessler's reagent and 4M KOH solutions in 2:1 ratio. For the analysis, 4ml polymer solution of desired concentration was mixed vigorously with 4 ml of Nessler's assay and the absorbance was measured at 420 nm, using a Shimadzu (UV 260) UV-visible spectrophotometer. The concentration of the PEG solution was determined using a calibration curve.

The concentration of chitosan, a cationic polyelectrolyte was analysed following the colorimetric procedure given by Muzzarelli [30]. In this method, 5ml of chitosan solution of desired concentration was mixed vigorously with 3ml of Cibacron brilliant red 3B-A dye solution. The absorbances were measured using a Shimadzu (UV 260) UV-visible spectrophotometer at a wavelength of 575 nm. The concentration of chitosan was obtained from the calibration curve.

The analysis of chitosan using the colorimetric procedure given by Muzzarelli [30], was not affected by the presence of PEG in the solution. But the presence of chitosan in the solution significantly affected the analysis of PEG by the procedure described earlier [29]. The concentration of PEG in the presence of chitosan was therefore analysed using a Tekmar Total Organic Carbon (TOC) analyzer, based on calibration curve constructed for the purpose.

3.2. Adsorption Studies

For these tests, 1 g of SiC was taken in a 250 ml Erlenmeyer flask and mixed with 50 ml of 10^{-3}M KNO$_3$ electrolyte solutions. 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 hours at 28°C. A desired concentration of 50 ml of PEG or chitosan polymer solution was prepared and the pH of the solution was adjusted equivalent to the corresponding suspension pH value, with the background electrolyte concentration maintained at 10^{-3}M KNO$_3$. The prepared polymer solution was then mixed with the suspension of corresponding pH value. The suspension was equilibrated in a Remi orbital shaking incubator for a specified time. After equilibration, the suspension was centrifuged in a Remi centrifuge at 5000 rpm for 45 min. The clear supernatant polymer solution was analysed for PEG or chitosan as per the procedure described earlier. Adsorption of the polymers onto SiC was measured as a function of interaction time, suspension pH and polymer concentration. For the competitive adsorption studies, the polymers were added to the SiC suspension either simultaneously or sequentially.

3.3. Desorption Experiments

Desorption of the adsorbed polymers (PEG or chitosan) from the SiC surface was estimated at different pH values to examine the reversibility of the adsorption process. Each of the residues obtained after centrifuging the polymer interacted suspension of different pH values, was mixed with 20 ml of deionised, double distilled water of corresponding pH and re-agitated in the Remi orbital shaking incubator at 180 rpm, for 1h, at 28°C. Subsequently, the suspension was centrifuged and the supernatant was analysed for the PEG or chitosan concentration. The percentage desorption was calculated from the adsorbed and desorbed amount of the polymers.

3.4. Electrokinetic Tests

Electrokinetic experiments were carried out using a Malvern 3000 model zetasizer, U. K. A dilute suspension of SiC was prepared with deionized double distilled water (10 mg in 100 ml) with the background electrolyte concentration kept constant at 10^{-3}M KNO$_3$. The pH of these suspensions were adjusted to the desired values and equilibrated. The zeta potential values of the suspensions were measured as a function of pH and the isoelectric point (i.e.p.) of SiC was determined. To ascertain the effect of PEG and/or chitosan on the electrokineticbehaviour of SiC suspension, initially 10 mg of SiC in 50 ml deionised double distilled water was prepared. Then 50 ml of PEG and/or chitosan solution of desired concentration, whose pH was preadjusted to the suspension pH value was added to the suspension and allowed to equilibrate for a specified time. The zeta potential values were measured as a function of pH and polymer concentration.

3.5. Dispersion Tests

A suspension of 100 mg of SiC powder in 100 ml deionised double distilled water was prepared in a 100 ml measuring cylinder. The pH of the suspension was adjusted to a desired value. To study the effect of PEG and/or chitosan on the dispersion stability of the suspension, the required concentration of the polymer solution with the pH preadjusted to the corresponding suspension pH value, was mixed with it such that the total suspension volume was 100 ml. Then the measuring cylinder was gently tumbled 30 times 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 this time, the top 25 ml of the suspension was siphoned out and diluted to 50 ml. The turbidity of the diluted suspension was directly measured in a Systronics turbidity meter-132, which was calibrated with Formazine standard. The turbidity values expressed in terms of Nephelometric Turbidity Units (NTU) were measured as a function of pH and polymer concentration.

3.6. FTIR Spectroscopic Studies

FT-IR spectra of SiC before and after interaction with PEG or chitosan were recorded using a JASCO-410 FT-IR spectrometer, UK, in the wavenumber range of 4000 to 400 cm^{-1}. To record the spectra of adsorbed samples, the SiC suspensions interacted with the polymers (PEG or chitosan) were filtered through Whatman 42 filter paper and the solid residues were air dried and stored in a vacuum desiccator. All the samples were further dried using an IR lamp, after mixing with spectroscopic grade KBr and then the spectra were recorded.

4. Results and Discussion

4.1. Adsorption Studies

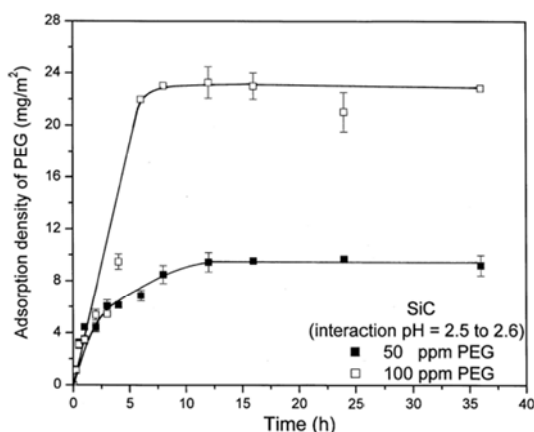#### 4.1.1. Adsorption Kinetics

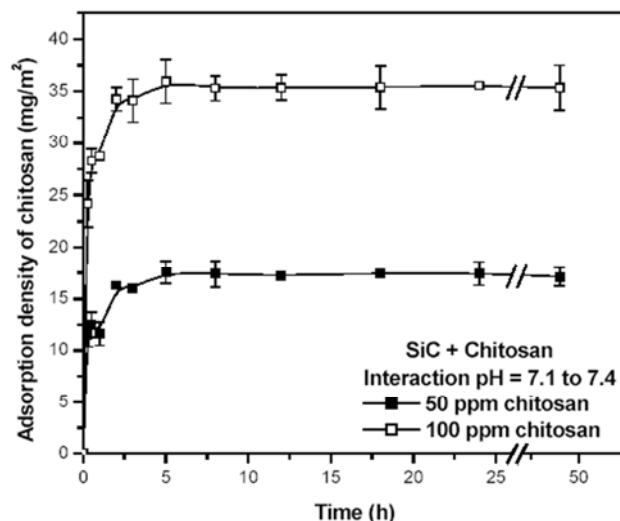**Figure 1(a).** *Adsorption density of PEG for silicon carbide as a function time.*

Figure 1(b). *Adsorption density of chitosan for silicon carbide as a function of time.*

Figures 1(a) and (b) portray the adsorption density of PEG and chitosan respectively onto SiC, as a function of time. It is evident from the figures that the adsorption of PEG onto SiC becomes saturated at around 12 h, while that of chitosan attains saturation value around 5 h. Based on the adsorption kinetics, the equilibration time for further adsorption experiments was fixed as 12 h in the case of PEG and 5 h in the case of chitosan for their interaction with SiC. It is also evident that with the increase in the initial polymer concentration from 50 ppm to 100 ppm, the adsorption density is correspondingly increased, though the time taken to attain the saturation value is not altered.

4.1.2. Effect of pH

Figure 2 (a) illustrates the adsorption density of PEG onto SiC suspension as a function of pH for three different polymer concentrations namely 25 ppm, 50 ppm and 100 ppm.
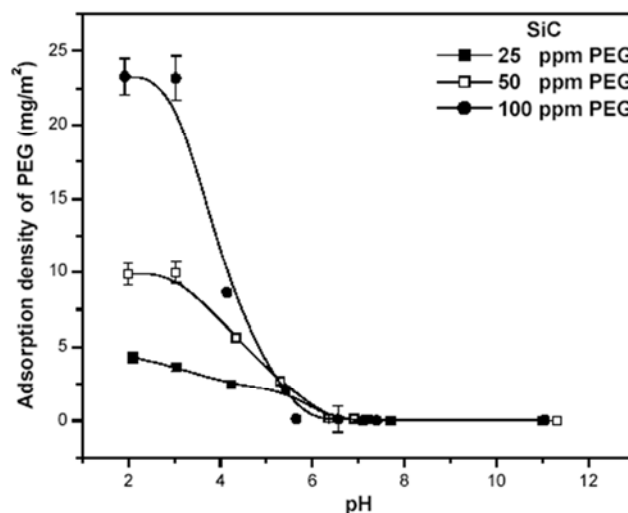

Figure 2(a). *Adsorption density of PEG for silicon carbide as a function of pH.*

For all the three concentrations investigated, the adsorption density of PEG decreases as the pH increases and the adsorption density is higher between pH 2 to 3. For 25 ppm initial PEG concentration, the adsorption density steadily decreases from pH 2 onwards and reaches a minimum value at pH 6 and beyond. On the other hand, a steeper decrease in the adsorption density can be observed for the 50 ppm and 100 ppm initial PEG concentrations, from pH 3 to 6. Beyond pH 6, the adsorption density is almost negligible, irrespective of the initial PEG concentrations investigated. The natural oxidation of SiC surface results in the formation of silica layer, which gets hydroxylated as surface silanol groups, as has been well documented in the literature [31-34]. The active functional group available in the repeating unit of PEG is ether oxygen. On considering the surface functionality of SiC and the functional group of PEG, it can be expected that hydrogen bonding will be the dominating force of interaction between the hydrogen of surface silanol groups of SiC and ether oxygen of the polymer. The hydrogen bonding mechanism between silica and PEO (high molecular weight analogue of PEG) has been explained in detail in the literature by several workers [35-37]. The earlier studies of Howard and McConnell [38], revealed the importance of the surface –OH groups, for the hydrogen bonding interaction between silica and the ether oxygen of polyethers. The decrease in the density of surface silanol groups as the pH is increased could be the underlying reason for the observed decrease in the adsorption density of PEG with the increase in pH. It has been reported that the pKa value of surface Si-OH groups varies from pH 6.5 at 0% neutralization to about pH 9.2 at 50% neutralization [39]. The ionization of Si-OH groups leads to the formation of SiO$^-$, which hampers interaction with the ether oxygen of the polymer. The slight anionicity of the ether oxygen of PEO is invoked in the electrostatic interaction process with the oxide surfaces [36, 37]. The repulsion between the ethoxy oxygen of Synperonic NP8 (nonyl phenol ethoxylate with an average of eight ethylene oxide groups per molecule) and the dissociated silanol groups has been explained in another study [40]. Tadros [41] has attributed the decrease in the hydrogen bonding between PVA and silica surface, to the ionization of the silanol groups. The negligible adsorption of PEG onto SiC, in the pH region of 6 to 11, can thus be understood.

The adsorption densities of chitosan onto SiC as a function of pH, for 25 ppm, 50 ppm and 100 ppm initial polymer concentrations are shown in the Figure 2(b). A gradual increase in the adsorption density is observed in the pH region of 2 to 6, followed by a drastic increase between pH 6 and 7, with the adsorption densities exhibiting a characteristic maximum value at around pH 7. Thereafter, the adsorption density decreases steeply till pH 11. It is evident that the effect of the polymer concentration on the adsorption density is more pronounced in the pH region of 6 to 9.5, namely that the amount adsorbed increases with increase in the polymer concentration from 25 ppm to 100 ppm. 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 [14, 42]. Thus, below pH 7.5, chitosan is positively charged due to ionization of the amino group. It is evident from the electrokinetic studies that the isoelectric point of SiC is located at pH 3 and beyond that pH the surface becomes increasingly, negatively charged (Figure 6(a)). Thus, the higher adsorption of positively charged chitosan can be expected to take place
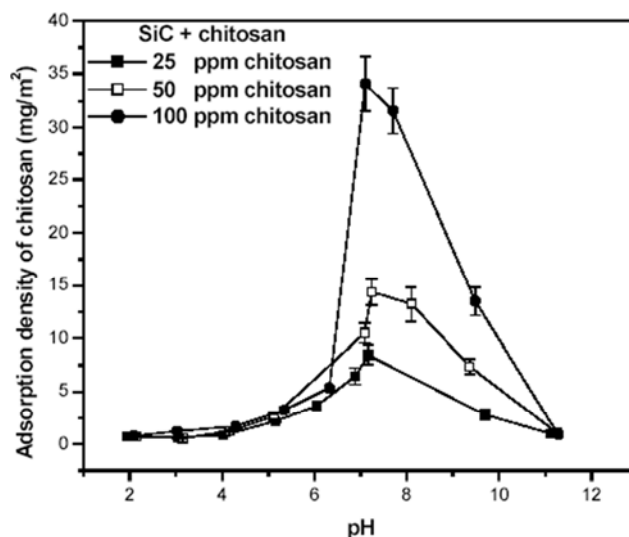

Figure 2(b). *Adsorption density of chitosan for silicon carbide as a function of pH.*

on negatively charged SiC surface in the pH range of 3-7. 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 that pH range. Apart from electrostatic and hydrogen bonding forces, hydrophobic interaction can also take place between the glucopyranose ring of chitosan and the hydrophobic areas of SiC surface. The ionization of the Si-OH groups to siloxane (Si-O-Si) in the alkaline pH range reduces the affinity of SiC with chitosan. Considering 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 can be expected. The importance of electrostatic forces of interaction for the adsorption of other cationic polymers with silica and SiC has been reported in the literature [43-46]. Electrostatic attraction has been considered as a dominant interaction mechanism between chitosan and kaolin surfaces by Domard *et al* [47] in their work. On the other hand, Sun et al [43] have explained the interaction of SiC with polyethylene imine through hydrogen bonding between the surface silanol or silaxane groups and the polymer.

4.2. Co-adsorption Studies

4.2.1. Effect of pH

Figures 3(a) and 3(b) illustrate the adsorption density of PEG/chitosan onto SiC as a function of pH, at three different initial PEG/chitosan concentrations, in the absence and presence of different concentrations of chitosan/PEG

respectively. It is clearly evident from the figures that the additional presence of chitosan or PEG, irrespective of their concentrations, does not alter the adsorption density of PEG or chitosan respectively onto SiC. The adsorption trends with respect to pH are also similar to those observed earlier (Figures 2(a) and 2(b)). The fact that the pH regimes for higher adsorption of PEG, namely 2 to 6 and that for chitosan ($\approx$ 7 to 7.5) are different, the magnitude of the adsorption densities of each polymer when interacted individually is not affected by the combined addition of PEG and chitosan.
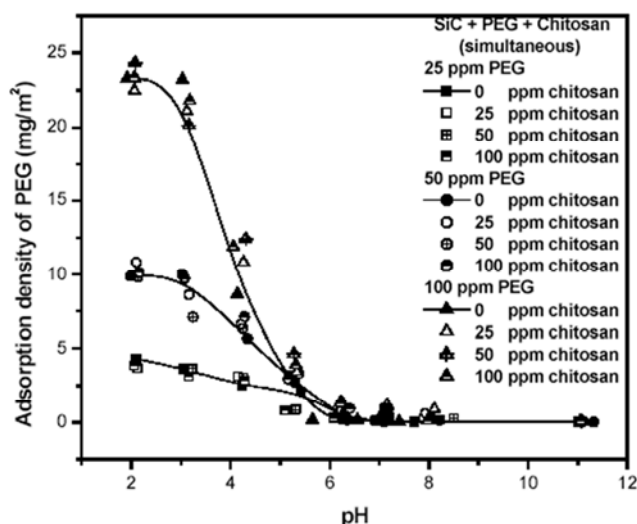

Figure 3(a). *Adsorption density of PEG for silicon carbide as a function of pH, in the absence and presence of different concentrations of chitosan.*
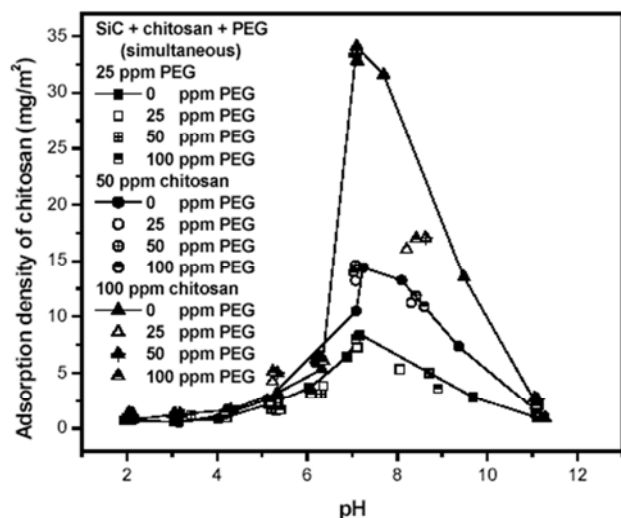

Figure 3(b). *Adsorption density of chitosan for silicon carbide as a function of pH, in the absence and presence of different concentrations of PEG.*

It can be summarised from the observed behaviour that these polymers are adsorbing on silicon carbide through different surface functionalities, even through hydrogen bonding is the underlying mechanism of interaction. In the case of PEG below pH 6, hydrogen bonding takes place between the hydrogen of the surface Si-OH groups present on silicon carbide and the ether oxygen of PEG. On the other hand, chitosan has both –OH and -NH$_2$ groups (which can

protonate less than pH $\sim$ 7.5) in the chain, facilitating hydrogen bonding either through the hydrogen of –OH or protonated –NH$_2$, with the oxygen of Si-OH or ionized Si-OH (SiO$^-$) groups of silicon carbide surface. It is pertinent to recall that the Si-OH density decreases as the pH increases and also Si-OH starts ionizing from pH 6.5 (section 4.7.1.2). The fact that the pH regimes for higher adsorption of PEG, namely 2-6 and that for chitosan ($\approx$ 7-7.5) are different, the magnitude of the adsorption densities of each polymer when interacted individually is not affected by the combined addition of PEG and chitosan.
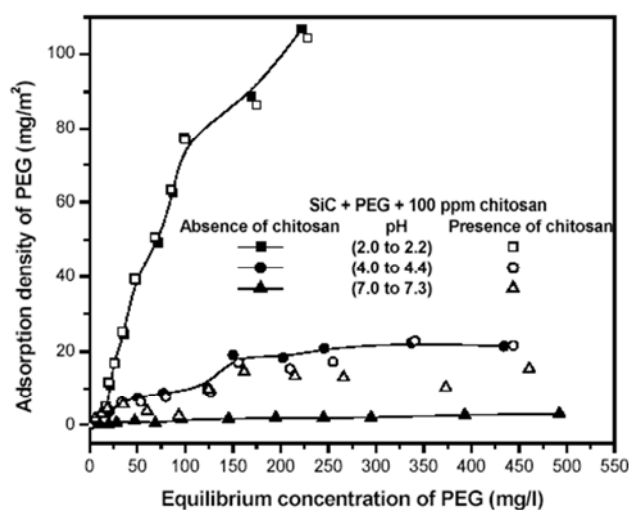
4.2.2. Adsorption Isotherms

Figure 4(a). *Adsorption isotherms of PEG for silicon carbide at different pH values, in the absence and presence of 100 ppm chitosan.*

Figure 4(a) shows the adsorption isotherms for PEG onto SiC, at three different pH values, in the absence and presence of 100 ppm chitosan. At pH 2-2.2, the adsorption density of PEG onto SiC continuously increases with the increase in polymer concentration and saturation level is not observed in the concentration –range investigated. On the other hand, for the pH values 4-4.4, the saturation in the adsorption can be observed beyond an equilibrium concentration of ~150 mg/l. The adsorption isotherm obtained at pH 7-7.3, shows relatively very low adsorption density. These results corroborate the pH trend obtained in the earlier experiments (Figure 2(a)). It is evident from the figure that the presence of 100 ppm chitosan does not alter the adsorption isotherms for PEG onto SiC at pH 2-2.2 and 4-4.4. However, at pH 7-7.3, the adsorption density of PEG is increased in the presence of chitosan, especially beyond a certain equilibrium concentration of PEG. It is interesting to recall that this is the pH region where a characteristic higher adsorption of chitosan onto SiC was observed (Figure 2(b)). The possibility of the hydrogen bonding interaction between ether oxygen of PEG and hydrogen of –OH or –NH$_3^+$ groups of chitosan has been suggested by Jiang and Han [48]. The observed increase in the adsorption density of PEG onto SiC, in the presence of chitosan, can thus be expected, due to the bridging of PEG with the adsorbed chitosan at pH 7-7.3.
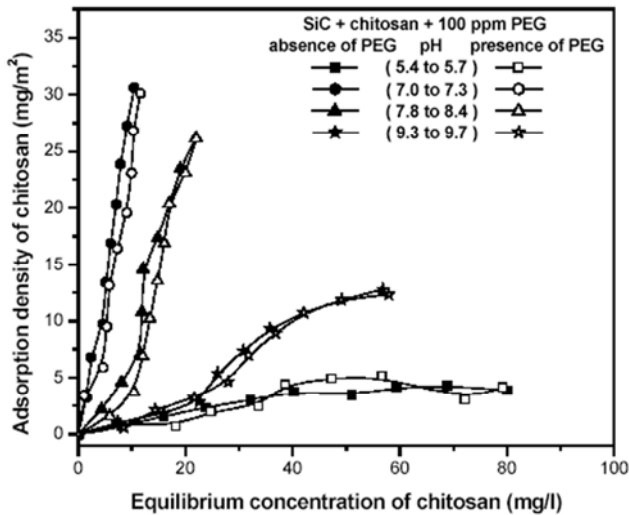
Figure 4(b). *Adsorption isotherms of chitosan for silicon carbide at different pH values, in the absence and presence of 100 ppm PEG.*

Figure 4(b) illustrates the adsorption isotherms for chitosan onto SiC at four different pH values, in the absence and presence of PEG. The isotherms exhibit Langmuirianbehaviour. The adsorption isotherms attain a saturation level beyond a certain equilibrium concentration of chitosan at pH 5.4-5.7 (~40 mg/l) and at pH 9.3-9.7 (~50 mg/l). On the other hand, for the isotherms obtained at ~ pH 7 and 8, the adsorption densities of chitosan are found to increase steeply and the saturation is not observed in the chitosan concentration range investigated. These results are in line with the observed trends of adsorption density of chitosan as a function of pH (Figure 2(b)). Domard et al [47], have found similar trends for the adsorption of chitosan onto kaolin. Their experimental studies revealed that there was no plateau in the adsorption density of chitosan at pH 6, while the plateau was attained beyond a certain equilibrium concentration of chitosan at pH 4. From the results of the above experiments, it is pertinent that the amount of unadsorbed polymers present in the suspension is higher around pH 5.5 and 9.5, when compared to that around pH 7 and 8, which could facilitate the stabilization of the suspension. It is noteworthy that the adsorption isotherms for chitosan onto SiC in the presence of 100 ppm PEG almost overlap those of chitosan alone for all the pH values investigated.

4.3. Desorption Studies

The adsorption density of 100 ppm PEG or chitosan onto SiC, as a function of pH and the corresponding percentage desorption of the adsorbed polymers from SiC, has been illustrated in Figure 5. It is evident from the figure that the percentage desorption of PEG increases from ~10% at pH 2 to ~24% at pH 4. From the adsorption and desorption trends for the SiC-PEG system, it is evident that as the pH increases both the adsorption density and the strength of interaction decreases. As mentioned earlier (section 4.1.2.), when the pH increases, the number of silanol groups on the

surface of SiC, which take part in the hydrogen bonding interaction with the ether oxygen of PEG, is decreased and thus results in the decrease in the adsorption density. On the other hand, the decrease in the strength of interaction with the increase in pH, may be due to the repulsion between the slightly anionic PEG and the increasingly negatively charged SiC surface.
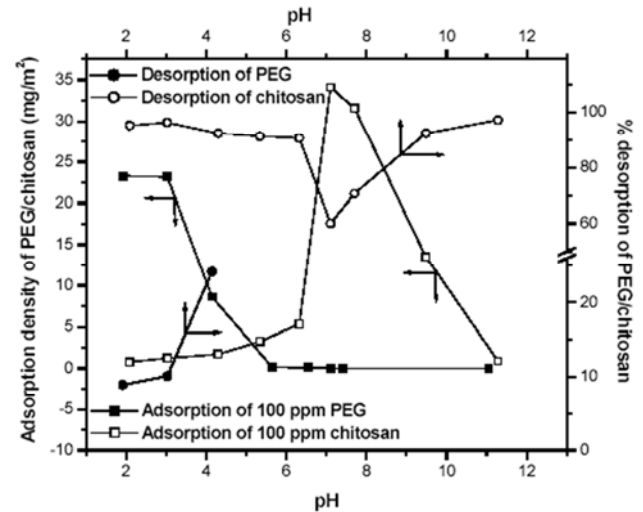

Figure 5. *Adsorption density of 100 ppm PEG/chitosan for silicon carbide and the corresponding percentage desorption of PEG/chitosan respectively, as a function of pH.*

It is evident from the figure that the percentage desorption of chitosan from SiC remains constant ~ 90 - 95%, over the pH range of 2 to 6. At pH 7, it attains the minimum desorption percentage of ~ 60. Thereafter, again it gradually increases to ~ 97% at pH 11. It is evident from the figure that the reversibility of chitosan is higher in the lower adsorption region, while in the characteristic higher adsorption region (pH~7) the reversibility of polymer adsorption is minimum. At pH 7, the combination of electrostatic, hydrogen bonding and hydrophobic forces of interaction facilitate the higher binding strength of chitosan onto SiC surface. On the contrary, in the other pH regions (2-6 and 8-11), hydrogen bonding is the dominating force of interaction, which is of comparatively lower strength, and this leads to the higher reversibility of adsorption.

On comparing the desorption percentages of PEG and chitosan, it is noteworthy that the hydrogen bonding between the functional groups of PEG and SiC is stronger than that of SiC-chitosan system. Voronin et al, [49]have described the stronger hydrogen bonding force between PEO and fumed silica through quantum chemical calculations. Based on the conformation of these two polymers, presumably the steric hindrance exhibited by the glucosamine ring of chitosan for adsorption may be higher, compared to that of the simpler linear structure of PEG. Moreover, the segmental interaction energies for the corresponding functional groups of the polymers with the functional groups of SiC surface should also be taken into consideration.
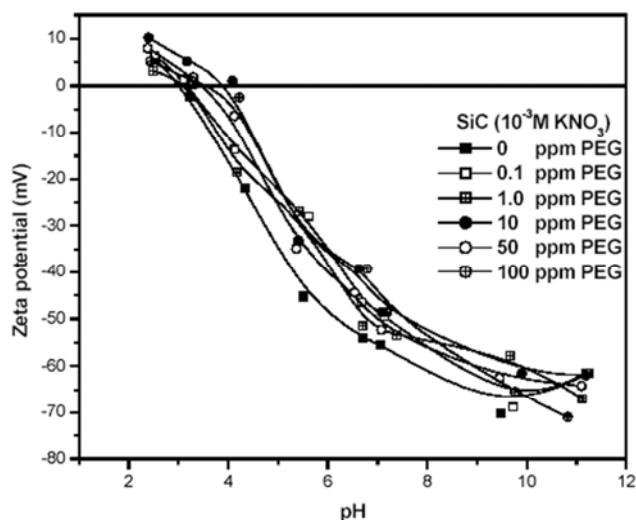
4.4. Electrokinetic Tests

Figure 6(a). *Zeta potential of silicon carbide as a function of pH in the absence and presence of different concentrations of PEG.*

Figrue 6(a) portrays the zeta potential values of SiC surface as a function of pH, at different PEG concentrations. In the absence of polymer the zeta potential value is positive at pH 2. The isoelectric point (i.e.p.) of SiC surface is found to be located at pH 3. This value is in agreement with the values cited in the literature [43, 45, 50-54]. As the pH increases beyond 3, the negative zeta potential values increase steadily and reach a maximum value of around –70 mV at pH 9.5 and thereafter a slight decrease is observed at pH 11. In the presence of different concentrations of PEG, the zeta potential values of SiC surface are marginally reduced to less negative values or even slightly positive values as a function of pH. Additionally, the i.e.p. of SiC is shifted to less acidic values namely pH 4.1 with the addition of 10 ppm PEG concentration.
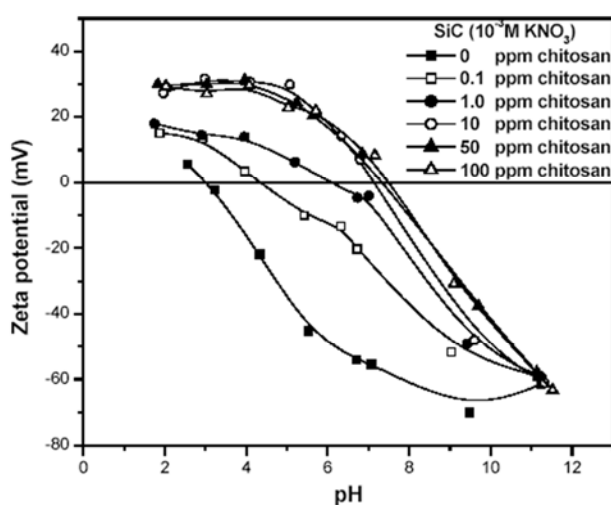

Figure 6(b). *Zeta potential values of silicon carbide as a function of pH, in the absence and presence of different concentrations of chitosan.*

Figure 6(b) illustrates the zeta potential values of SiC suspension as a function of pH in the absence and presence of different concentrations of chitosan. Since chitosan is a cationic polymer, it is expected to shift the i.e.p. of the SiC suspension more towards the alkaline pH region in proportion with the added polymer concentration as evidenced from the figure. It can be observed that the i.e.p. is shifted from pH 3 in the absence of chitosan, to pH ~7.5 with the addition of 100 ppm chitosan. These shifts in i.e.p. have been observed by other workers [43, 45] also for SiC surface with the addition of cationic polyethylene imine and dodecyl amine. The presence of cationic functionality (amine group) in these systems is responsible for the shift in the i.e.p. towards alkaline pH values. More importantly, the presence of chitosan increases the magnitude of the zeta potential values towards more positive values. For instance, at pH 3 the zeta potential value of SiC surface is zero in the absence of chitosan, but in the presence of chitosan beyond 10 ppm concentration, it increases to a value of about + 30 mV. This value remains constant in the pH region of 2 to 4.5 in the chitosan concentration range of 10 to 100 ppm. In the pH range of 9.5 to 11.5 in the presence of different concentrations of chitosan, the zeta potential values of SiC surfaces become highly electronegative, namely about – 40 mV.
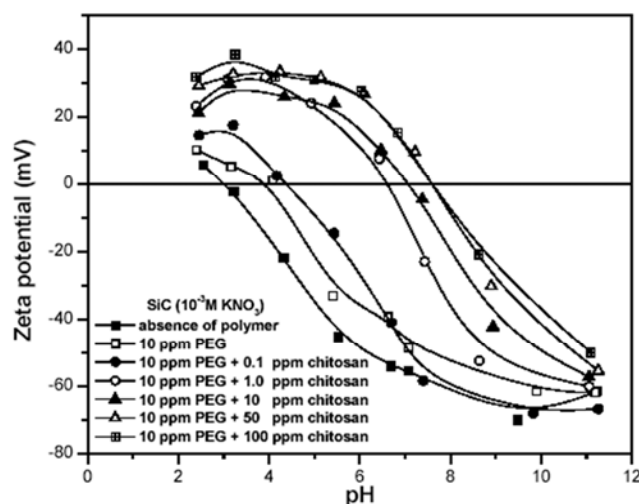

Figure 6(c). *Zeta potential of silicon carbide-10ppm PEG system as a function of pH, in the absence and presence of different concentrations of chitosan.*

Figure 6(c) portrays the zeta potential values of the SiC-chitosan system as a function of pH in the absence and presence of different concentrations of PEG. It is evident from the figure that the presence of PEG in the concentration range investigated, has only slightly altered the electrokineticbehaviour of the SiC-chitosan system throughout the pH range. In an analogous manner, Figure 6(d) shows the electrokineticbehaviour of SiC-100 ppm PEG system with different concentrations of chitosan and it closely resembles the trends exhibited by SiC surface with different chitosan concentrations. These results reveal that the electrokineticbehaviour of SiC in the combined presence of chitosan and PEG, is governed more by chitosan rather than PEG.
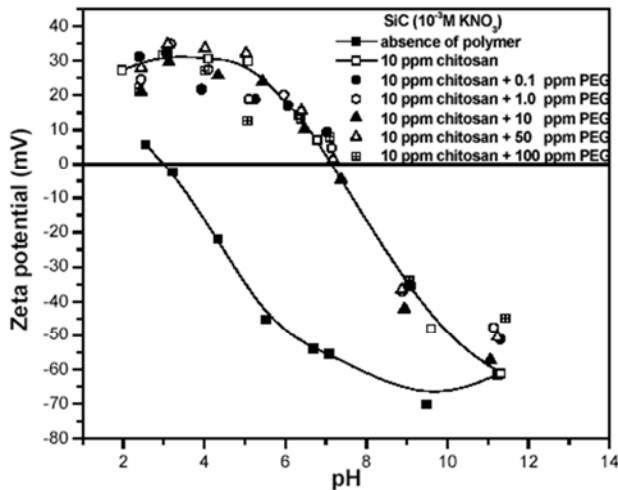
Figure 6(d). Zeta potential of silicon carbide-10ppm chitosan system as a function of pH, in the absence and presence of different concentrations of PEG.

4.5. Dispersion Tests

Figure 7(a) illustrates the dispersion behaviour of SiC suspension in the absence and presence of different concentrations of PEG as a function of pH. It is evident from the figure that in the absence of PEG, the turbidity value of SiC suspension increases steeply from 190 NTU at pH 2 to a value of about 300 NTU at pH 4. Beyond that pH, the turbidity increases gradually to a maximum value of about 350 NTU at pH ~11. The turbidity trend for SiC suspension, as a function of pH is in agreement with its electrokineticbehaviour (Figure 6(a)). The dispersion characteristics of the suspension are thus controlled by the surface charge of SiC particles as a function of pH. It can be observed from the figure that the addition of different concentrations of PEG to the SiC suspension has only a marginal effect on the dispersion properties. Li et al [55], have also observed that there was no change in the colloidal behaviour of SiC suspension in the presence of PEG.
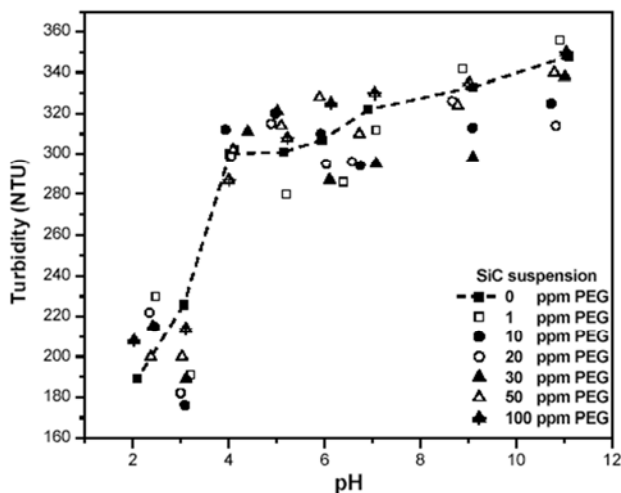

Figure 7(a). Turbidity values of silicon carbide suspensions as a function of pH, in the absence and presence of different concentrations of PEG.

The effect of addition of different concentrations of chitosan to the SiC suspension and its dispersion behaviour as the function of pH, are depicted in Figure 7(b). The following observations are noteworthy: (1) An increase in the turbidity values of SiC suspension can be observed in the pH region of 2-6, with the addition of upto 30 ppm chitosan. It is pertinent to recall that the addition of chitosan increased the zeta potential values of SiC surface to a value of about +30 mV in this pH region. This increase in surface charge results in the electrosteric stabilization of the suspension. Domard et al [47], similarly explained the enhanced stability of kaolin suspension to the increase in the zeta potential values of kaolin, in the presence of chitosan at pH 4. It is noteworthy that the adsorption density of chitosan was relatively low in this pH region (Figure 2(b)), which indicates the presence of a large amount of unadsorbed free polymer in the suspension. This factor also needs to be taken into consideration for the increased stabilization of the suspension, through the "depletion stabilization" mechanism [56]. Moreover in this pH region, chitosan is in the ionized form and this favours the increased repulsion between the free polymeric chains present in the bulk solution, which would enhance the depletion stabilization effect. The theoretical aspects of the depletion stabilization mechanism have been well brought out [57, 58].
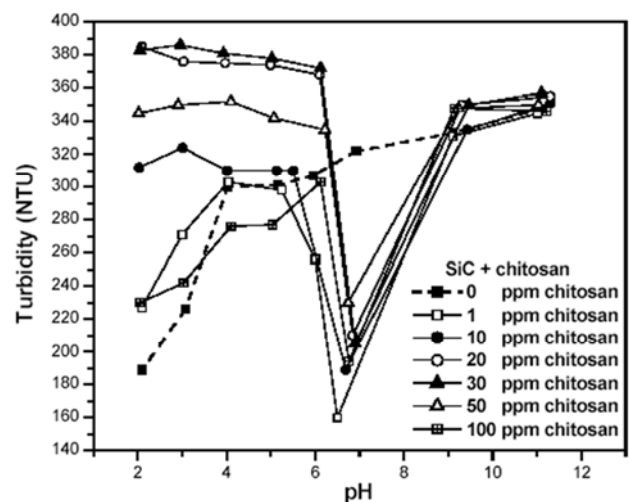

Figure 7(b). Turbidity values of silicon carbide suspensions as a function of pH in the absence and presence of different concentrations of chitosan.

The experimental results of Sato and Kohnosu [56], revealed that the stability of titanium dioxide increased with the increased amount of unadsorbed free polyvinyl pyrrollidone (PVP). Hackley [59], has also attributed the enhanced stability of silicon nitride suspension to the presence of completely ionized, unadsorbedpolyacrylic acid (PAA), facilitating the depletion stabilization mechanism. (2) For chitosan concentration from 50 to 100 ppm, a decrease in the turbidity values can be found in the pH range of 2-6. This attests to the fact that the addition of excess concentration of the polymer leads to the destabilization of the suspension and consequently the turbidity values are decreased. (3) A sharp characteristic minimum in the turbidity values observed

around pH 6.5 to 7, with the different concentrations of chitosan, reveals the enhanced flocculation of particles by the polymer. It is worth recalling that at this pH region, the adsorption density of chitosan showed a distinct maximum for all the concentrations, namely 25, 50 and 100 ppm (Figure 2(b)) and also a lower percentage of desorption (Figure 5). Flocculation by polymer bridging could result in the decreased turbidity values. Moreover the i.e.p. of the SiC-chitosan system was observed to be shifted to pH 7-7.5, consequent to the addition of 10-100 ppm of the polymer, due to electrostatic attraction resulting in the destabilization of the suspension at this pH region. It was also observed by

Domard *et al* [47], that the maximum flocculation of kaolin occurred at pH 6 due to the higher adsorption of chitosan. (4) In the pH region of 7-11, the suspension turbidity steeply increases from the characteristic minimum to higher values, both in the absence and presence of chitosan. This is in conformity with the electrokineticbehaviour of the SiC suspension, wherein highly negative zeta potential values were observed in the alkaline pH range (Figure 6(b)). From these results it is evident that the favourable regions for better stabilization of the SiC suspension are between pH 2 to 6 and 9.5 to 11.5, in the presence of optimum chitosan concentration.
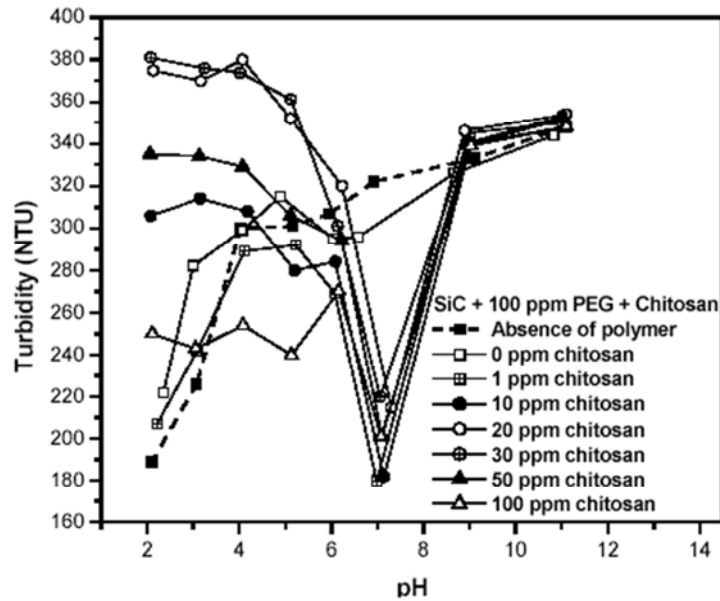

Figure 7(c). *Turbidity of silicon carbide-100 ppm PEG system as a function of pH, in the absence and presence of different concentrations of chitosan.*
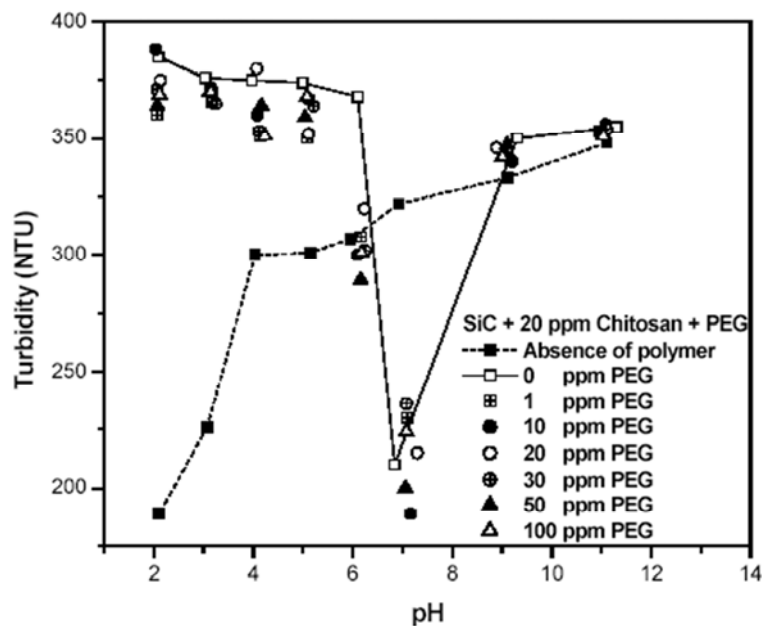

Figure 7(d). *Turbidity of silicon carbide-20 ppm chitosan system as a function of pH, in the absence and presence of different concentrations of PEG.*

Figures 7 (c) and 7(d) illustrate the effect of the addition of different concentrations of PEG and chitosan on the

dispersion behaviour of SiC-20 ppm chitosan and SiC-20 ppm PEG systems respectively. It is evident that the addition

of different concentrations of PEG to the SiC-20 ppm chitosan system has not altered its dispersion behaviour. On the contrary, the dispersion behaviour of SiC-20 ppm PEG suspension in the presence of different concentrations of chitosan closely resembles that of the SiC-chitosan system. These results indicate that the presence of PEG does not hamper the dispersing ability of chitosan for SiC suspension in the pH regimes of 2 to 6 and 9-11.
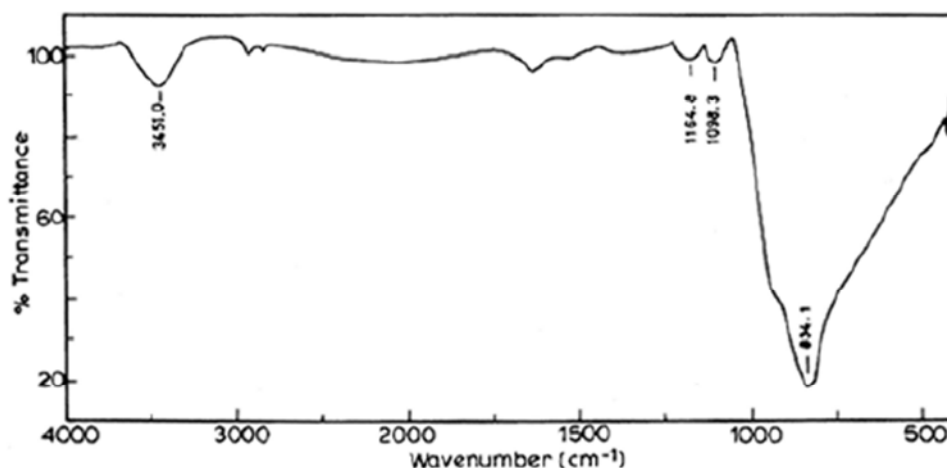
4.6.1. SiC

Figure 8. FTIR spectrum of silicon carbide.

Figure 8 portrays the FTIR spectrum of SiC. The medium band that appears at 3451 cm^{-1} is attributable to the –OH vibrations of surface silanol groups (Si-OH). The small band appears at 1629 cm^{-1} can be traced to the –OH scissoring of moisture present on the surface. The band that appears at
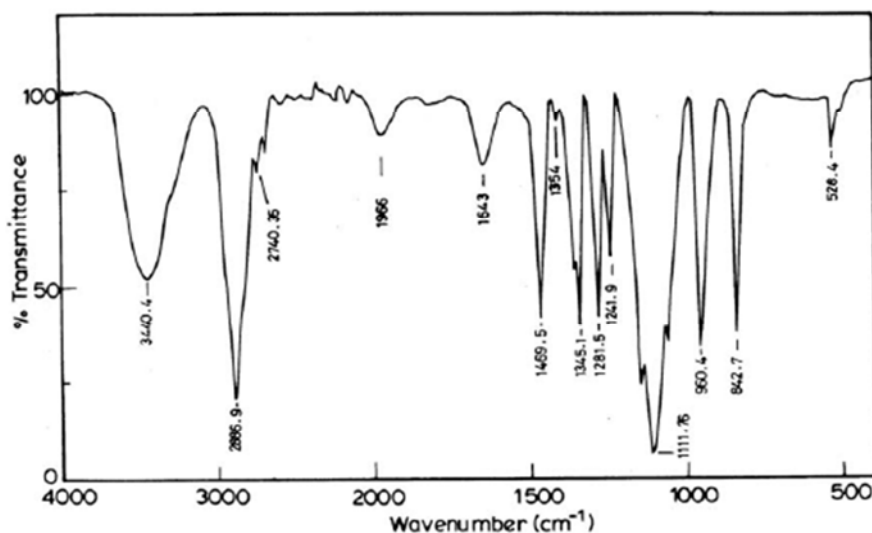
4.6.2. SiC-poly (Ethylene Glycol)

Figure 9(a). FTIR spectrum of PEG.

Figure 9(a) shows the FT-IR spectrum of the PEG polymer. The medium band appearing at 3440 cm^{-1}, is due to the presence of bonded hydroxyl group vibrations of the

4.6. FTIR Studies

The FTIR spectroscopic studies were carried out on SiC before and after interactions with the polymers namely, PEG and chitosan. The spectra of the polymers before interaction was also recorded. The peak assignments were made based on available literature [60-62].

1165 cm^{-1} can be attributed to the Si-O-C-O stretching vibrations. The smaller peak at 1098 cm^{-1} is due to the Si-O-C and Si-O-Si stretching vibrations. The highly intense peak that appears at 834 cm^{-1} is attributable to Si-C stretching vibrations.

polymer. The sharp and intense band at 2887 cm^{-1} corresponds to the CH$_2$ symmetrical stretching vibrations. The weak band at 2740 cm^{-1} can be assigned to the overtone

of CH_2 deformation on CH_2 stretching vibration. The small band at 1966 cm^{-1} corresponds to C-H stretching vibration. The band at 1643 cm^{-1} represents the scissoring of two O-H bonds, of water molecules [Smith 63]. The sharp and intense band at 1469 cm^{-1} is due to in-plane scissoring of CH_2 group,

while those at 1354 cm^{-1}, 1345 cm^{-1} and 1282 cm^{-1} can be attributed to in-plane O-H deformation. The intense bands at 1242 cm^{-1} and 1112 cm^{-1} are assigned to C-O-C asymmetric stretching vibrations. The sharp bands at 960, 843 and 528 cm^{-1} are due to C-C skeletal stretching vibrations.
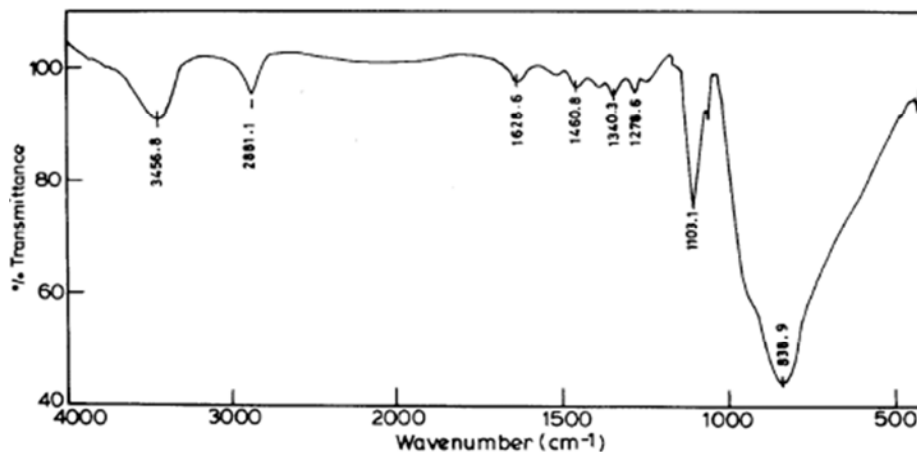

Figure 9(b). *FTIR spectrum of silicon carbide interacted with PEG.*

Figure 9(b) depicts the FT-IR spectrum of SiC after interaction with PEG. The medium band observed at 3457 cm^{-1} can be attributed to the –OH stretching vibrations exerted from both PEG polymer and Si-OH of SiC surface. The sharp and intense band, which appeared at 2887 cm^{-1}, corresponding to CH_2 symmetrical stretching vibrations for PEG, is reduced in intensity and is shifted to 2881 cm^{-1} after interaction with SiC. The peak that appears at 1629 cm^{-1} can be attributed to the presence of moisture in the sample [63]. The sharp and intense band at 1469 cm^{-1} due to in-plane scissoring of CH_2 group of PEG, after interaction with SiC has reduced in intensity and is shifted to 1461 cm^{-1}. The peaks at 1345 cm^{-1} and 1282 cm^{-1} corresponding to in-plane O-H deformation of PEG have shifted to lower wave

numbers and appear at 1340 cm^{-1} and 1279 cm^{-1} respectively, in the adsorbed state. Similarly, the sharp peak that appeared at 1112 cm^{-1}, attributable to C-O-C asymmetric stretching vibrations of PEG has reduced in intensity and shifted to a lower wave number of 1103 cm^{-1} after interaction with the SiC. These lower shifts strongly suggest the presence of hydrogen bonding forces between PEG and SiC surface. The small peak at 1098 cm^{-1} corresponding to Si-O-C and Si-O-Si stretching vibrations of SiC has shifted to a lower wave number and appears as a shoulder centered at 1061 cm^{-1} after interaction with the PEG, due to hydrogen bonding. The intense peak at 834 cm^{-1} attributable to the Si-C stretching vibrations has shifted slightly and appears with the same intensity at 839 cm^{-1} after interaction with PEG.
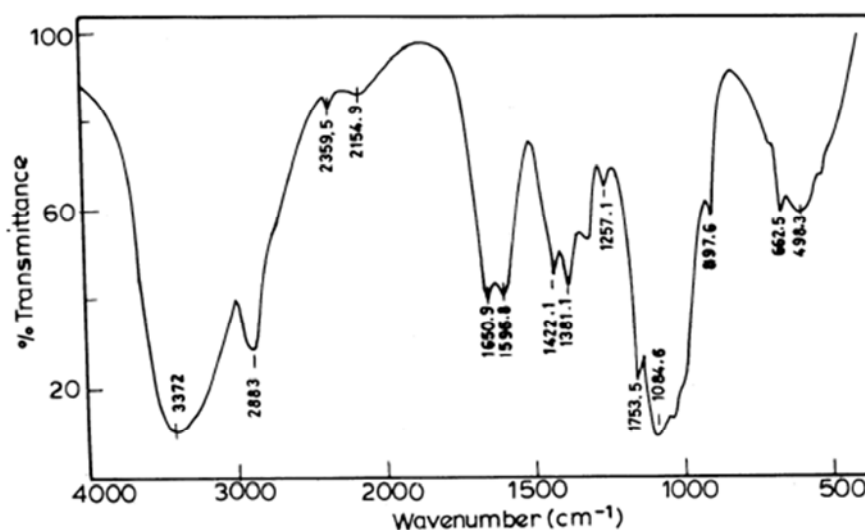
4.6.3. SiC-chitosan

Figure 10(a). *FTIR spectrum of chitosan.*

Figure 10(a) portrays the FT-IR spectrum of the chitosan polymer. The intense peak at 3372 cm^{-1} can be attributed to the stretching vibrations of hydroxyl groups present in the polymer. The band that appears at 2883 cm^{-1}, is due to the –CH$_3$assymmetric deformation. The bands 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 [62]. The intense broad band centered at 1085 cm^{-1} is assignable to primary alcoholic groups (-CH$_2$OH) vibrations.
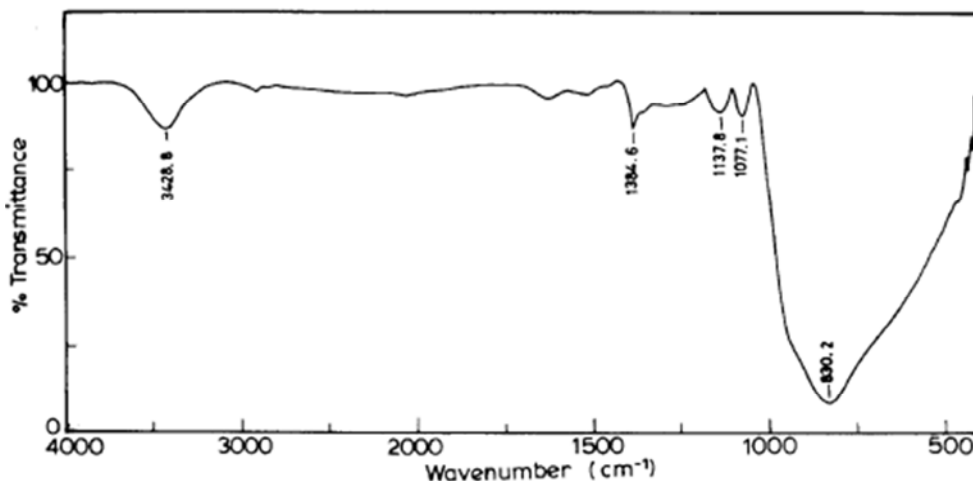

Figure 10(b). FTIR spectrum silicon carbide interacted with chitosan.

The FT-IR spectrum of SiC interacted with chitosan is depicted in the Figure 10(b). 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 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 hydrogen bonding between the oxygen present on the surface of SiC and the proton 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}.

4.7. Interaction Mechanisms

For the discussion of the interaction mechanisms between PEG or chitosan and SiC at the solid-liquid interface, the active sites available on the SiC surface and the functional groups of PEG or chitosan have to be considered. The acid-base properties of both SiC surface and PEG or chitosan are the common and important factors influencing the interaction between them [64], apart from the hydrophobic and electrostatic forces. It is well known that SiC surface has a layer of SiO$_2$ due to the natural oxidation [31, 32]. The silanol (SiOH) groups are the active sites available on the SiO$_2$ surface [39], as well as in the SiC surface [65]. Apart from silanol groups, unreacted carbon is also present on the surface of SiC in the silica layer [32], which exhibits some hydrophobicity for the surface.
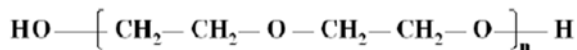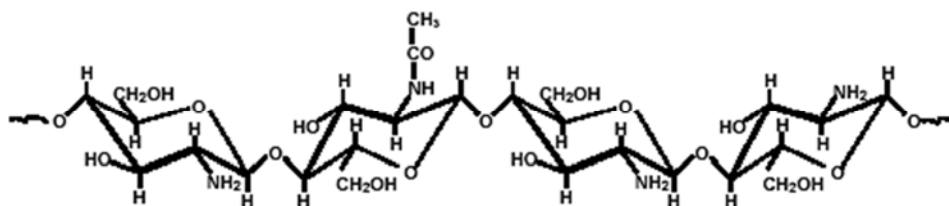

Figure 11(a). Chemical structure of PEG.

Figure 11(b). Chemical structure of chitosan.

The polymeric structures of polyethylene glycol (PEG) and chitosan are shown in Figure 11(a) and (b) respectively. The ether oxygen is the functional group available in the repeating unit of PEG, which can act as a base center and accept protons from the proton donor. The electronegativity of ether oxygen can be considered for the electrostatic interaction for PEG with the SiC surfaces when they are positively charged [36, 37]. The CH_2-CH_2 part between the ether oxygen can take part in the hydrophobic interaction with the hydrophobic centers of SiC surfaces. Hydroxyl and amine groups are the functional groups present in the glucosamine ring, which is the repeating unit of chitosan. Both the functional groups are capable of donating or accepting protons [66, 39] depending on the functionalities available on the solid surfaces. The ionization of chitosan (to positive charge) less than its pKa value favours the electrostatic interaction of the polymer with negatively charged SiC surfaces. The possibility of hydrophobic interaction can also be considered between the hydrophobic centers of the SiC surface and the glucosamine ring [39].

Based on the above factors and the experimental evidences the plausible interaction mechanisms between SiC and PEG or chitosan can be summarized as follows:

SiC-PEG system:
(1) The hydrogen bonding between surface silanol (SiOH) groups on SiC and the ether oxygen of PEG.
(2) The electrostatic interaction between the feebly negatively charged ether oxygen of PEG and the positively charged SiC particles, below pH 3.
(3) The hydrophobic interaction between CH_2-CH_2 groups and the hydrophobic carbon (unreacted surface carbon) present on the surface of SiC.

SiC-chitosan system:
(1) The hydrogen bonding interaction between hydrogen of the surface silanol (SiOH) groups on SiC and oxygen of –OH groups or nitrogen of -NH_2 groups of chitosan, where SiC acts as proton donor and the polymer acts as acceptor. Another possibility is the hydrogen bonding through the oxygen of SiO^- of SiC surface and hydrogen of –OH groups or hydrogen of -NH_2 groups of chitosan, where SiC acts as proton acceptor and the polymer acts as donor.
(2) The electrostatic interaction between positively charged –NH_3^+ groups (below pKa) of chitosan and negatively charged SiC surfaces, between pH 3 and 7.
(3) The hydrophobic interaction between glucosamine ring of chitosan and the hydrophobic carbon (unreacted carbon) on the surface of SiC.

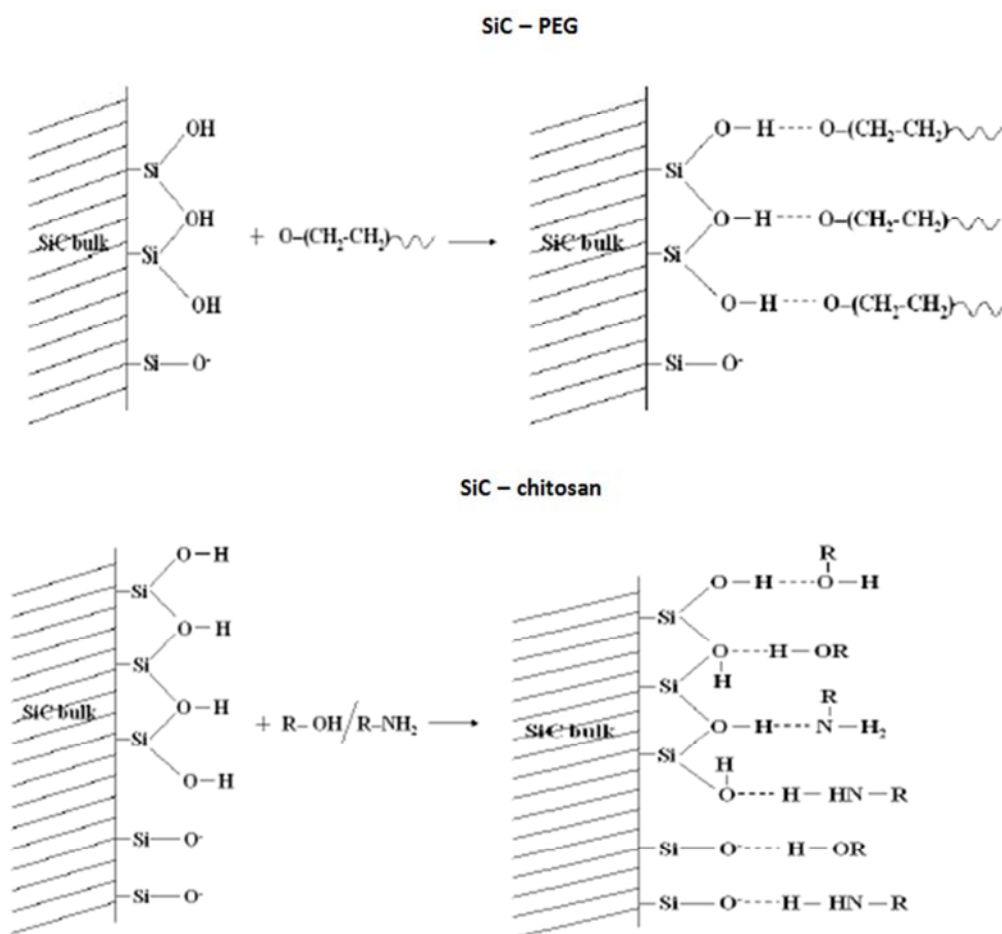The schematic representation of the interaction mechanisms is shown in the Figure 12.

Figure 12. Schematic representation of interaction mechanisms.

5. Conclusions

The following conclusions can be drawn from the detailed studies carried out:

The adsorption density of PEG onto SiC decreases steeply from pH 2 to 6 and remains unaltered beyond that pH. On the contrary, a characteristic maximum in the adsorption density of chitosan onto SiC is observed at pH ~ 7-7.5. The adsorption behaviour of either PEG or chitosan onto SiC, is not altered in the combined presence of PEG and chitosan. The percentage desorption of PEG from SiC varies between ~10% at pH 2 to ~24% at pH 4. On the other hand, a higher percentage desorption of chitosan (90 – 97%) is observed in the pH range of 2-6 and 9-11, compared to 60% at pH ~7. The i.e.p. 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 chitosan added. In the pH range of 2-5, the zeta potential values become positive (~ + 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. On the other hand, the addition of PEG only marginally alters the electrokineticbehaviour of the SiC suspension. The electrokineticbehviour of SiC suspension in the combined presence of PEG and chitsoan essentially follows the trends observed in the presence of chitosan alone. 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, both in the absence and presence of PEG. FTIR spectral data provide evidence in support of the hydrogen bonding forces of interaction between PEG or chitosan and SiC.

Acknowledgements

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