JOURNAL OF MATERIALS SCIENCE 31 (1996) 471–478

Infrared spectral investigation of polyacrylate adsorption on alumina

D. H. LEE, R. A. CONDRATE. Sr., J. S. REED
NYS College of Ceramics at Alfred University, Alfred, NY 14802, USA

Diffuse reflectance infrared Fourier transform spectroscopy was used to investigate the structural nature of polyacrylates adsorbed on alumina from aqueous solution. The presence of sodium bicarbonate or sodium ions on the alumina surface could inhibit the carboxylate groups on the polymer chains from forming covalent bonds with aluminium ions on the surface. More carboxylate groups of the chains were adsorbed on surface sites at lower polymer concentration and higher pH. Also, an increased loop formation of the polyacrylate chains occurred with a decrease in treatment of pH and an increase in polymer concentration. When the pH changed from higher to lower values in steps, the adsorbed polymer did not increase as much from the stretched-out form to the coiled form as was noted if one initially only treated the aqueous polyacrylate/alumina slurry at the lower pH. The adsorption of water on the polyacrylate-treated surface changed the ratio between covalently and ionically bonded carboxylate groups, causing more ionically bonded species.

1. Introduction

Many kinds of organic additives are used to ensure appropriate conditions for various ceramic processes. The addition of a dispersant is usually needed to control the stability of the slurry by steric or electrosteric stabilization. Polyacrylate is often used in ceramic processes such as casting to achieve a homogeneous microstructure after sintering. The dispersion state of powders such as alumina is very closely related to the adsorption state of the polymer on the powder surface. Understanding of the adsorption state includes knowledge of the amount and configuration of the adsorbed polymer, the final surface charge on the powder, the bonding mechanism for the adsorption, etc. Polyacrylate that is adsorbed on alumina or other types of oxides adopts various configurations, ranging from a stretched-out form to a coiled form depending upon the pH of the slurry, which is one of the important factors for steric stabilization. Furthermore, this configuration variability shows, to some extent, irreversibility. The potential differences in surface states of the alumina powder due to variation in the treatment conditions such as concentrations of the polymer, impurities, etc., can also influence the nature of the adsorption of the polymer on to the alumina from the aqueous slurry. The purpose of the current investigation was to study the adsorption of polyacrylates on alumina powders using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy to determine the variations in the surface species that would be present upon adsorption of polyacrylates on alumina surfaces, and information about variations produced by various treatment conditions.

2. Experimental procedure

Two different lots of a specific alumina preparation were selected for the applied experiments. Both of the investigated alumina powders were alpha-alumina samples that were produced by the Bayer process. The investigated polymers were commercially available sodium and ammonium polyacrylates which were prepared as 43 and 40 wt% aqueous solutions, respectively. Their molecular weights were approximately 6000.

The sample preparation procedure is illustrated in Fig. 1. A 5 vol% slurry was made by mixing 2 g alumina powder with 9.8 ml distilled water. These slurries were mixed using an ultrasonic probe for 30 s to break down agglomerates, and then either sodium or ammonium polyacrylate was added at the desired concentrations. After the pH values of the slurries were adjusted using HCl and NH_4OH, they were agitated on a shaking table for 48 h, and then centrifuged for 30 min. The supernatant parts of the slurries were separated, and the sedimented parts were washed using distilled water whose pH values were preadjusted to the same pH as those of the slurries. The washed sediment parts were dried overnight in a dry oven at 80 °C. DRIFT spectra were measured for these dried powders.

In order to investigate the reversibility of the polyacrylate adsorption process, 8 g alumina was mixed with distilled water to produce a 5 vol % slurry. After ultrasonic mixing for 1 min, sodium polyacrylate was added. The pH of the slurry was adjusted initially to pH 2. The slurry was agitated on a shaking table for 24 h, and then the pH of the mother slurry was readjusted to a pH of 5, 8 and 11. Before readjusting the

0022–2461

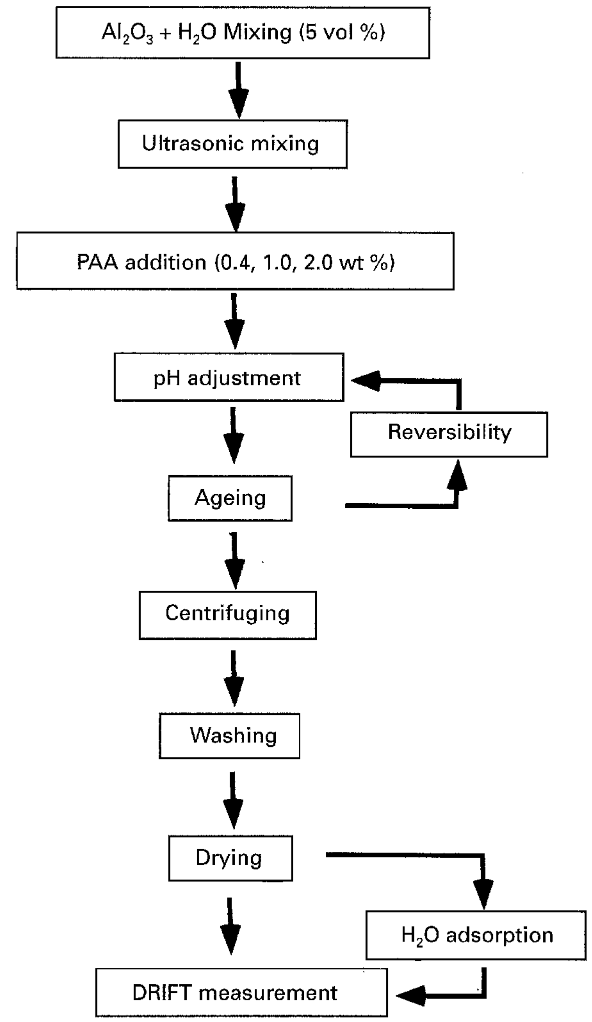

Figure 1 Preparation procedure for polyacrylate-adsorbed powders.

pH of the slurry, 10 ml slurry were separated at every step, and dried powders were made by the above-mentioned procedures for DRIFT measurement. A similar experiment was done with the sample prepared at initially a pH of 11. The pH of the slurry was readjusted in a reverse direction.

The effect of water adsorption of polyacrylate-adsorbed aluminas was also investigated. Alumina powder on which sodium polyacrylate was adsorbed was stored above water for 7 h in a tightly closed desiccator, one-third of which was filled with distilled water. The pH of the water was preadjusted to the same pH as occurred in the slurry from which the dried powder was prepared. The powder was not further dried after this treatment before the DRIFT measurements were made.

The transmission and the DRIFT spectra were measured in the 400–4000 cm^{-1} region using a Nicolet 60 SXR FT–IR (Fourier transform–infrared) spectrometer. Transmission spectra were measured on thin films of either sodium or ammonium polyacrylate that were dried on silicon windows. Each spectrum was scanned 32 times. DRIFT spectra were obtained for the powders by using a Spectra-Tech diffuse reflectance accessory. The investigated powder was placed in a micro-sample holder without diluting with KBr. Each spectrum was scanned 2048 times to increase the signal-to-noise ratio. For the powders on which the polyacrylate was adsorbed, a difference spectrum was obtained by subtracting the spectrum of a pure alumina powder from the spectrum of the alumina powder with the polymer. For investigating the powder on which water was adsorbed, the DRIFT spectrum was collected as soon as the sample was mounted on the DRIFT accessory in order to prevent the water adsorbed on the powder surface from being evaporated into the dry nitrogen found in the chamber of the instrument. A spectrum of a raw alumina powder that was wetted by water was selected as the difference reference spectrum.

3. Results and discussion

Useful structural information can be found with respect to the polyacrylate species found on the surface of treated alumina using infrared spectroscopy. This section will deal with such spectral studies involving polyacrylates in the different material environments.

3.1. The infrared transmission spectra for polyacrylate films

The infrared transmission spectra of sodium and ammonium polyacrylate films that were dried on silicon windows are illustrated in Fig. 2. The wave number of the C=O stretching mode for a protonated carboxylate group is shifted by hydrogen-bonding. Bands at 1710 and 1740 cm^{-1} are characteristic of such C=O stretching modes for protonated carboxylate groups which form cyclic dimers and side-ways chains, respectively. Bands for the C=O stretching mode of the monomers of the protonated carboxylate group appear at 1760–1780 cm^{-1} [1, 2]. When ionization occurs, generating COO^- ions, resonance equilibrium is possible between the two oxygen atoms attached to the carbon atom in these ions. As a result, the characteristic carbonyl adsorption band associated with a protonated carboxylate species disappears, and is replaced by two bands occurring in the 1550–1610 and 1400–1300 cm^{-1} regions, which correspond to the asymmetric and symmetric C–O stretching modes, respectively, for the COO^- ions. Of these bands, the former band, which is generally more constant in wave number, is more diagnostic than the latter one which has many other skeletal vibrations occurring in the same range.

The bands at 1552 and 1572 cm^{-1} for the ammonium and sodium polyacrylate are associated with the asymmetric C–O stretching modes of carboxylate groups which bond with sodium and ammonium ions, respectively. The location of the band for the bidentate complex for sodium polyacrylate is slightly shifted from that for ammonium polyacrylate. It is difficult for the ammonium ion to form the bidentate complex efficiently with the carboxylate group due to its large size. This effect makes the carboxylate group remain as a free ion. In an aqueous solution, the asymmetric C–O stretching mode for acetate ions locates at 1556 cm^{-1}, but in the sodium salt, at 1578 cm^{-1} [3]. The symmetric C–O stretching mode of the

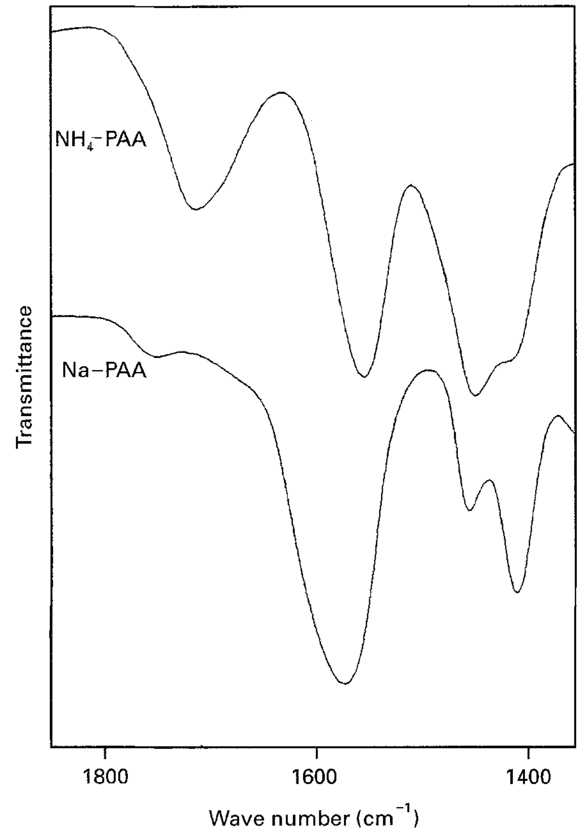

Figure 2 Transmission spectra for dried sodium and ammonium polyacrylate films.

carboxylate group appears at 1416 and 1410 cm^{-1} for the ammonium and sodium polyacrylate, respectively. The relative intensity of this band follows that of the asymmetric C–O stretching mode [1, 2, 4].

Infrared bands at 1711 cm^{-1} for ammonium polyacrylate, and at 1749 cm^{-1} for sodium polyacrylate are related with the C=O stretching modes of protonated carboxylate groups which form cyclic dimers and side-ways chains, respectively. Ammonium polyacrylate has a stronger band due to protonated carboxylate groups than sodium polyacrylate, indicating that a large number of its carboxylate groups do not bond to ammonium ions. This effect occurs because some ammonia evaporates from the polyacrylate leaving behind a hydrogen ion which bonds to a carboxylate group. The different locations of the bands can also be explained by the different degree of ionization of the each polyacrylate. When the polyacrylate chain is more ionized, its configuration changes from a coiled to a stretched-out form due to the electrostatic repulsion between the ionized carboxylate groups adjacent to each other. Therefore, the hydrogen bonding between the protonated carboxylate groups changes from cyclic dimer to the side-ways chain, resulting in an absorption band at a higher wave number for the sodium polyacrylate.

3.2. Bonding mechanisms for polyacrylates on alumina surfaces

Figs 3 and 4 demonstrate the DRIFT spectra for different weight per cents of sodium and ammonium polyacrylates that were adsorbed on the as-received alumina from solutions that are prepared at different pH values. Two major differences are observed when comparing the infrared spectra of the pure polyacrylate salts with those of the corresponding adsorbates on the alumina surfaces. First, the band location and intensity for the C=O stretching mode of the protonated carboxylate group varies with pH of the solution from which the polymer is adsorbed. Second, a new band appears at lower wave number (1602–1606 cm^{-1}) in the infrared spectra for the adsorbed sodium and ammonium polyacrylates. Also,

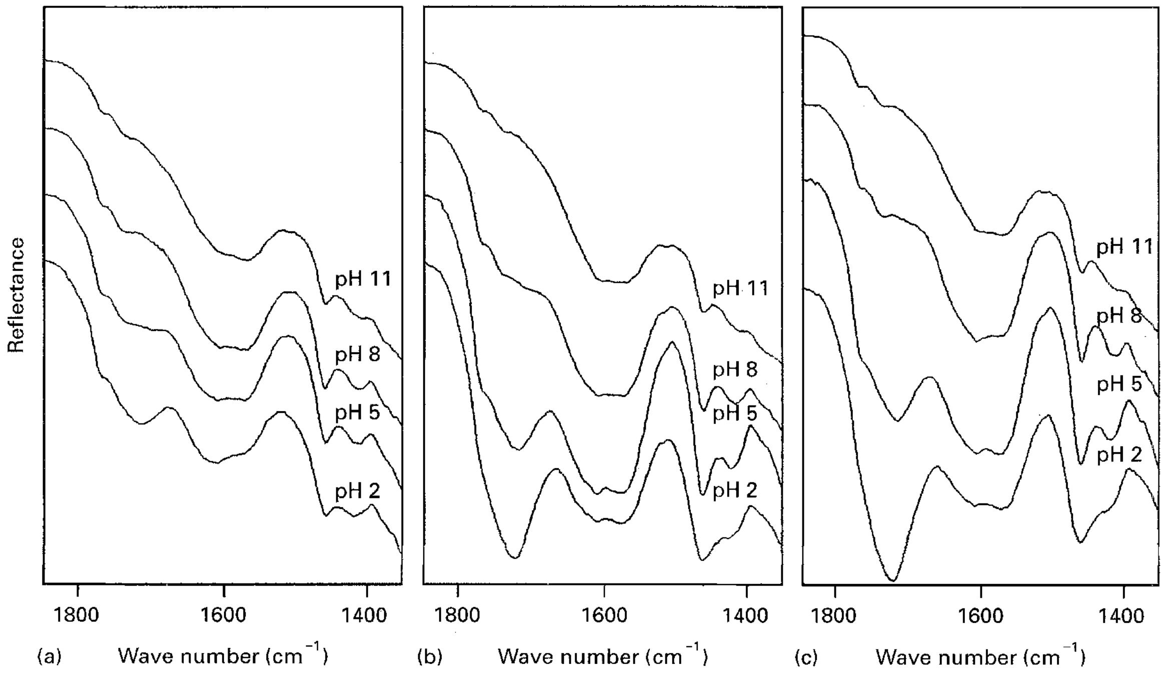

Figure 3 DRIFT spectra for various amounts of sodium polyacrylate adsorbed on alumina from aqueous solutions at various pH values. (a) 0.4 wt %, (b) 1.0 wt %, (c) 2.0 wt %.

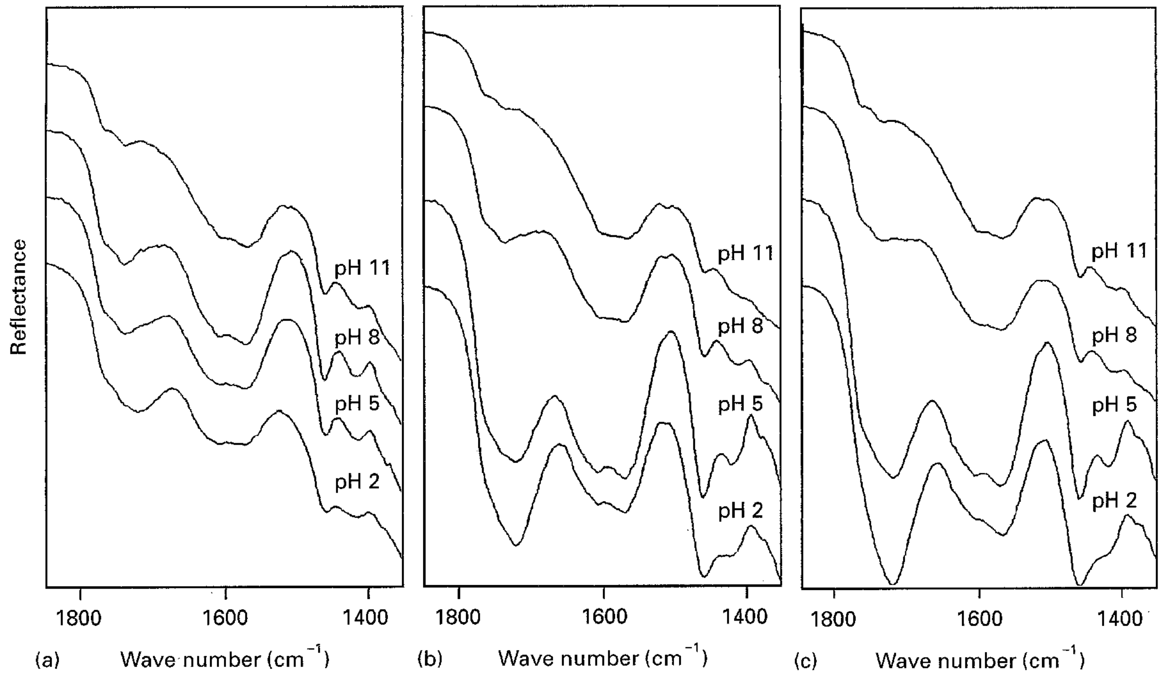

Figure 4 DRIFT spectra for various amounts of ammonium polyacrylate adsorbed on alumina from aqueous solutions at various pH values. (a) 0.4 wt %, (b) 1.0 wt %, (c) 2.0 wt %.

other differences can be noted in the spectra of the ammonium polyacrylate that was adsorbed on the surface. The infrared band observed in the spectrum of the pure ammonium polyacrylate at 1552 cm^{-1} disappears, and new bands appear in the spectra of the corresponding adsorbed species at 1566–1572 cm^{-1}.

Figs 3 and 4 illustrate that the relative band intensities of the protonated and ionized (deprotonated) carboxylate groups follow the expected trends as a function of pH and the concentration of the polyacrylate in original solutions of the slurry. For adsorbed powders prepared at pH 2 from slurries containing 2.0 wt% sodium or ammonium polyacrylate, the resulting spectra possess strong bands at 1720–1722 cm^{-1} associated with the C=O stretching mode of the cyclic dimer, and weak bands at 1604–1606 and 1568–1570 cm^{-1} which are due to C–O stretching modes of deprotonated carboxylate groups. As the pH increases and the concentration of the polymer in the slurries decreases, comparisons of the related spectra demonstrate that the band intensities at 1720–1722 cm^{-1} decrease, showing weak bands at 1736–1740 and 1766–1770 cm^{-1} which are related to side-ways chains and monomer units, respectively. In contrast, the intensities of the bands at 1604–1606 and 1568–1570 cm^{-1} increase. The reduction with pH in relative intensities of the bands due to the protonated carboxylate groups with respect to those of the bands due to the deprotonated carboxylate groups is greatest at 2.0 wt % polyacrylate slurry content, while at pH 2. The DRIFT spectra suggest an increase in the ionization of the polyacrylate on the alumina surface with increasing pH values in the slurry, and decreasing slurry concentration of the polymer. Increasing the pH of the slurry increases the dissociation constant of the polyacrylate. Because polyelectrolytes, such as polyacrylate, ionize progressively, the first group on the polymer molecular does so with an ease similar to that of the small-molecule analogue. However, as progressively more groups are ionized, the increasing total negative charge on the polymer molecule makes it progressively more difficult to remove protons from particular protonated carboxylate groups [5]. Therefore, when the concentration of the polyacrylate increases in the slurry solution, ionization of the polymer is more difficult, resulting in a decrease of the ionization constant due to crowding of the polymer chain.

Some portion of the bands at 1572 cm^{-1} assigned to the asymmetric C–O stretching mode of the carboxylate group of the sodium polyacrylate species shifts to higher wave numbers when the polymer is adsorbed on the alumina surface. The new band at 1604–1606 cm^{-1} can be assigned to the asymmetric C–O stretching mode for carboxylate groups which bond covalently with aluminium ions on the surface of the alumina [2, 6–8]. This change indicates that carboxylate groups in the polyacrylate form complexes with aluminium ions on the surface when the polymer is adsorbed on the alumina. If the metal–carboxylate bonds are not purely ionic, and coordinated complexes occur, then these complexes have some covalent character, and the wave number of the C–O stretching mode shifts. The sodium–carboxylate complexes are purely ionic in an aqueous solution. An earlier study of aluminium polyacrylate showed that when the complex possesses a bridging configuration, the infrared band for the complex appears at 1599 cm^{-1} [9]. Mechanisms are suggested for the formation of the aluminium–carboxylate groups. Some carboxylate groups of the polyacrylate are ionized (deprotonated), so they are negatively charged with increasing pH of the solution. These carboxylate groups bond directly with the positively charged aluminium ion site ($AlOH_2^+$) on the alumina surface in the slurry solution. By drying the slurry, these electrostatically bonded carboxylate groups can convert into covalently bonded carboxylate groups (i.e. the aluminium–carboxylate complexes). This chemistry will be discussed in another section. On the other hand, another early study observed that free protonated carboxylate groups of polyacrylates were adsorbed by dissociatively reacting with the aluminium ions on the aluminium oxide through an acid/base reaction which produced aluminium–carboxylate complexes [6]. Other infrared [10–13] and IETS (inelastic electron tunnelling spectrometry) [14–17] studies also observed that chemisorption occurred by proton dissociation to form carboxylate species when the carboxylate group was adsorbed on the aluminium oxide.

3.3. Variations in the configurations of the adsorbed polyacrylates

3.3.1. *Variations in powders prepared at fixed pH*

As far as determining the nature of the configurations of the adsorbed polyacrylate species on the alumina surfaces with respect to sample preparation is concerned, variations of the observed band locations and intensities for the C=O stretching modes of the protonated carboxylate group with its hydrogen-bonded variations are very useful to predict them for the adsorbed polymer. If geometric and thermodynamic conditions are right, the protonated carboxylate group has a tendency to form a cyclic dimer between the groups by strong hydrogen bond formation [1]. At low pH, pure polyacrylate in an aqueous solution is less ionized, and the polyacrylate species has a low charge density so that it thus adopts a coiled configuration. The protonated carboxylate groups then form cyclic dimers. On increasing pH, more protonated carboxylate groups are ionized, resulting in an increased charge density on the polymer species. Therefore, the polymer forms a stretched-out configuration due to the electrostatic repulsion between ionized carboxylate groups. The protonated carboxylate groups then exist in side-ways chains or isolated monomer units. The isolated monomer units appear when the protonated carboxylate groups are between ionized carboxylate groups. This tendency increases with increasing pH. Therefore, one can see that knowledge of the hydrogen-bonding characteristics for the protonated carboxylate groups for a polyacrylate species can be applied to predict the configurations of the polyacrylate adsorbed on the alumina surface. A higher ratio of the cyclic dimer to the side-ways chain and monomer unit means that the polyacrylate is adsorbed in a more coiled configuration. In contrast, a lower ratio means that the polymer is adsorbed in a more stretched-out configuration.

Figs 3 and 4 show a strong band at 1711–1722 cm^{-1} that is associated with the cyclic dimer for alumina prepared from 2.0 wt % polyacrylate slurry prepared at a pH of 2. On increasing the pH of the slurry, the band at 1711–1722 cm^{-1} vanishes, and a new band begins to appear at 1736–1740 cm^{-1} due to the side-ways chains. The bands at 1766–1768 cm^{-1} for the monomer unit of the protonated carboxylate group are shown under all investigated conditions. These bands become stronger in intensity with respect to the bands for the other protonated carboxylate species as the pH of the slurry increases. With decreasing concentration of the polymer, the intensities of the bands associated with cyclic dimers decrease over all investigated pH values, and the bands due to the side-ways chains and the monomer units begin to appear at lower pH. The reduction in relative band intensities with pH for the cyclic dimers with respect to those for the side-ways chains and the monomer units is greatest for the alumina prepared from 2.0 wt % polyacrylate slurries. On the other hand, the reduction with a fixed concentration of the polyacrylates is greatest at pH 2.

Various configurations occur for the adsorbed polyacrylates at different preparation conditions. The DRIFT spectra indicate that at lower pH or higher concentration of the polyacrylate, the polymer is adsorbed in a more coiled configuration on the alumina surface. On decreasing pH or increasing the concentration of the polymer, the adsorbed polymer has a less coiled configuration (i.e. a more stretched-out configuration). This result indicates that the configurations of the adsorbed polymer depend strongly on the degree of ionization of carboxylate groups and the surface charge of the alumina. Varying the solution pH affects not only the degree of ionization of the polymer but also the surface charge on the alumina particles. The observed point of zero charge (p.z.c.) of the as-received alumina powder is 9.5. The pK_a of polyacrylate is reported to be approximately 4.5 [18, 19]. At pH 2, the surface of the alumina is positively charged. On the other hand, the polymer is almost uncharged, resulting in a decrease of the molecular dimensions (i.e. coiled configuration) because of fewer electrostatic repulsions between ionized carboxylate groups. The carboxylate groups of the polymer having residual negative charges are attracted on to the positively charged sites on the surface. Consequently, the polymer chain is adsorbed in a relatively coiled configuration with an enhanced loop formation, accounting for the relatively higher intensity of the band at 1711–1717 cm^{-1} for the cyclic dimer. As the pH increases, the polymer is significantly ionized as the pH reaches 4–5. The electrostatic repulsion between the charged carboxylate groups, and the attraction to the positively charged sites on the surface inhibits loop formation of the adsorbed polyacrylate. The polymer is adsorbed in a stretched-out configuration on the surface, resulting in the increased intensities of the bands due to the side-ways chains and monomer units of the protonated carboxylate groups. Adsorption of polymer is inhibited when the charge of the alumina surface is negative enough in magnitude for electrostatic repulsive forces. The DRIFT spectra shows that even at pH 11 (above the p.z.c. of the alumina), the polyacrylate is adsorbed on the surface of the alumina. At this pH, the polymer can be adsorbed on a few positively charged sites even though the net surface charge of the alumina is negative. Even at pH 11, at which all of the carboxylate groups are ionized, bands due to the side-ways chains and monomer units are observed in the spectra of the adsorbed polyacrylate species for all polyacrylate concentrations. Other studies showed that the amount of polyacrylate adsorbed on an oxide increased when the polymer chain was adsorbed in a coiled configuration [20, 21]. On the other hand, as the polymer concentration increases, more competition for adsorption takes place on the surface. Furthermore, it makes the polyacrylate more difficult to be ionized, resulting in the formation of more coiled configurations of the polymer chain. Consequently, this leads the polymer to be adsorbed in a more looped formation and with a thickening of the adsorption layers, resulting in increased intensity for the bands of the cyclic dimer.

3.3.2. Variations in powders prepared from slurries in which the pH is changed

DRIFT spectra were investigated for aluminas prepared from 1.0 wt % sodium polyacrylate slurries, where the pH values were changed in steps from initially 2 to 11, and from initially 11 to 2 after ageing the slurries for 24 h. The ratios of the intensities of the bands for the monomer units and side-ways chains to those of the bands for the cyclic dimers are higher when the pH is changed initially from 11 to 2. Also, the intensities of the band due to the cyclic dimers with respect to those of the bands at 1603–1608 cm^{-1} due to the covalently bonded carboxylate groups and at 1568–1577 cm^{-1} due to the ionically bonded carboxylate groups are stronger for the samples initially prepared at pH 11 and then changed to pH 2. This result indicates that the sodium polyacrylate adsorbed from the solution prepared initially at pH 11 and then changed to pH 2 has less-coiled configurations than that from the slurry initially prepared at pH 2.

The various configurations of the polyacrylates adsorbed at fixed pH and changing pH are illustrated in Fig. 5. When the sample is prepared initially at pH 2, a few negatively charged carboxylate groups of the polyacrylates are attracted to the positively charged sites on the alumina surface in a coiled configuration. As the pH increases, the polymer is significantly ionized so that the number of the negatively charged carboxylate groups and the adsorption sites on the alumina surface increase. The polymer chain which is adsorbed then stretches out on the surface because of the increased electrostatic repulsion between negatively charged carboxylate groups. Newly ionized carboxylate groups are attracted on the positively charged sites on the surface, until all of the positively charged sites on the surface are consumed by the adsorption of the newly ionized carboxylate groups. Then, the configurations of the adsorbed polymer species become flat. In contrast, when the sample is prepared at initially pH 11, the carboxylate groups bond with a few positively charged sites on the surface. The polyacrylate is then adsorbed in a stretched out configuration. With decreasing pH of the solution, the polymer is less ionized, and the number of the negatively charged carboxylate groups decreases. The polymer chain will try to coil because of the reduced electrostatic repulsion between the carboxylate groups. However, relatively strong bonding between the negatively charged carboxylate groups and the positively charged sites on the surface resist the coiling of the polyacrylate, resulting in a less-coiled configuration than that obtained from the slurry initially prepared at pH 2.

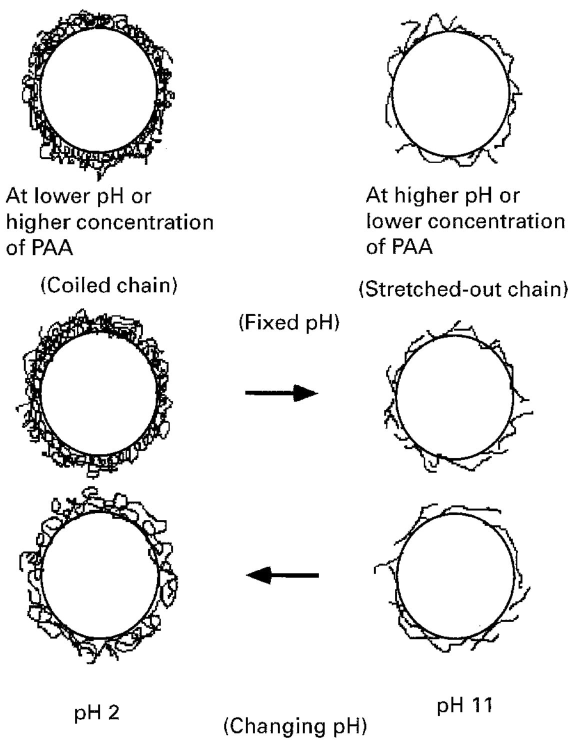

Figure 5 Various configurations for polyacrylate adsorbed at fixed and changing pH values.

3.4. Effects on the ratio between covalently and ionically bonded carboxylate groups in the polyacrylate species

Figs 3 and 4 reveal bands associated with the covalently bonded carboxylate groups involving aluminium ions at 1602–1606 cm^{-1}, and bands associated with ionically bonded carboxylate groups on the alumina surface at 1567–1571 cm^{-1}. For the alumina powders prepared from 0.4 wt % sodium polyacrylate slurries at pH 2, the intensity of the band for the covalently bonded carboxylate groups is stronger with respect to that of the band for the ionically bonded carboxylate groups. Upon increasing the pH, the band intensity at ~1606 cm^{-1} decreases. In contrast, the band due to the ionically bonded carboxylate groups becomes stronger. At higher polymer concentration with increasing pH, the band intensity at ~1570 cm^{-1} decreases with respect to that at ~1606 cm^{-1}, indicating that the concentration of the covalently bonded carboxylate group increase.

These trends can be explained on the basis of the amounts of the ionically bonded COO$^-$–Na$^+$ and the covalently bonded COO–Al in the adsorbed polyacrylate. These concentration variations can be related to the ionization behaviour of the polymer, the typical adsorption isotherm for the polymer on alumina, and the degree of coiling for the adsorbed polymer. Adsorption isotherm studies by early investigators [8] showed that the adsorbed amount of the polymer increases with decreasing pH and increasing concentration of the polymer. On increasing pH, the amount of the adsorbed polymer decreases more suddenly at higher polymer concentration than at lower polymer concentration. On the other hand, as the polymer concentration increases, the amount of the adsorbed polymer increases more at lower pH rather than at higher pH.

For the aluminas prepared from 0.4 wt % sodium polyacrylate slurries at pH 2, most of the ionized carboxylate groups (COO^-) bond with positively charged aluminium ion sites ($AlOH_2^+$) on the surface in the solution. These species bond to each other by electrostatic attraction, and are converted to the covalently bonded aluminium–carboxylate complexes by the drying procedure, which contribute to the band at 1606–1610 cm^{-1}. A few carboxylate ions isolated with aluminium ions can possibly remain as ionically bonded COO^-–Na^+ species. These differences account for the relatively higher band intensity at 1606 cm^{-1} to that for the band at 1570 cm^{-1}. Increasing the pH above the p.z.c. increases the negatively charged sites on the polymer and the alumina surface. Therefore, all of the carboxylate groups cannot bond with Al–OH_2^+ species, resulting in the increased ionically bonded COO^-–Na^+ species. On increasing the concentration of the polymer to 2.0 wt % in the slurry at pH 2, the amount of the adsorbed polymer greatly increases. Furthermore, as a result of the competitive adsorption between carboxylate groups, the polymer is highly coiled, and the adsorbed layer is thickened. Therefore, all of the ionized carboxylate groups cannot bond effectively with $AlOH_2^+$ sites, so that some of them remain as COO^-–Na^+ bonds. These conditions result in the increased intensity for the band due to the ionically bonded carboxylate groups even though the polymer is less ionized compared to that for aluminas with lower polymer concentration. As the pH increases with a slurry whose polymer concentration is 2.0 wt %, the adsorbed amount and the degree of coiling of the polymer decrease to a great extent. These conditions result in increased amounts of covalently bonded carboxylate groups even though electrostatic repulsion exists between the polymer species and the alumina surface.

3.5. Differences between sodium and ammonium polyacrylate powders

Ammonium polyacrylate shows the same trends as the sodium polyacrylate in terms of the configurations of the adsorbed polymer on the surface of the alumina, and the ratio with respect to the ionically and covalently bonded species. However, there are some differences that are observed. First, the relative intensity of the band associated with the cyclic dimers with respect to those due to the side-ways chains and the monomer units is stronger for the ammonium polyacrylate than for the sodium polyacrylate. Second, the relative intensity of the band for the ionically bonded carboxylate groups with respect to that for the covalently bonded carboxylate groups is stronger in the spectra for the ammonium polyacrylate than the sodium polyacrylate. These results indicate that ammonium polyacrylate is adsorbed in more coiled configurations, and bonds more ionically on the alumina surface than sodium polyacrylate.

3.6. Effect of surface impurities on polyacrylate adsorption

DRIFT spectra were measured for polyacrylate-treated aluminas (two different lots initially containing different amounts of sodium ion) that were prepared from aqueous slurries containing 1.0 wt % sodium polyacrylate at various pH values. The relative intensity for the band at 1570 cm^{-1} associated with ionically bonded carboxylate groups with respect to that for the band at ~1600–1610 cm^{-1} associated with covalently bonded carboxylate groups is stronger in the DRIFT spectra for the alumina containing more sodium ions for all investigated pH values. The former as-received alumina contains significantly more $NaHCO_3$ on its surface than the latter one, and slightly more Na^+ ions were leached out of it by water. These observations indicate that $NaHCO_3$ or Na^+ ions on alumina surfaces play important roles in the adsorption process with respect to the carboxylate groups in the polyacrylates. The Na^+ ions or $NaHCO_3$ on the alumina surfaces inhibit the carboxylate groups in the sodium polyacrylate chains from easily bonding with the aluminium ions on the surface.

3.7. Effect of water vapour on polyacrylate adsorption

The effect of water adsorption on polyacrylate adsorption on alumina powder is spectrally illustrated in Fig. 6. After water vapour-treatment of dried powders, on which polyacrylate was adsorbed, the relative intensity of the band due to ionically bonded carboxylate groups increases with respect to that of the band due to covalently bonded carboxylate groups. By water adsorption, some covalent bonds between aluminium ions and carboxylate groups are broken, generating ionic carboxylate groups. In this investigation, the dried powder after water adsorption can be considered as being analogous to a green compact. The preceding observations indirectly indicate that in an aqueous alumina slurry, a large number of the carboxylate groups on the adsorbed polyacrylate chains are ionic. On the other hand, in the green compact which is formed after drying the slurry, a significant number of ionically bonded carboxylate groups convert into covalently bonded carboxylate groups.

4. Conclusions

1. DRIFT spectroscopy is a very useful and powerful technique to study the adsorption of polymers such as polyacrylates on ceramic powders such as alumina.

2. The presence of sodium ions or sodium bicarbonates on the alumina surface inhibits carboxylate

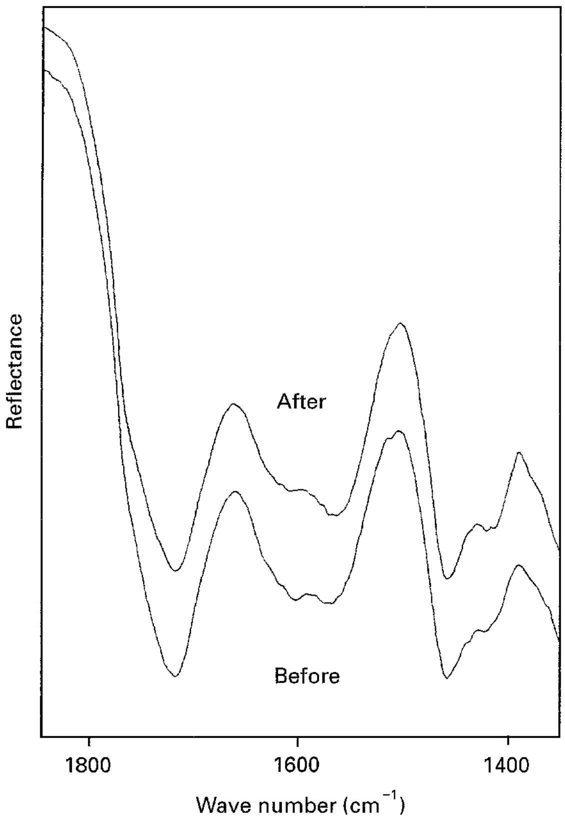

Figure 6 DRIFT spectra for sodium polyacrylate (1.0 wt %) adsorbed on surfaces of alumina from aqueous solutions with and without adsorption of water vapour.

groups in the polyacrylate chain from bonding with aluminium ions on the surface.

3. In alumina powders prepared from aqueous slurries at lower pH values or with higher concentrations of the polyacrylate, the formation of the coiled polymer form is preferred to that of the stretched-out form. The adsorbed polymer chains from sodium polyacrylate have much more stretched-out configurations than adsorbed chains from ammonium polyacrylate.

4. When the slurry pH changes from 2 to 11, the adsorbed polyacrylate species change from coiled configurations to stretched-out configurations. However, in the reverse process when the pH changes from 11 to 2, the adsorbed polyacrylate does not change as completely from stretched-out configurations to coiled configurations as is observed if the polyacrylate is initially at pH 2.

5. With increasing slurry pH and lower concentrations of the polyacrylate, ionic bonding increases for the carboxylate groups. In contrast, at higher concentration of polyacrylate, covalent bonding increases for them. More carboxylate groups of polyacrylate chains are bonded ionically on the alumina surface from ammonium polyacrylate than from sodium polyacrylate.

6. Adsorbed water on the surface of polyacrylate-treated aluminas changes some covalently bonded carboxylate groups into ionically bonded carboxylate groups.

References

1. L. J. BELLAMY, "The Infra-red Spectra of Complex Molecules" (Chapman & Hall, London, 1975).
2. M. A. ROMERO, B. CHABERT and A. DOMARD, *J. Appl. Polym. Sci.* **47** (1993) 543.
3. K. ITO and H. J. BERNSTEIN, *Can. J. Chem.* **34** (1956) 170.
4. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" (Wiley Interscience, New York, 1978).
5. P. MOLYNEUX, "Water-Soluble Synthetic Polymers: Properties and Behavior", Vol. II (CRC Press, Boca Raton, FL, 1984) pp. 751–756.
6. D. L. ALLARA, in "Adhesion and Adsorption of Polymers", edited by Lieng-Huang Lee (Plenum Press, New York, 1980).
7. S. CRIPS, H. J. PROSSER and A. D. WILSON, *J. Mater. Sci.* **11** (1976) 36.
8. N. SHASHIDAR, J. R. VARNER, R. A. CONDRATE Sr, in "Ceramic Powder Science-III", "Ceramic Transactions", Vol. 12, edited by G. L. Messing, S. I. Hirano and H. Hausner (American Ceramic Society, Westerville, OH, 1990) pp. 443–446.
9. P. H. McCLUSKEY, R. L. SNYDER and R. A. CONDRATE Sr, *J. Solid State Chem.* **83** (1989) 332.
10. D. L. ALLARA and R. G. NUZZO, *Langmuir* **1** (1985) 52.
11. Y. NOTO, K. FUKUDA, T. ONISHI and K. TAMARU, *J. Chem. Soc. Farad. Trans. I.* **63** (1967) 2300.
12. K. KONSTADINIDIS, B. THAKKAR, A. CHAKRABORTY, L. W. POTTS, R. TANNENBAUM, M. TIRRELL and J. F. EVANS, *Langmuir* **8** (1992) 1307.
13. A. V. KISELEV and A. V. UVAROV, *Surf. Sci.* **6** (1967) 399.
14. B. F. LEWIS, M. MOSESMAN and W. H. WEINBERG, *ibid.* **41** (1974) 142.
15. N. M. D. BROWN, R. B. FLOYD and D. G. WALMSLEY, *J. Chem. Soc. Farad. Trans. II.* **75** (1979) 17.
16. *Idem, ibid.* **75** (1979) 32.
17. R. F. COLLETTI, H. S. GOLD and C. DYBOWSKI, *Appl. Spectrosc.* **41** (1987) 1185.
18. A. S. MICHAELS and O. MERELOS, *Ind. Eng. Chem.* **47** (1955) 1801.
19. C. J. BLOYSVAN TRESLONG and A. J. STAVERMAN, *Rec. Trav. Chim. Pay-Bas* **93** (1974) 171.
20. J. CESARANO III, I. A. AKSAY and A. BLEIER, *J. Am. Ceram. Soc.* **71** (1988) 250.
21. J. E. GEBHARDT and D. W. FUERSTENAU, *Colloids Surf.* **7** (1983) 221.
22. R. R. VEDULA and H. G. SPENCER, *ibid.* **58** (1991) 99.

Received 13 July 1994
and accepted 15 August 1995