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Nature of interfacial interaction mechanisms between polyacrylic acid macromolecules and oxide metal surfaces

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The mechanism for the adhesion of polyacrylic acid (PAA) coatings to oxidized metal surfaces has been studied. The work entailed studies of the mechanical and chemical interactions occurring at the interfaces between PAA polyelectrolyte macromolecules and iron (III) orthophosphate dihydrate or zinc phosphate hydrate (hopeite) crystalline films that were deposited on the metal surfaces. With respect to mechanical interactions, it was determined that the surface topography of the highly crystallized hopeite layers consisted of an open microstructure. This resulted in enhanced wettability of the oxide film by the polyelectrolyte macromolecules, thereby increasing the mechanical interlocking bond forces. Studies of the interfacial chemical reactions indicated that the conformation changes in the PAA macromolecules relate directly to the frequency of the magnitude of acid–base and divalent metallic ion crosslinking interactions between the proton-donating pendent COOH groups in PAA molecules and polar OH groups at hydrated oxide surface sites. Namely, the presence of numerous free nucleophilic ions existing on the deposited oxide film leads to a substantial increase in the coil-up and entanglement macromolecule density. These entangled complex macromolecules at the interfaces result in a decrease in the degree of chemisorption at the oxide film surfaces, whereas regularly oriented COOH groups produce strong interfacial chemisorption with the polar OH groups. Since the polyelectrolyte macromolecules have hydrophilic pendent COOH groups, the polymer structure which appears best for use as an adhesive and coating should have only enough hydrophilic COOH groups to occupy all available polar OH groups at the oxide metal surface sites.

1. Introduction

The effects of functional carboyxlic acid (COOH) groups located in the pendent of polyacrylic acid (PAA) on ionic reactions and adsorption are of primary interest in understanding the fundamental adhesion mechanisms between polar oxide metal surfaces and functional polyacid macromolecules. The PAA molecule, which is generally expressed as a polyelectrolyte macromolecule, is characterized by a simple chemical structure consisting of a stabilized hydrophobic main chain $(-CH_2-CH-)_n$ and the hydrophilic pendent (COOH) groups. Several studies of the reactions between ions and polyelectrolyte macromolecules have been made, using spectroscopic and polarographic techniques and with pH titration curves [1–5]. Other reports dealing with polymer adsorption in which the adsorbed segments interact in the surface layers have emphasized theoretical studies [6–10].

When divalent metallic ions such as Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+} and Mg^{2+} are introduced into macromolecules, it has been reported [11] that ion-exchange reactions occur between the proton donor COOH groups and the essentially electrostatic ions. The active ions of higher valency contribute to the formation of inter- and intra-

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molecular crosslinking of the polyelectrolyte macromolecules caused by the salt-bridge structure which replaces two hydrogens in the COOH groups. Once the polyacid is ionically crosslinked, this complexed macromolecule has enhanced mechanical properties, higher glass transition temperatures, hydrolytic stability and resistance to chemicals. These composite materials, all based on metal ion–polyanion reaction systems, are currently being used for dental applications, for example, as filling materials for restoring teeth and for cementing inlays and crowns into place [12–16]. In the dental cement applications, calcinated aluminosilicate glass [17] and ZnO–SnF_2 [18] compound powders are used as a source of ion-exchangeable metal cations which are rapidly dissociated in an aqueous solution of polyacid. The influence of these ion-leachable powders on the salt-bridged polymer formation can be interpreted by the acid–base and ion-exchange reactions associated with charge transfer mechanisms.

Recently, the ability of polyacid to function as an adhesive at an ionic interface was investigated by using Fourier Transform IR Spectroscopy techniques [19]. This study emphasized that the degree of neutralized polyelectrolyte macromolecule conformation results in a fraction of bound segments on the adsorbed molecules.

Since one of the main factors affecting the durability of protective coatings is the adhesion force to metal substrates, it is very important to understand the nature of the adhesion mechanisms and how they effect the interactions between the functional polyacids and the metal surfaces. Hence, in the present work we have made a systematic assessment of how the adhesive and absorption mechanisms at the polyelectrolyte macromolecule-treated oxide metal interfaces affect the interfacial bond strength and the role of the interface in adhesion processes. This elucidation of the interfacial interaction mechanisms will provide the ability to utilize polyelectrolyte macromolecules as an adhesive and a coating.

Generally, good bonding can be attributed to the following four elements: (i) mechanical interlocking associated with the surface topography of metals, (ii) surface wettability of metal by the polymers, (iii) strong chemisorption, and (iv) type and degree of polymer–metal interfacial interaction. Modifications to the metal surfaces are very important to successful bonding. Therefore, two types of chemically oxidized metal surfaces were evaluated in this study: (a) iron phosphating crystalline and (b) zinc phosphating crystalline layers. The investigation of the interaction at the polyacid–oxide metal interfaces was conducted by using scanning electron microscopy, X-ray fluorescence, X-ray powder diffraction, contact angle analysis, infrared spectroscopy and lap shear bond strength methods.

2. Experimental procedure

2.1. Materials

Commercial polyacrylic acid (PAA), 45% solution in water, having an average molecular weight of 104 000, was supplied by Scientific Polymer Products, Inc. The pendent carboxylic acid (COOH) groups on the macromolecules were partially neutralized by adding the calculated amount of sodium hydroxide (NaOH). The degrees of neutralization used were 0, 20, 40, 60 and 80%.

In order to deposit iron phosphate and zinc phosphate crystalline films onto metal substrate surfaces, the metal surfaces were polished with ultrafine emery paper and then chemically treated in an oven at 60° C for up to 24 h. In the iron phosphate experiments, the polished metal surface was immersed in a dilute (pH ~ 2.5) solution of phosphoric acid (H_3PO_4). The zinc phosphate was deposited by immersing the metal in an acidic solution consisting of 9 parts zinc orthophosphate dihydrate [$Zn_3(PO_4)_2 \cdot 2H_2O$] and 91 parts 15% H_3PO_4 solution. The pH of this solution was ~ 2.0.

2.2. Measurements

The surface topography and morphology for the chemically treated metal adherends were analysed by AMR 10 nm scanning electron microscopy (SEM) associated with TN-2000 energy dispersive X-ray spectrometer (EDX).

A Perkin-Elmer Model 257 Spectrometer was used for infrared spectroscopic (IR) analysis. To obtain the basic information regarding the interfacial reaction mechanisms, IR spectra were obtained for the samples prepared in the form of KBr discs. The samples were powdered before mixing and grinding with KBr.

The magnitude of the wetting force of the oxidized metal surfaces by polyelectrolyte macromolecules and water molecules was measured using a Contact Angle Analyzer in a 60% RH and 24° C environment. All of the data were determined within 30 sec after drop application.

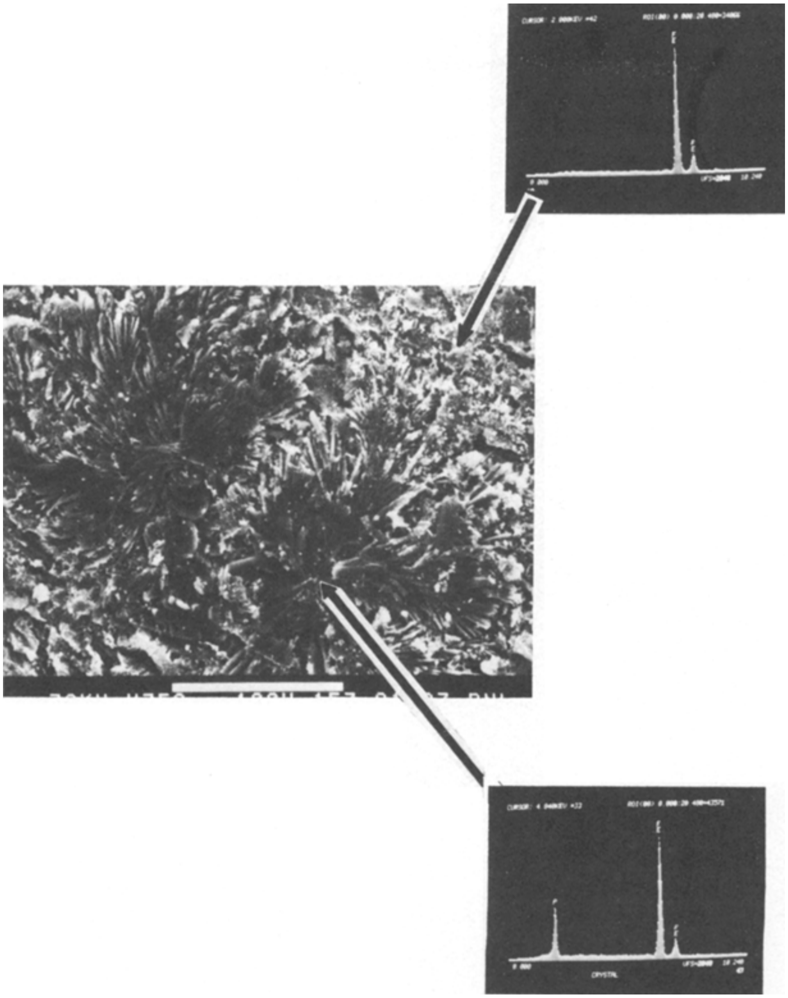


Figure 1 Scanning electron micrograph and EDX peak of H_3PO_4-treated metal surfaces.

X-ray powder diffraction (XRD) analyses were employed to identify the oxide compound layers deposited on the treated metal surface. To prepare the fine powder samples, the deposited oxide layers were removed by scraping the surfaces and were then ground to a size of ~ 325 mesh (0.044 mm).

The lap shear tensile strength of metal-to-metal adhesives was determined in accordance with the modified ASTM method D-1002. Prior to overlapping between metal strips 50 mm long, 15 mm wide and 2 mm thick, the $10 \times 15\,mm^2$ lap area was coated with the neutralized polyelectrolyte macromolecular adhesives. The thickness of the overlapped film ranged from 1 to 3 mil. The bond strength values for the lap shear specimens are the maximum load at failure divided by the total bonding area of $150\,mm^2$.

2.3. Surface topography

Since the nature of the surface micromorphology [20, 21] and the thickness [22, 23] of the deposited oxide layers relate directly to the bonding forces at the interface, two different oxide film surfaces were examined by SEM and EDX. As illustrated in Figs. 1 and 2, the micromorphology and topography yielded by these two surface preparations appeared to be very different. The topographical image of the H_3PO_4-treated surface (see Fig. 1) seems to consist of two discriminable layers. Analyses of EDX peaks indicated that one of the layers consisted of irregularly deposited iron phosphate crystals and the other of iron oxide. The former was composed of crystals characterized by circular radiating and thin plate-like features. On the basis of the strong spacing at

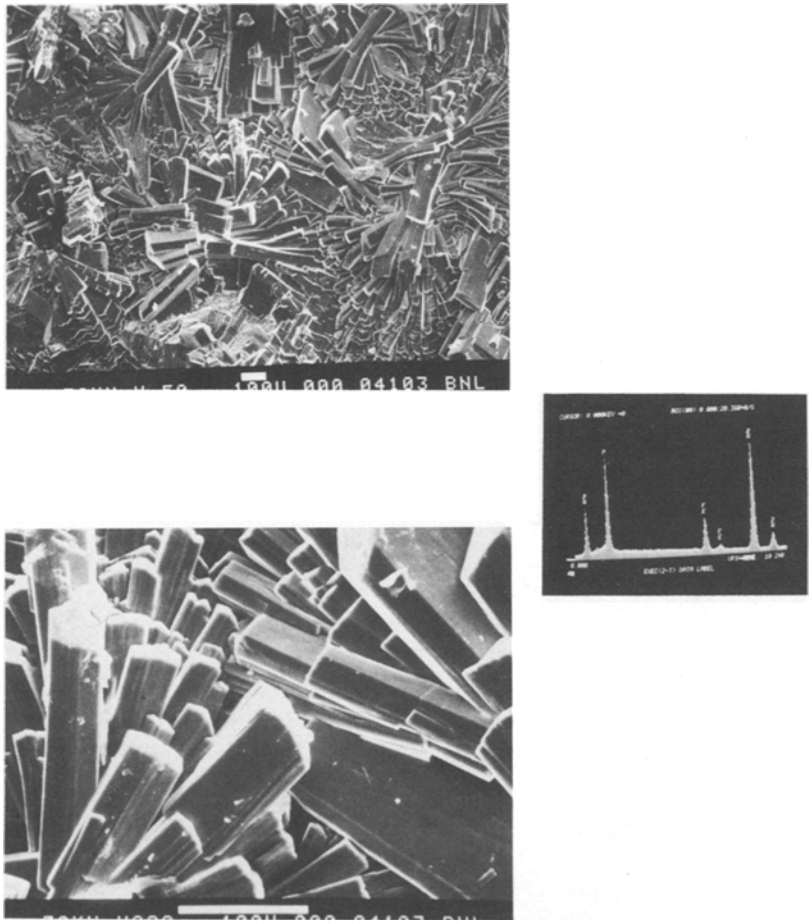


Figure 2 SEM photomicrographs and EDX diffraction peak of a lamellate block-like hopeite crystal prepared on metal.

0.328 and 0.360 nm on XRD patterns in the diffraction range 0.884 to 0.154 nm, the crystallized compound layer was identified as iron (III) orthophosphate dihydrate ($FePO_4 \cdot 2H_2O$). This was also confirmed by IR spectra analysis, which will be discussed in later sections of the paper. From SEM observations, it appears that the concentration of the crystal clusters of $FePO_4 \cdot 2H_2O$ cover ~ 70% of the treated metal surface. Therefore, the H_3PO_4-treated surface appears to consist of a hybrid layer of $FePO_4$–Fe_2O_3–H_2O absorbed on porous Fe oxide.

Fig. 2 shows large lamellate block crystal growths of zinc phosphate hydrate compound layers arrayed uniformly on all surfaces of the modified metal sites. The XRD patterns for these crystalline powder samples disclosed a strong peak intensity at 0.457 and 0.283 nm. Accordingly, the highly crystallized layers indicated the formation of hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$. As seen in the figure, the main microstructure features of deposited hopeite films, compared with those for iron phosphate films, are extreme roughness, greater crystal thickness and a more open surface structure. Because of these topographical features, it is expected that the regularly interlocked hopeite crystals will provide a larger surface area for bonding and give sufficient mechanical interlocking with adhesives. Also, penetration of adhesives into the pores on the open surface microstructure will help to enhance the bond at the polymer–hopeite interfaces. In addition to the information obtained from XRD, it appears from EDX peaks that some zinc is likely to be replaced by ferrous ions. By comparing the microstructure and surface topography of these two different hydrated oxide layers, work was initiated to define the micromorphological features that contribute to the adhesion behaviour at the polyelectrolyte macromolecule–oxidized metal interfaces.

2.4. Wetting behaviour

The wettability and the adsorption behaviour of polyelectrolyte macromolecules on oxide layers were investigated on the basis of contact angle measurements made 30 sec after deposition on the test surfaces. For this work, a 10% PAA solution was prepared by diluting 45% PAA with distilled water. The primary purpose of this study was to evaluate quantitatively the degree of interfacial interactions of the functional COOH groups and to assess the correlations that may exist between the surface morphological features of oxide films and the dispersion forces of polyelectrolyte macromolecules. Both the conformation and orientation of the pendent polar groups in polyacid macromolecules will contribute to the magnitude of surface wettability and spreadability onto the oxide films. Thus, in order to describe how the regularly oriented macromolecule affects the dispersion function and efficiency, the pendent COOH groups were neutralized by adding NaOH. The changes in conformation of PAA molecules neutralized in the range of 0 to 80% were apparently verified by the shift in IR spectra for these samples, as shown in Fig. 3. The most pronounced changes in these frequencies were an increase in the peak intensity of two new bands at 1550 and 1400 cm^{-1} with an increase in the degree of neutralization. In addition, the carbonyl C=O group frequency at 1710 cm^{-1} tends to shorten with increased degrees of neutralization. The absorption bands at 1550 and 1400 cm^{-1} can be assigned to the asymmetrical and symmetrical stretching vibrations of carboxylic anions, COO^-. The spectra from the 80% neutralization sample indicates the almost complete disappearance of the conventional band at 1710 cm^{-1}. These results clearly demonstrate that salt complex formations having $\text{COO}^-\ \text{Na}^+$ groups were yielded by the acid–base reaction between the carboxylate anions formed by proton donor characteristics of the arrayed carboxylic acid groups and the active neucleophilic Na^+ ions dissociated with NaOH in the PAA solutions. These conformational changes contribute to the subsequent entanglement and coiling of the macromolecules. Since the extent of the intermolecule entanglement increases with the degree of neutralization, the loss of functional groups at available absorption sites in the molecular chains may result in decreased dispersion and wettability forces on oxide surfaces by PAA polymers.

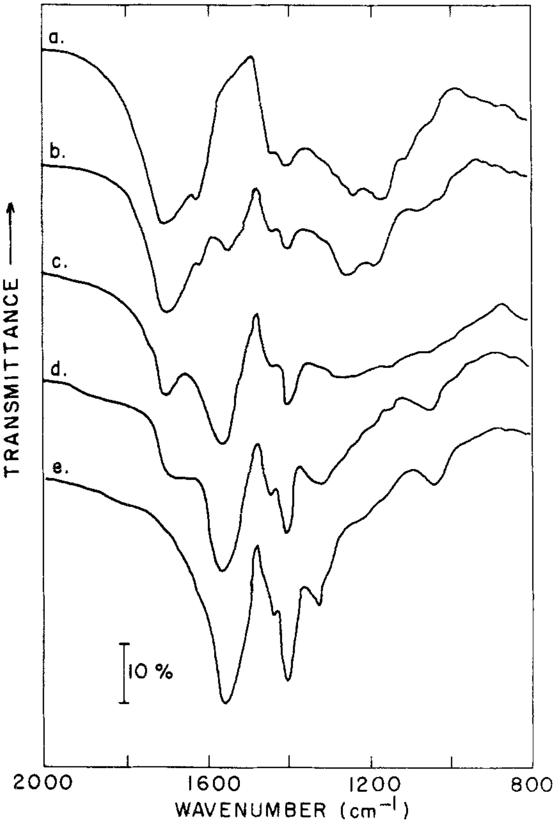


Figure 3 Infrared spectra of PAA polymers neutralized by NaOH; (a) 0%, (b) 20%, (c) 40%, (d) 60% and (e) 80% neutralization.

The improved wettability of metals by the macromolecules is attributed not only to interfacial interactions between the polar groups in the polymer and the oxide layers, but also to the enhanced activation of modified metal surface sites at which the energetics of adsorption are particularly favourable. The contact angles on the metal surface were measured as a function of the age of the chemical treatment. PAA solutions with 0, 20 and 40% neutralization were employed in this test series. The data, shown in Fig. 4, indicate that the contact angles for both the H_3PO_4- and $Zn_3(PO_4)_2 \cdot 4H_2O$-treated surfaces tend to decrease with increasing treatment times. When a non-neutralized PAA solution was used, the contact angles after a 24 h surface treatment were reduced by ~ 63% and ~ 81% for the H_3PO_4- and $Zn_3(PO_4)_2 \cdot 4H_2O$-modified surface layers, respectively, when compared with those from polished surfaces. Although the contact angles were measured using a neutralized PAA, the magnitude of the angle reduction for the $Zn_3(PO_4)_2 \cdot 4H_2O$

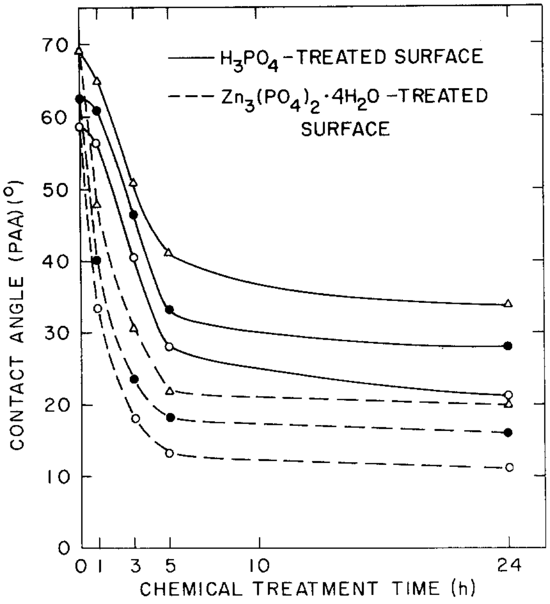


Figure 4 Changes in contact angle of oxide layers by non-neutralized and neutralized PAA as a function of the age of chemical treatment; (○) 0%, (●) 20% and (△) 40% neutralization.

layers is considerably higher than that for H_3PO_4-treated layers at the same age. This indicates that the open surface microstructure of hopeite crystals is easier to wet. The data further indicate that an increased degree of neutralization results in an increase in the contact angle. From these observations, it can be concluded that the migration of collectively entangled macromolecules leads to a decrease in the magnitude of the spreading and capillary forces, the magnitude of the interfacial wetting force is primarily dependent on the conformation changes in adhesive molecules and the surface topography of the deposited oxide films, and the presence of highly crystallized hopeite layers which have an open surface microstructure increases the wettability and dispersion of polyelectrolyte macromolecules.

2.5. Chemisorption

The purpose of the chemical treatment is not only to increase the roughness of the metal surface, thereby enhancing mechanical interlocking bonds, but also to modify the surface chemical composition. Thus, it was considered that the increase in wettability discussed above may also have been due to interfacial interactions and conformation changes induced by chemical reactions between the functional COOH groups and the oxidized metal layers. To elucidate the nature of the interfacial chemical reaction mechanisms, these oxide layers were removed by scraping the metal surfaces, and the removed oxide metal powders were then ground to a size of ~ 325 mesh (0.044 mm). Samples were prepared by mixing PAA polymers with the finely powdered oxide compounds and subsequently curing them in an oven at 70° C for 10 h.

Fig. 5 shows IR spectra for iron phosphate compounds, bulk PAA polymers and iron phosphate–PAA composites. IR analysis showed conspicuous bands at frequencies of 3400 and 1030 cm^{-1} in the spectra for the iron phosphating powder. These indicate the formation of iron (III) orthophosphate. The broad band near 3400 cm^{-1} can be ascribed to the vibration of the bonded hydroxyl (OH) groups of the hydrated oxide films, while the band at 1030 cm^{-1} may be due to the vibration of PO_4^{-3} in $FePO_4 \cdot 2H_2O$ compound formations. Although frequencies under 600 cm^{-1} are not shown in the figure, the presence of divalent Fe ions was confirmed by two adsorption bands at ~ 570 and 375 cm^{-1}.

The bulk PAA polymer samples exhibited major

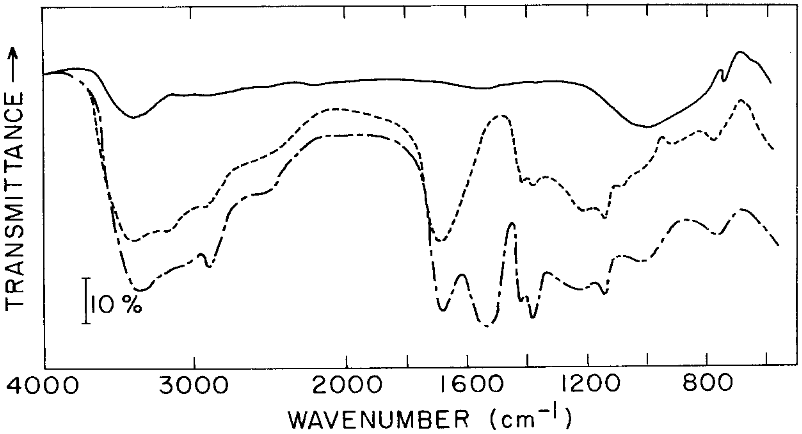
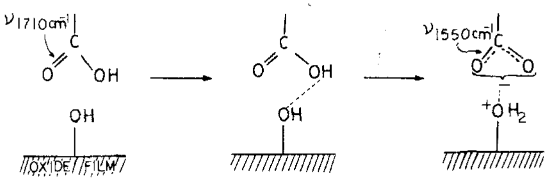


Figure 5 IR spectra of iron phosphate/PAA composite samples; (———) iron phosphate hydrate compounds, (– – –) bulk PAA polymers, and (–·–·–) PAA composites containing hydrated iron phosphate powders.

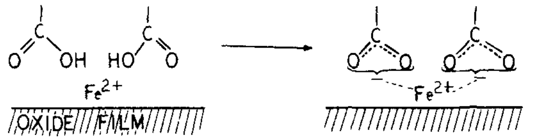
IR bands at frequencies of 3400, 1710, 1430, 1380 and 1160 cm^{-1}. The band around 3400 cm^{-1} is characteristic of O–H stretching. The adsorbance of carboxyl (C=O) groups is represented by the intense peak at 1710 cm^{-1}, and the bands at 1430 and 1380 cm^{-1} are associated with the dimeric OH in-plane bending coupled with C–O stretching, and the vibration of methyl groups, respectively. The band at 1160 cm^{-1} may be assigned to the O–H in-plane deformation mode.

When compared with the above two spectra, the spectrum for the iron phosphate–PAA composite samples was characterized by the pronounced presence of two new bands at 1550 and 1398 cm^{-1} and a shorter band intensity for C=O groups at 1710 cm^{-1}. Since these new peaks are attributed to the asymmetrical and symmetrical vibrations characteristic of carboxylate anion (COO^-) groups, it is presumed that interfacial interaction between the COOH groups and the hydrated oxide layers is due to the following two hypothetical mechanisms:

Type A: Acid–base surface interaction mechanisms



Type B: Salt-bridge intermolecular reaction mechanisms by free ferrous ions



Type A consists of a strong ionic interaction associated with charge transfer bonding mechanisms which predominate over weaker dipole interactions. Thus, it is believed that the carboxylate anions (COO^-) produced by acid–base surface interactions occurring between the functional carboxylic acid (COOH) groups and the polar hydroxyl (OH) groups on hydrated oxide surface sites are strongly chemisorbed to oxidized metal surfaces. This significantly enhances the wettability and the bonding properties.

As an alternative possibility, mechanism **B** is the salt-bridge formation brought about by ionic bonding between the free Fe^{2+} ions existing on the oxide surface sites and the COO^- anions. This formation leads to a substantial increase in the coil-up and the entanglement intermacromolecule density. The entangled molecules at the interface result in a decrease in the polymer adsorption values to metal surfaces. Accordingly, this spherical molecule phenomenon contributes to the formation of a weak boundary layer under the surface due to insufficient polymer filling of the cavities in the oxide film layers. However, the rate of the formation of the ionic interaction regions and the density of entanglement macromolecules at interfaces are not evident for the limited data. Nevertheless, there is no doubt that, when the reactive surface oxide layer chemically interacts with the oriented COOH groups to form metal–oxygen–polymer interfacial complex bonds, the yielded ionic bonds contribute particularly to an increase in adhesion.

IR spectra for the PAA–$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ composite systems are given in Fig. 6. The vibra-

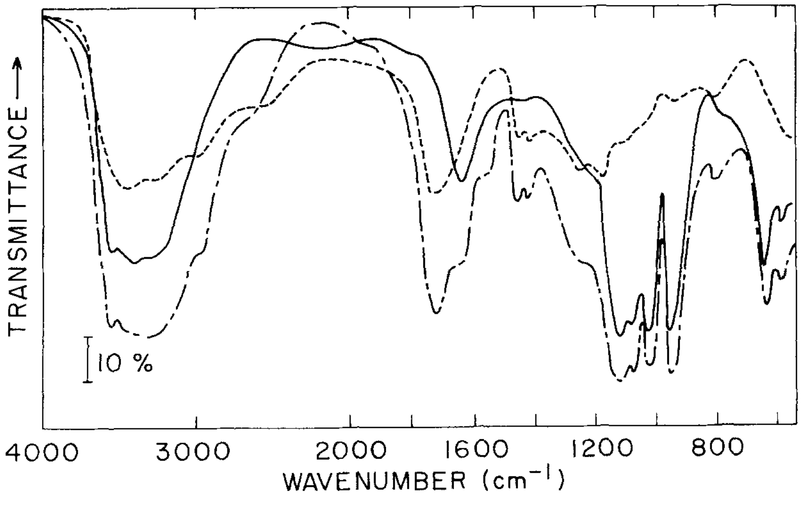


Figure 6 Comparison of IR spectra of (———) hopeite, (– – –) bulk PAA polymer, and (– - – -) PAA–hopeite composite.

tional frequency in inert hopeite powder is represented by the marked peaks at 3560, 3400, 1630, 1110, 1010 and 950 cm^{-1}. The bonds at 3560 and 1630 cm^{-1} are assigned to the coordinated water expressed in terms of the hydration water. The latter bond in particular can be taken as another important means of identifying water of crystallization. The 3400 cm^{-1} bond is consistent with the hydroxyl stretching vibration of hydrated inorganic compounds. An absorption bond in the region 1100 to 1000 cm^{-1} can be explained by assuming the presence of tetrahedral phosphate ions such as PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ in the hydrated zinc phosphate compounds. Since the P–O–(metal) linkage appears to have the stretching frequencies for a P–O bond and an O–(metal) bond in the frequency range 1055 to 950 cm^{-1}, the two bonds at 1010 and 950 cm^{-1} are likely to represent the stretching vibration of the P–O–(Zn) bond.

The spectrum for the PAA–hopeite composite samples indicates a new shoulder band at 1550 cm^{-1}, when compared with those for the hopeite and bulk PAA samples. The band at a frequency of 1550 cm^{-1} corresponds to an asymmetric stretching vibration of COO^- groups in accordance with Type A interaction mechanisms. As indicated by earlier SEM and EDX studies, very little, if any, free ferrous ions exist on the oxide film surfaces. The presence of free zinc ions would also act to inhibit the spreading forces of the oxide films by PAA polymer, thereby resulting in the entanglement of macromolecules. However, the concentration of the free zinc ions adsorbed onto the hopeite surface sites was not determined in this study. In addition, the charge transfer leading to the nature of acid–base reaction mechanisms between the polyelectrolyte macromolecules and the regularly oriented polar OH groups of hydrated oxide film sites, is more likely to be associated with the carboxylic anions converted from carboxylic acid groups rather than from the carbonyl group. Consequently, it was found that the presence of minimized divalent metallic ions at the interfaces not only tends to increase the magnitude of wettability and chemisorption of the oxide film by the functional macromolecules, but also enhances the environmental durability of the oxide–polymer bonds. In fact, the strong intensity band of C=O groups at 1710 cm^{-1} seems to suggest that even though oriented active COOH groups are present and may undergo acid–base interaction at all available –OH surface sites, the rate of the chemisorption at the interface regions will be small. Despite this small chemisorption rate, the energy evolved by the chemical interaction is enough to improve the interfacial bond forces.

2.6. Lap shear bond strength

In support of the studies of the nature of the adhesion mechanisms and interfacial interaction processes described above, the lap shear bond strengths when PAA polymers with varying degrees of neutralization were used as metal-to-metal adhesives were determined. The average PAA adhesive thickness for the overlap ranged from 1 to 3 mil, and the tests on the lapped samples were performed after curing for 7 days at room temperature.

Fig. 7 shows the lap shear bonding forces at the chemically treated metal–PAA polymer interfaces as a function of the degree of neutralization of the macromolecules. Correlation between the bond strength and the neutralization rate of COOH groups were found for both treated and untreated metal surfaces. In both cases, the bond strengths

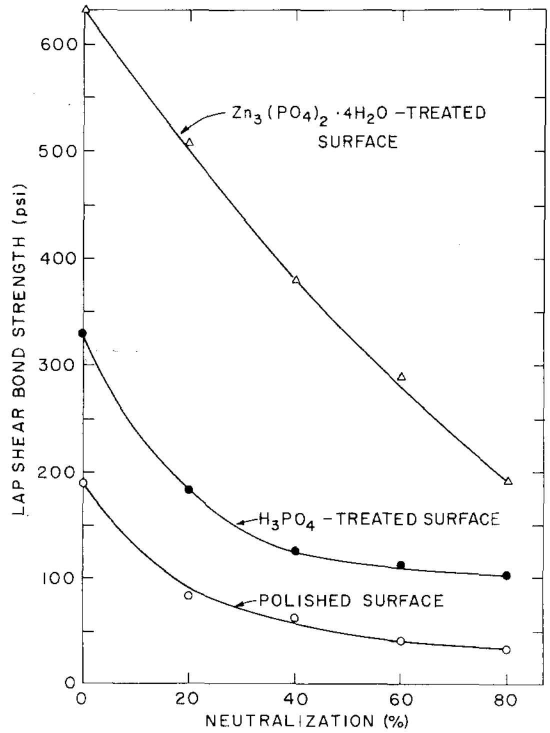


Figure 7 Lap shear bond strength change in chemically treated metal-to-metal PAA adhesives as a function of the degree of neutralization with NaOH.

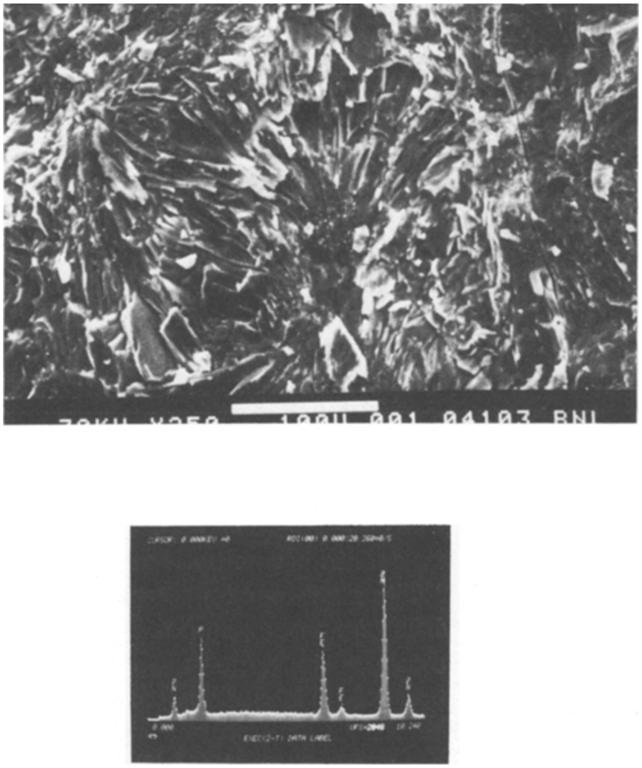


Figure 8 SEM image and EDX analysis of bonded surface side of PAA film.

decrease with increasing NaOH neutralization of the PAA. As already noted in the earlier section on wetting behaviour, the strength reduction is due to the poor spreading and adsorbing characteristics of PAA adhesives resulting from the increased density of conformational entanglement macromolecules. The spreading force is primarily dependent upon the degree of neutralization, but is independent of the degree of surface roughness of the deposited oxide films. In fact, the highest strength reduction rate of ~ 81% was obtained from the polished surface substrate bonded with 80% neutralized PAA polymers. Similar results were obtained for both treated surfaces. As an example, hopeite layers having a highly crystallized surface roughness exhibited a loss in strength of ~ 71% at the same degree of neutralization.

Without neutralization of the PAA, the adhesion force to the polished metal surface is low because of the absence of mechanical interlocking and chemical bonding at the interface. A strong bond results when the metal surfaces are given a chemical treatment to produce a thick crystal surface oxide. The maximum bond strength of 650 psi (4.48 MPa) in this test series was attained with the hopeite-deposited metal surface. This value corresponds to improvements of ~ 4 and ~ 2 times over those obtained from polished and H_3PO_4-modified surfaces, respectively.

To obtain further information regarding the polymer–hopeite interfacial bonding mechanisms, non-neutralized PAA polymer was applied to the hopeite surfaces and, after curing, the polymeric coating was physically stripped from the hopeite surfaces. Both the bonded surface side of the stripped polymer film and the coated hopeite side after stripping were studied by SEM associated with EDX. Since most of the thin polymer film remains on the hopeite surfaces, the presence of the jointed pieces of hopeite crystals could be detected visually on the stripped polymer film surfaces. Morphological and energy-dispersive X-ray studies of the adhesive sites on the polymer films was therefore focused upon the bonded hopeite pieces which were randomly distributed on the film surfaces. As seen in Fig. 8, the micromorphological image from the SEM resembles the surface microstructure of hopeite deposited on

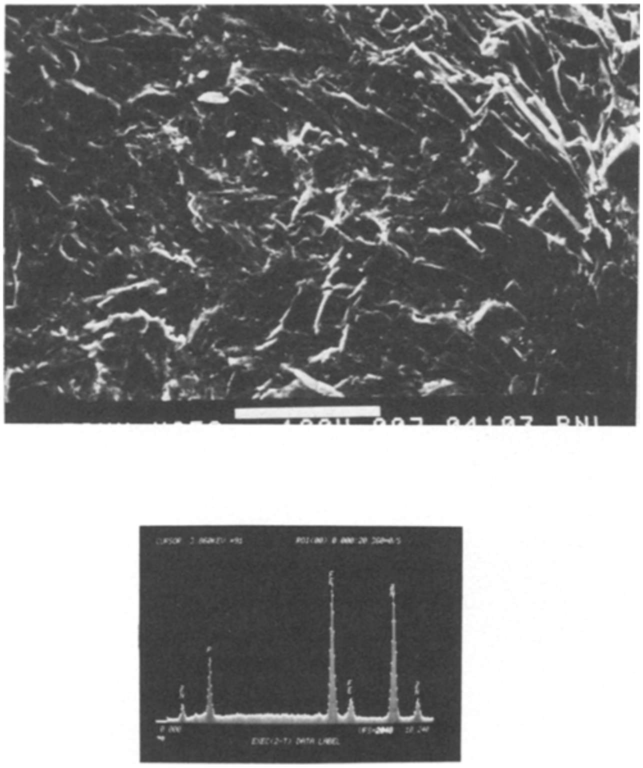


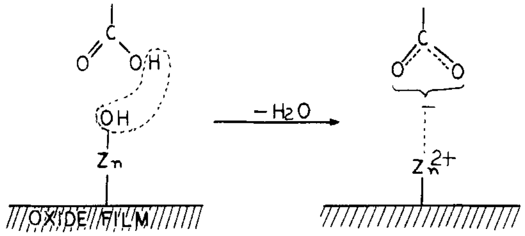
Figure 9 Surface topography with EDX peaks of coated hopeite layer site after stripping polymer.

the metal surfaces turned upside down. The roughness of the polymer surface definitely verifies that the polyelectrolyte macromolecules adhere very well to hopeite surfaces.

The relatively modest technique of EDX has a high potential for detecting the distributions and concentrations of the major chemical constituents which exist at the solid material surface. When compared to the EDX peaks for hopeite itself (see Fig. 2), it appears that the peak intensity for the zinc atom is stronger than those for phosphorus and iron atoms. This may mean that although other transitional metal ions can be present, larger quantities of zinc atoms may be transferred to the polymer films from the hopeite surfaces.

In contrast, the coated side of the hopeite, as shown in Fig. 9, displayed microstructure features completely different from those of the original hopeite crystal structures. EDX results indicated that the intensity of iron atom peaks increases significantly, whereas the zinc and phosphorus atom peak intensities become less. Consequently, an alternative hypothetical interfacial interaction mechanism consistent with the above observation may be proposed.

Type C: Divalent metallic ion crosslinking reactions



In the hypothetical Type C model, the carboxylic anion/hydroxyl group interfacial ionic bonds which have a relatively high mobility may be converted into more rigid divalent metallic bridge formations. From the results described above, the strong adhesion is essentially associated with the topography of the deposited oxide hydrate compound films, the nature of interfacial interactions and the type of degree of chemisorption at the interfaces.

2.7. Surface hydrophilicity

PAA polymeric structures having numerous hydrophilic COOH groups located in the pendent group of the oriented macromolecular chains are commonly referred to as hydrogel-type polymers.

Namely, the COOH groups are easily hydrolysed by water molecules, which leads to the fragmentation of the main chains. In applications of PAA polymers for dental cements, it is well known [24–27] that the incorporation of divalent metallic ion-leachable powders into polyacid solutions produces ion-complexed and -chelated PAA molecular structures which are moisture resistant. It is evident from this literature that the hydrolytic stability of metal ion–polyacid complexed systems is due to the conformation of the strong inter- and intra-ionic crosslinking in which the proton-donating hydrogen atoms in COOH groups are replaced by free divalent metallic ions. Induced salt-bridge crosslinking formations do not lead to the fragmentation into discrete units.

Generally, the hydrophilic properties of solid surfaces are estimated by comparing the magnitudes of wettability at the liquid–solid boundary. Thus, to assess the transformation to hydrophobic from hydrophilic characteristics of PAA macromolecules, water contact angle measurements of polymer surfaces containing a divalent metallic ion were made at an ambient temperature of 24° C, as a function of the ion–polyacid reaction time. The composite samples were prepared by mixing 60 parts PAA with 40 parts of a thermally activated metal oxide powder (92% zinc oxide, 4% SnF_2 and 4% silica). Commercially available $ZnO–SnF_2–SiO_2$ compound powder which is used as a dental cement was supplied as a sample by Premier Co., Ltd. After mixing, the materials formed a highly reticulated Zn–PAA complex.

The test results from these sample surfaces are given in Fig. 10. The data indicate that the water contact angles increase dramatically with elapsed time for ~ 5 min after deposition. An angle of ~ 61° was obtained for a hardened sample surface at an age of 20 min. This value is 12 times greater than that at an age of 10 sec. From this, it can be interpreted that an increasing equilibrium water contact angle is achieved by increasing the degree of inter- and intra-molecular crosslinking in the PAA macromolecules associated with the formation of salt bridges. The enhanced crosslinking density relates directly to the decrease in the hydrophilic groups caused by ion-exchange reactions occurring between the H^+ ions from COOH groups and Zn^{2+} ions dissociated from calcinated $ZnO–SnF_2–SiO_2$ compound grain surfaces. The salt-bridge crosslinking may occur in the vicinity of the grain surfaces.

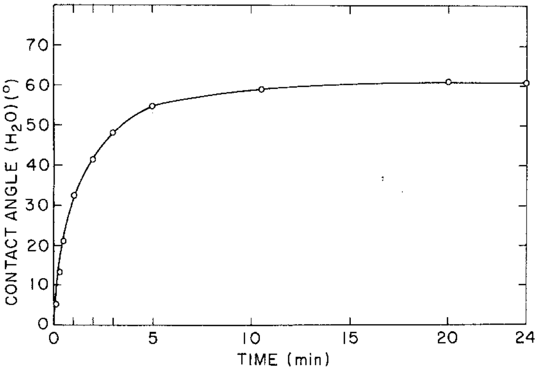


Figure 10 Changes in water contact angle of $PAA–ZnO–SnF_2–SiO_2$ composite surfaces as a function of crosslinking time.

The above data suggest that the presence of large numbers of hydrophilic groups in the polymer results in coatings that are susceptible to excessive hydrolysis and consequently increased water permeability, swelling, softening and transport rates when immersed in water. The reduction in hydrophilic groups caused by substituting COOH groups for metallic ion crosslinking formations $COO^-–Zn^{2+}–{}^-OOC$ yields outstandingly good water stability. Accordingly, for resistance to moisture stress, macromolecule structures for adhesives and coatings should have only enough hydrophilic COOH groups to occupy all available polar OH group sites at the hydrated oxide metal film surfaces.

3. Conclusions

It appears that for a metal substrate surface to achieve good bonding with polyelectrolyte macromolecules, the interface and interfacial regions should have the following surface activation elements: (i) a highly crystallized oxide layer consisting of an open surface structure, (ii) an adequate crystal thickness, (iii) the presence of rich polar hydroxyl groups formed on the metal oxide surfaces, and (iv) minimal free divalent metallic ions on the oxide films.

An essential prerequisite for attaining good adhesion of macromolecules to hydrated oxide metal surfaces is that macromolecules having regularly oriented pendent COOH groups must continuously wet the rough surface by spreading on and penetrating in the open surface microstructure and microfissures of the oxide films. Subsequently, the proton-donating COOH groups chemisorbed strongly by the polar OH groups at hydrated oxide surface sites must be converted into carboxylic anions which induce strong ionic bonding as a result of acid–base and charge transfer interaction mechanisms. The mechanical interlocking and chemical ionic bonds formed at the pore wall, which are normal to the oxide hydrate films, are primarily responsible for the molecular orientation. The preferred macromolecule orientations in the polymer layer contribute significantly to the development of the interfacial bond strength, whereas the conformation change caused by the free-ion-complexed molecular structure, resulting in coiled-up macromolecules, is likely to result in a decrease in interfacial bonding forces.

In addition, a requirement for utilization of PAA as adhesives and protective coatings is that the designed macromolecules should have only enough functional groups to occupy all available hydroxyl groups at the oxidized surface sites. The presence of additional COOH groups in the macromolecules leads to increases in the magnitude of hydrophilicity and can therefore cause a reduction in resistance to water.

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