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Drift Spectral Study of Polyacrylate (PAA) and Polymethyl Methacrylate (PMMA) on Various Ceramics and Glasses

Donghun Lee* and Robert A. Condrate, Sr.

NYS College of Ceramics at Alfred University, Alfred, NY 14802, USA

SUMMARY: Carboxylate-containing organic coatings can be used for their dispersion, lubrication, durability or hydrophobic applications with ceramic or glass surfaces. Such applications intimately depend upon the nature of the structural interaction of the organic coating on the surface of the inorganic material. In this study, organic polymers such as polymethyl methacrylate (PMMA) and polyacrylate (PAA) were coated on either ceramic or silicate-containing glass powders. Investigated ceramic materials included alumina, barium titanate and bismuth oxide-containing cuprate superconductors. The structural interactions between the organic coatings and the inorganic materials were determined by analyzing and interpreting Diffuse Reflection Infrared Fourier Transform (DRIFT) spectra. Depending upon the nature of the investigated materials, various metal-carboxylate complexes were formed at the interfaces along with hydrogen-bonded or non-hydrogen-bonded protonated PAA or PMMA.

Introduction

Many kinds of organic additives are used either to ensure the appropriate treatment conditions for various ceramic or glass processes or to control the surface properties of the investigated inorganic material. The resulting properties of the coated material intimately depend upon the nature of the bonding of the coating with the material at their interface. In this investigation, organic coatings mainly involving polymers such as polyacrylic acid (PAA) or polymethyl methacrylate (PMMA) have been applied. Structural information was obtained regarding the coating/material interface, using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. Ceramics such as alumina, barium titanate and bismuth oxide-containing

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cuprate superconductors along with silicate-containing glasses have been applied as substrates for coating.

Useful infrared-active vibrational modes involving carboxylate groups

Infrared bands involving the carboxylate groups of carboxylate-containing organic materials are useful for obtaining structural information concerning the organic/material interface. For instance, the infrared band corresponding to the C=O stretching mode of monomeric units involving isolated protonated carboxylate groups appears at 1760-1780 cm^{-1} [1,2]. The wavenumber of the C=O stretching mode for a protonated carboxylate group is shifted by hydrogen bonding. Infrared bands at ca. 1710 and 1740 cm^{-1} are characteristic of such C=O stretching modes for protonated carboxylate groups, which form hydrogen-bonded cyclic dimers, and side-ways chains respectively on the polymeric chains[3]. When metal-carboxylate complex formation occurs, resonance equilibrium occurs between the two oxygen atoms attached to the carbon in this complex group. Consequently, the characteristic band associated with protonated carboxylate groups disappears, and is replaced by two bands that occur in the 1550-1610 and 1400-1300 cm^{-1} regions which correspond to the asymmetric and symmetric CO_2^- stretching modes, respectively, of complexed metal-carboxylate groups[4]. Such infrared bands are useful for determining the nature of the bonding at the coating/substrate interface.

Polyacrylate coatings on alumina

Fig. 1 illustrates the DRIFT spectra for polyacrylate-coated alumina powders that were prepared from aqueous suspension solutions of different pH's and with different weight percents of sodium polyacrylate. Some portion of the band at 1572 cm^{-1} assigned to the asymmetric CO_2^- stretching mode of the carboxylate group of the sodium polyacrylate species shifts to higher wavenumbers when the polymer is adsorbed on the alumina surface. The new infrared band at 1604-1606 cm^{-1} can be assigned to the asymmetric CO_2^- stretching mode for carboxylates that bond covalently with aluminum ions on the surfaces of the alumina particles[4]. This change indicates that carboxylate groups in the polyacrylate chain form complexes and strong bonds with aluminum ions on the surface when the polymer is adsorbed on the alumina. The aluminum ions also form strong covalent bonds with oxygen ions that are contained in the structural network of alumina. The spectral data also indicate that at higher pH and/or lower polyacrylate concentration, the concentrations of the isolated protonated carboxylate species and the side-ways hydrogen-bonded protonated carboxylate species are dominant with respect to the protonated carboxylate dimeric species. Conversely, at lower pH and higher polyacrylate concentrations, the reverse is true. This variation in

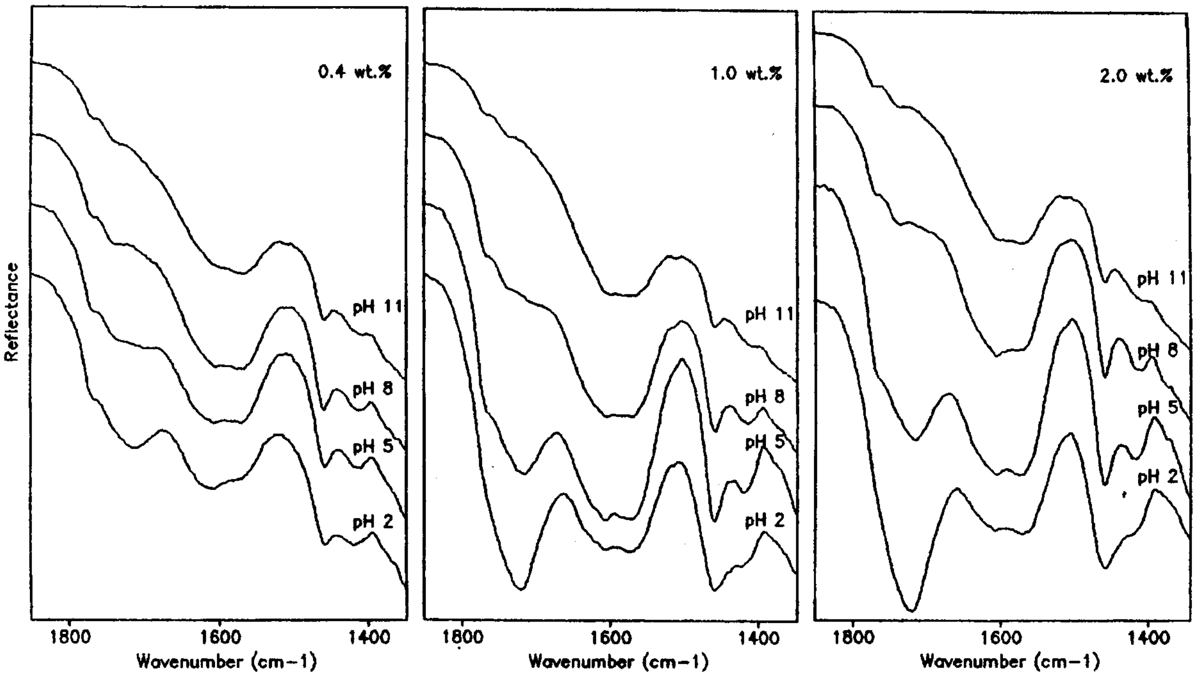

Fig. 1: DRIFT spectra for various amounts of sodium polyacrylate adsorbed on alumina from aqueous solutions at various pH values. (a) 0.4 wt%, (b) 1.0 wt%, and (c) 2.0 wt%.

infrared band intensities describes a structural model in which the polyacrylate chains are stretched out on the alumina surface at high pH and low polyacrylate concentration mainly forming metal-carboxylate bonds along the chain. While, at low pH and high polyacrylate concentration, the chains are more coiled up, allowing the formation of hydrogen-bonded acid dimeric units across the chain. In all cases, strong covalent aluminum-carboxylate bonds are formed at the interface.

There appears to be some hysteresis with respect to the concentrations of the various generated carboxylate species on the surface, if one treats a suspension solution for a short period at one pH, and then changes to another pH. With respect to a sample treated at only the latter pH, the relative concentrations of the related carboxylate species for the samples, which are treated first at one pH and then at another, are slightly shifted compared to those for the samples obtained at the initial pH.

Carboxylate-containing coatings on silicate-containing glasses

Organic coatings can also be placed on silicate glass surfaces to enhance durability, lubrication or hydrophobicity for the glass. Again, such properties intimately depend upon the structural interactions at the coating/glass interface. Oleic acid is used to improve lubricity of glasses. **Fig.** 2 illustrates the DRIFT spectra obtained for a freshly-ground soda lime silicate (Sodium-calcium-silicate) glass that was treated with oleic acid from ethyl alcohol along with spectra for various metal oleate precipitates. Clearly, the spectral data indicates the formation of a metal-oleate complex that is expected for each major cation in the glass composition along with its relative concentration.

Variations in treatment conditions for these glasses can alter the relative concentrations of the various carboxylate species on the glass surface. **Fig.** 3 illustrates the DRIFT spectrum for an oleate-coated soda lime silicate (SLS) glass that was aged in air for two months at room temperature. One may note that with aging, the infrared band which is associated with sodium-oleate complexes increases in intensity with respect to bands which are associated with other oleate species. Also, the infrared band associated with the protonated oleate species decreases, indicating an increase in the concentration of the sodium-oleate complex on glass surface with a related decrease in the concentration of the protonated oleate species.

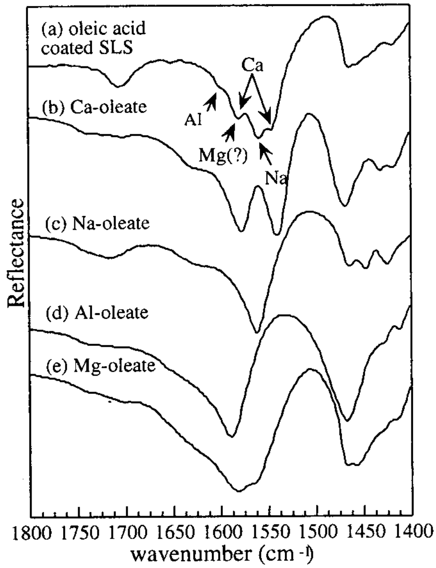

Fig. 2: DRIFT spectra for oleate-coated SLS glass and related metal-oleate precipitates.

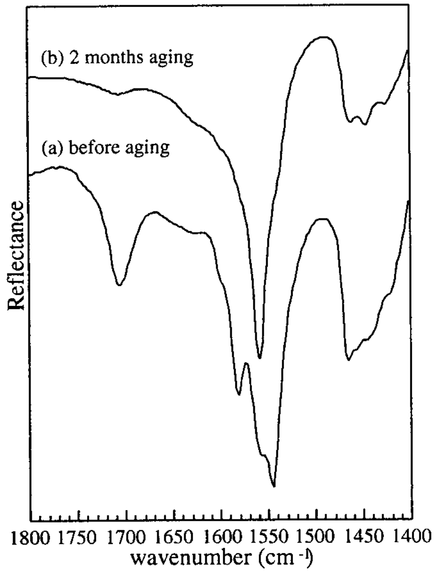

Fig. 3: DRIFT spectra of SLS glass powders coated with oleic acid from ethyl alcohol, (a) before aging, and (b) after two months aging in air.

This structural change can be explained if sodium ions, which possess a higher diffusion constant than the other metal cations in the glass, diffuse to the surface of the glass from the bulk of the glass, while protons diffuse into the bulk of the glass. The resulting reaction for the oleate-coated glass involves sodium-oleate complexes being formed on the glass surface with silanol groups being formed in the bulk of the glass. How polyacrylate chains bond to SLS glass from aqueous solution depends upon treatment variables such as pH.

Fig. 4 illustrates the DRIFT spectra for SLS glasses coated with polyacrylate from aqueous solutions at different pH's. The spectral data clearly indicates that protonated carboxylate groups dominate the adsorbed chains at low pH, while metal-carboxylate groups dominate the adsorbed chains at high pH.

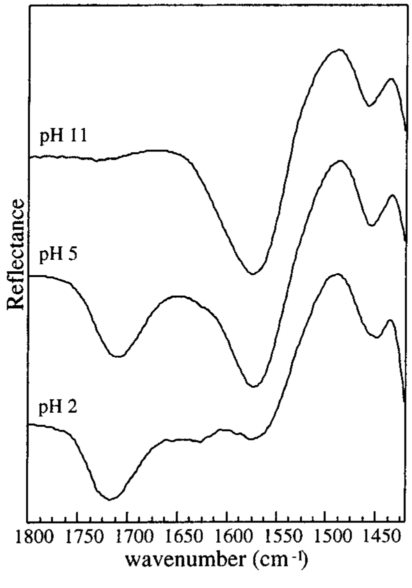

Fig. 4: DRIFT spectra for polyacrylate coated SLS glass from aqueous solutions at different pH values.

Bonding of PMMA chains at the coating/glass interface depends upon the structural nature of the glass. **Fig.** 5 illustrates the DRIFT spectra that were obtained for PMMA-coated silica and SLS glass. One may note that for coated silica, only the infrared band that is associated with the C=O stretching mode for the ester unit is observed in the DRIFT spectrum, indicating that only physically adsorbed PMMA chains occur on the glass surface. However, in the case of

PMMA-coated SLS glass, along with the band associated with ester units, a band also occurs in the 1550-1610 cm^{-1} region. This latter band is associated with metal-carboxylate complexes that are formed on the glass surface due to the replacement of some of the ester methyl groups in the PMMA chain by metal ions in the glass, thereby forming stronger bonds to the glass surface.

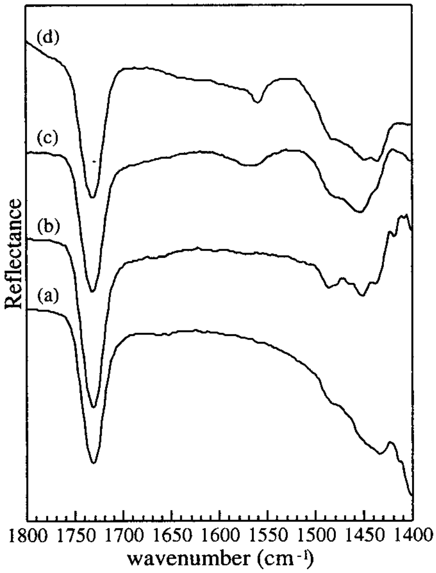

Fig. 5: DRIFT spectra for PMMA coated on (a and b) the silica glass and (c and d) the SLS glass: (a and c) before and (b and d) after aging in air for nine months.

This spectral interpretation is consistent with the DRIFT spectra that are observed after aging these two types of coated glasses in air for two months at room temperature. No spectral change is observed for the coated silica glass with aging in the higher-wavenumber carbonyl stretching region. This is consistent with no metal cations being able to diffuse to the glass surface to form metal-carboxylate bonds because of the chemical composition of silica glass. However, in the case of SLS glass, the band maximum for the infrared band in the 1550-1610 cm^{-1} region shifts to a lower wavenumber upon aging this glass in air. This result would be expected if similarly to aging oleate- coated SLS glass, sodium ions diffuse from the bulk of the glass, and then react to form sodium-carboxylate complexes. The band in the 1550-1610 cm^{-1} is a convoluted composite of all of the bands for the asymmetric CO_2^- stretching modes of all of the metal-carboxylate complexes on the chains. Since the infrared band that is associated with sodium-polyacrylate complexes (1572 cm^{-1}) occurs at a much lower wavenumber than with the other metal-complexes involving either Ca, Al or Mg, the resultant convoluted band will possess more added intensity from sodium-carboxylate complexes as compared to the non-aged sample. Therefore, the band maximum for the convoluted infrared band that is associated with the aged sample is at a lower wavenumber than the non-aged coated glass sample.

Coatings for protection of barium titanate or bismuth oxide- containing cuprate superconductors from surface degradation due to surface attack

The formation of degradation species on the surface of $BaTiO_3$ particles can alter their dispersion, sintering or electronic properties. Aging $BaTiO_3$ in water in an air atmosphere can alter such properties. The structural changes on the particle surfaces can either involve forming a surface carbonate species on the $BaTiO_3$ crystals or generating the $BaCO_3$ phase on their surface interfaces. The surface species and the $BaCO_3$ phase at the crystal interface can be identified by bands at 1433 and 1460 cm^{-1}, respectively. **Fig.** 6 illustrates the DRIFT spectra for $BaTiO_3$ powder with a Ba/Ti molar ratio of 1.007 that was aged for different periods of time in water at room temperature after calcination at 1200°C.

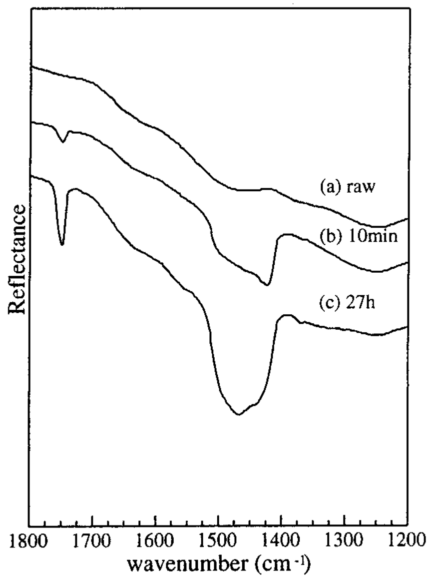

Fig. 6: DRIFT spectra for uncoated $BaTiO_3$ powders (Ba/Ti = 1.007) that was aged in humid air after calcination at 1200°C.

Initially, The surface carbonate species dominates the DRIFT spectrum. However, after longer aging times, as more $BaCO_3$ phase is formed, the infrared mode that is associated with this phase dominates the infrared band in the 1420-1480 cm^{-1} region, indicating the formation of more and more $BaCO_3$ phase.

Organic carboxylate species that are coated on the powders can prevent surface degradation of the $BaTiO_3$ powders. **Fig.** 7 illustrates the DRIFT spectrum that was obtained for a $BaTiO_3$ powder with the molar ratio of 1.007 that was coated with organic acid, and then aged in humid air for 24 hrs. Clearly, the spectral data indicates that in contrast to uncoated $BaTiO_3$, the amounts of surface carbonate species or $BaCO_3$ phase on coated powders are not measurable by DRIFT spectroscopy. The surface coating is protecting the $BaTiO_3$ powder from carbonate attack at their particle surfaces.

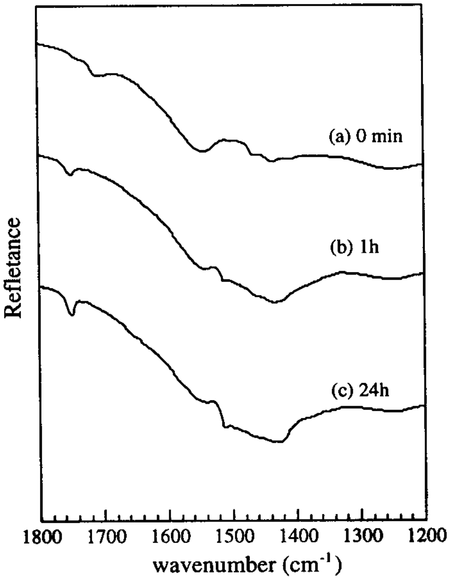

Fig. 7: DRIFT spectrum for coated $BaTiO_3$ powder that was aged in humid air.

The superconducting properties (T_c and J_c) of bismuth oxide-containing cuprate superconductors (for example, $Bi_2Sr_2CaCu_2O_x$) can degrade due to reaction of the surface of the superconducting materials with certain environments. Carbonate formation on the superconductor surface is one way that such properties can degrade. **Fig.** 8 illustrates the

DRIFT spectra for course uncoated $Bi_2Sr_2CaCu_2O_x$ powder that was aged for different periods of time in humid air. Spectral data indicates that initially, $CaCO_3$ is formed at a faster rate than $SrCO_3$. This is probably due to the fact that the Ca atoms are located on more reactive sites on the superconducting crystals than are Sr atoms. However, after their initial reaction, the higher concentration of the strontium atoms dominates, causing the concentration of $SrCO_3$ to be higher than that of $CaCO_3$. Again, when the coated powder was aged in humid air for different comparable periods of time, in contrast to uncoated superconductor powders, the DRIFT spectral measurements that were made for $Bi_2Sr_2CaCu_2O_x$ powder coated with various carboxylate-containing organic materials indicate that significant amounts of carbonate phases were not formed at the coating/material interface.

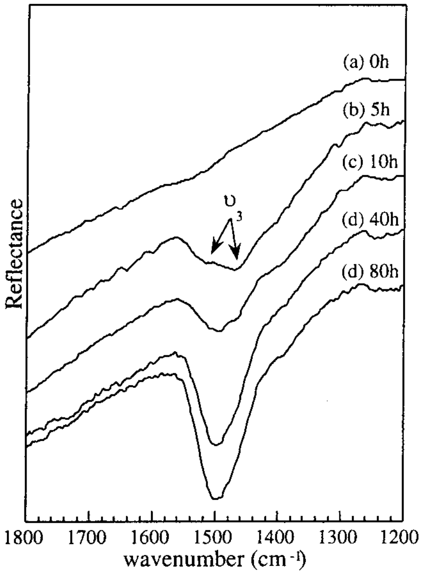

Fig. 8: DRIFT spectra for uncoated $Bi_2Sr_2CaCu_2O_x$ powders after aging for different periods of time in humid air.

Conclusions

The following conclusions can be drawn on the basis of this investigation:

1) DRIFT spectroscopy provides a useful and flexible tool to investigate organic surface species on ceramic or glass materials.

2) The surface species on alumina powders before and after coating with PAA under different conditions can be investigated by DRIFT spectroscopy, generating structural information concerning the bonding of the dispersant to the alumina surface.

3) Structural variations of the various organic species that can occur on a glass surface with changes in the treatment conditions can be determined from DRIFT spectral data.

4) DRIFT spectroscopy can be used to determine the structural interactions that occur during the degradation and the protective coating of either $BaTiO_3$ or bismuth cuprate superconductors. While in the case of $BaTiO_3$, $BaCO_3$ is formed during degradation, both $SrCO_3$ and $CaCO_3$ are formed during degradation of the superconductor.

Acknowledgement

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