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Poly(ethylene glycol) interactions with alumina and silica powders determined via DRIFT

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Diffuse reflection infrared spectroscopy (DRIFT) is used to determine interfacial interactions between poly(ethylene glycol) (PEG), alumina and silica powders. The interactions are created by grafting in high temperature and low moisture environments due to preferential adsorption between PEG and water. Under these grafting conditions, a shoulder appears on the C—O—C stretching band of the DRIFT spectrum. This is found to occur when PEG is in the presence of a hydrogen donor such as surface hydroxyls on alumina and silica. The shoulder is reported as an interaction band due to hydrogen bonding between the PEG etheric oxygen and the surface hydroxyls of alumina and silica. Specific band positions are measured when the PEG chain is interacting with alumina (1090 cm^{-1}), silica (1080 cm^{-1}), or water (1085 cm^{-1}).

1. Introduction

In a previous work, we used low concentrations of poly(ethylene glycol) (PEG) and water in a high-shear wet-granulation process to granulate sub-micron alumina powder [1]. The function of the PEG was to act as both a binder and a lubricant in order to improve the flow properties of the alumina. Although the granulation technique was successful, it was unclear whether PEG was binding to the alumina surface. The uncertainty arose because alumina and PEG both have a high solvent affinity to water. Therefore, they have preferential interaction with water rather than with each other. This behavior is seen in the literature published by Walker *et al.* [2] showing very low adsorbed amount of PEG onto alumina from aqueous solutions. However, they also studied PEG and silica interactions, which were found to be significantly higher than the interaction between PEG and alumina. Data have been found in the literature showing the bonding mechanism between ethylene oxide groups and silica. Fontana first postulated the bonding mechanism between PEG and silica by studying the adsorption of copolymers containing PEG side groups [3]. His work indicates a hydrogen bond between the PEG etheric oxygen groups and the silica surface hydroxyl groups as determined by FTIR. Later, Rubio and Kitchener studied PEG grafted to silica from non-aqueous solutions [4, 5]. They also found, by observation of the same 3000–3600 cm^{-1} region of the infrared spectrum, that the interaction was due to hydrogen bonding with the etheric oxygen of the PEG molecules. Our FTIR studies were inconclusive when analyzing just the 3000–3600 cm^{-1} region, but conclusive information was found in the fingerprint region.

The interesting situation of the granulation technique implemented here is that the loosely held water molecules evaporate from the alumina particles quickly due to high granulation temperatures. Because of this, the PEG chains, if thermodynamically driven, may possibly have a higher interaction with the alumina surface. It was our intention to identify the extent of interaction between PEG, alumina and silica powders. To this end, polymer/powder interactions between PEG and alumina or silica were facilitated through grafting procedures at high temperatures and low moisture content. The interactions were monitored by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT).

2. Experimental procedure

2.1. Materials

Poly(ethylene glycol) compounds* of molecular weights (M_w) 400 and 3350 g/mol were grafted to a reactive grade Bayer-process α-alumina from Alcoa called A-16 S.G.† The A-16 S. G. alumina was dried in a vacuum oven for 24 h at 150°C at a pressure of 94800 Pa, and was stored in a dessicator before grafting.

2.2. Grafting procedures

Two grafting procedures were used. The first involved a melt procedure in which PEG was heated above its melting temperature in the presence of the powder. The mixture was held at 100°C for 30 minutes and then slowly cooled to room temperature. The second was a wet-grafting technique utilizing high-shear wet-granulation. The wet-grafting technique was done by dispersing PEG in de-ionized water, heated to 80°C. This solution was then spray atomized on agitated

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*Carbowax® Union Carbide Corporation, S. Charleston, WV.

† A-16 S.G. Alumina, Alcoa Ind. Chemicals, Bauxite, AR.

alumina powder heated to 150°C. The powder continued to be mixed for an additional 15 minutes after adding the PEG. Concentrations of 0.5 mg/m^2 polymer to alumina were used for the wet-grafting. The grafted mixtures were stored in less than ten percent relative humidity atmosphere until FTIR analysis was conducted.

2.3. Fourier transform infrared spectroscopy

Powder samples were analyzed using DRIFT techniques. Spectra were collected using a Bruker Vector 22 FT-IR with a MCT detector ($D^* = 5 \times 10^9$ cm^{-1}/W/Hz). DRIFT measurements were performed using Pike Technology EasiDiff^{TM} accessory. Spectral analysis was performed using OPUS-NT spectroscopic software. The IR chamber was purged with dry nitrogen gas for 10 minutes to reduce effects of atmospheric moisture. 200 co-added scans were collected for a spectral range of 4000 cm^{-1} to 465 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussion

The absorbance spectrum for PEG 3350 in the region from 1250 cm^{-1} to 1000 cm^{-1} is given in Fig. 1. The bands that are identified are 1234 cm^{-1} due to CH_2 twist, 1148 cm^{-1} due to C—O stretch and CH_2 rocking, 1116 cm^{-1} due to C—O—C stretching and 1061 cm^{-1} due to C—OH stretching. If, in fact, the etheric oxygen is involved in the hydrogen bonding, then the C—O—C stretching band near 1100 cm^{-1} should be affected by the hydrogen bond. To test this assumption, a mix of phenol and PEG 400 in carbontetrachloride was analyzed using ATR-FTIR. Phenol is a good H-donor to hydrogen bonding, but shows little self-association. Therefore, when mixed with PEG, it is free to hydrogen bond with a H-acceptor such as the etheric oxygen. The phenol was added to the dispersed PEG solution using equal molar equivalents to the PEG ether group. The second derivative of the ATR-FTIR spectra for PEG, phenol and a mixture of the two are shown in Fig. 2. The spectral range of interest was very low in intensity, therefore 2nd derivative representations of the DRIFT spectra are used. The minima in these spectra represent the peak positions. The spectral region shown (1150 cm^{-1} to 1050 cm^{-1}) includes vibrational bands due to C—O—C stretching (1118 cm^{-1}and 1096 cm^{-1}) and νC-OH (1063 cm^{-1}) from the PEG molecule and νC-OH (1070 cm^{-1}) from phenol [6]. The PEG400 C—O—C band near 1096 cm^{-1} shifted to 1091 cm^{-1} after mixing with phenol. The band shift is complemented by a shift in the phenol —OH stretching band from 3600 cm^{-1} to 3350 cm^{-1} (not shown). The results indicate that the band shift is due to interaction between the etheric oxygen groups in poly(ethylene glycol) and hydroxyl groups from phenol. The C—O—C band shift was used to monitor PEG interactions with silica and alumina.

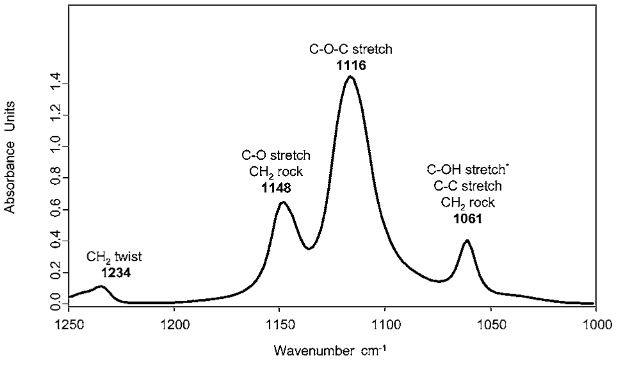

Figure 1 FTIR partial absorbance spectrum for PEG 3350.

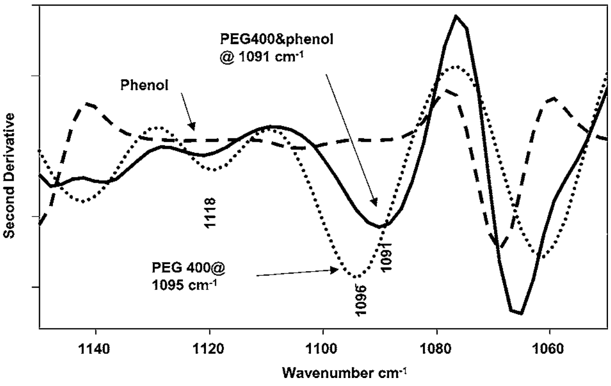

Figure 2 DRIFT 2nd derivative spectra for phenol, PEG400, and phenol & PEG400 mixture.

DRIFT spectroscopy was used to analyze the interactions between PEG 3350 and silica and α-alumina. As earlier mentioned, PEG adsorption was found to be much higher on silica than on alumina when dispersing the powder in an aqueous solution. The low adsorption between PEG and alumina was postulated to be a consequence of high adsorption affinity between alumina and water and that the polymer was not able to displace water molecules at the alumina surface. Because of these findings, the spectrum of PEG interacting with silica was collected along with PEG and alumina in order to determine if the band near 1091 cm^{-1} was present for both powders. A 5% PEG/95% by weight powder mixture was melt grafted under vacuum at 100°C. The 1150 to 1040 cm^{-1} region for the polymer grafted onto silica and alumina are shown in Figs 3 and 4 respectively.

In Fig. 3, a strong band at 1128 cm^{-1} is present from Si—O—Si stretching. The poly(ethylene glycol) (ca. $M_w = 3350$ g/mol) bands for C—O—C stretching at 1107 cm^{-1} and 1097 cm^{-1} and C—OH stretch near 1069 cm^{-1} are at slightly higher wavenumbers than PEG 400. An additional band near 1082 cm^{-1} is new

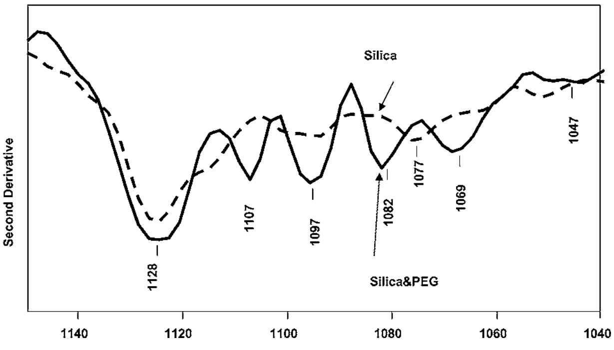

Figure 3 DRIFT 2nd derivative spectra for silica and PEG3350 grafted to silica.

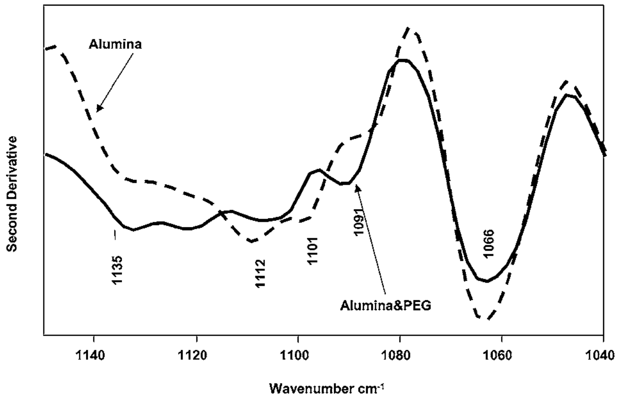

Figure 4 DRIFT 2nd derivative spectra for alumina and PEG3350 grafted to alumina.

to both the silica and PEG. The band near 1082 cm^{-1} appears to be as intense as the C—O—C stretching vibration indicating a significant number of interactions present between PEG and silica.

In Fig. 4 the spectrum of alumina displays a strong peak near 1066 cm^{-1} due to C—OH and Al—OH stretching. PEG is detected from the presence of bands near 1107 cm^{-1} and 1122 cm^{-1} from (the suggested) trans and gauche conformations respectively of the O—C—C—O group [6]. A weak band is evident near 1091 cm^{-1}. Here, the intensity is not as strong as detected between silica and PEG indicating few interactions between the PEG and alumina. The higher wavenumber position with respect to the silica/PEG system also indicates a weaker bond. The interaction band in the 1090–1100 cm^{-1} region is present in many spectra taken at different polymer contents and molecular weights, only varying slightly in intensity and the breadth of the peak. The peak was also present in a published paper, appearing as a shoulder in the spectrum (not a second derivative), but was not specifically identified in the paper [6]. The detection of a specific interaction between PEG and alumina has not been reported using FTIR techniques until now. The results from the melt grafting technique prove that FTIR techniques can be used to directly monitor the interactions between PEG and metal oxide powders. Quantitative analysis is difficult at this point due to the low intensities of the interaction band.

Additionally, it was important to investigate the effect that water has on the system during grafting. A second grafting technique was conducted to focus on the polymer/powder interaction under low moisture ($<5\%$ water) and high temperature (100–150°C) conditions. The DRIFT 2nd derivative spectrum for the polymer grafted onto alumina from a 10% aqueous solution of PEG3350 is shown in Fig. 5. Along with the grafted spectrum are displayed the spectra for neat alumina and PEG. A weak shoulder near 1090 cm^{-1} is again present. The band is not present in spectra of either of the original species. The band intensity is low compared to C—O—C stretch, again indicating the small number of interactions taking place. In retrospect, the combination of higher temperatures and low water content does facilitate PEG/alumina interactions just as well as the melt grafting technique.

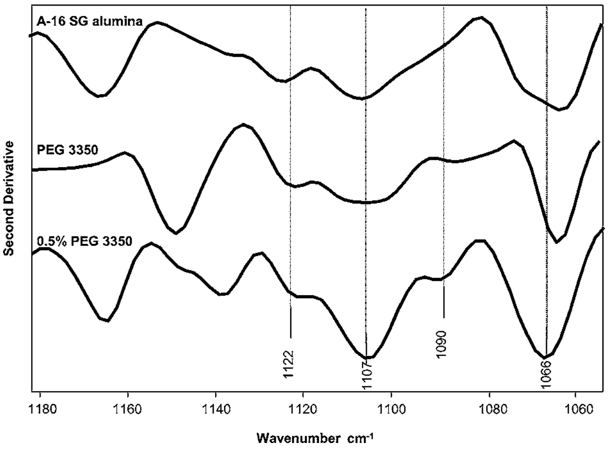

Figure 5 DRIFT 2nd derivative spectra for raw alumina, neat PEG3350 and grafted mixture using solution grafting technique. Dashed lines show positions of other relevant peaks.

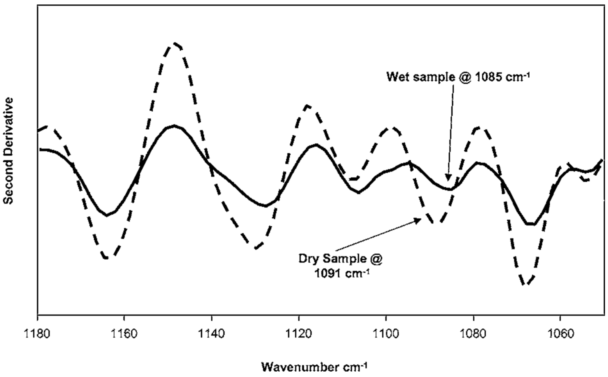

Figure 6 DRIFT 2nd derivative spectra for solution grafted PEG and alumina before (wet) and after drying (dry) at 50°C for 24 hours.

Finally, the wet-grafted system was dried to remove any physically adsorbed water introduced from the wet-granulation technique. Fig. 6 shows the 2nd derivative spectra for the original granulated system and the same material dried 24 hours at 50°C under vacuum. The drying procedure resulted in a shift in wavenumber and an increase in the intensity of the vibrational band near 1090 cm^{-1}. Therefore, water does have an effect on this region of the FTIR spectra. It has been stated that the lack on interactions between PEG and alumina is because they prefer to complex with water instead of one another. But, the band near 1090 cm^{-1} remains after drying and therefore, can be identified as an artifact of the interaction between PEG and alumina. The PEG/alumina interaction can be found near 1090 cm^{-1}, PEG/water 1085 cm^{-1} and PEG/silica near 1080 cm^{-1}. To this end, it is possible to use FTIR distinguish between PEG/alumina (or PEG/silica) interactions and interference with water. The ability to quantify this data would supply a much needed analysis technique to the ceramics industry.

4. Conclusions

Direct measurement of the interaction between poly (ethylene glycol) and metal oxide powders was achieved using DRIFT techniques. Specific hydrogen bonding interactions were identified for PEG and alumina as well as PEG and silica. A previously unreported vibrational band in the range of 1080–1090 cm^{-1} was identified. The band is related to hydrogen bonding interactions with the PEG etheric oxygen. The band is distinguishable for interactions between PEG and alumina (1090 cm^{-1}), PEG and silica (1080 cm^{-1}) and PEG and water (1085 cm^{-1}). Although we were able to identify whether an interaction was taking place, the interactions were still very weak and we were unable to quantify the extent of interaction.

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