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PMMA tacticity and alumina powder dispersion stability

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SUMMARY

Sedimentation experiments and X-ray photoelectron spectroscopy (XPS or ESCA) analyses have been used to study the effect of poly(methylmethacrylate) (PMMA) tacticity on aluminum oxide powder dispersion stability in a common solvent medium. The relative trends from sedimentation densities, and from surface analyses after solvent washing show that (PMMA) adsorption is greatest with isotactic polymer, where isotactic > atactic > syndiotactic adsorption. These results suggest that surface adsorption and hence dispersion stability can be influenced by polymer chain configuration as well as by chain conformation.

INTRODUCTION

The study of polymer adsorption onto metal surfaces often involves the consideration of specific interactions between polymer functional groups and metal oxide surface layers. These interactions are of practical importance since they can influence polymer to metal interfacial adhesion, or as in the case of ceramic slurries, the state of dispersion (1). Depending on the medium through which the polymer is deposited onto a surface, several competitive interactions can also have an influence on polymer adsorption. For example, when adsorption occurs from a solvent medium, the fraction of adsorbed polymer will depend on the strength of interactions between solvent with polymer, solvent with surface, and polymer with surface (2).

The conformation and configuration of polymer chains have also been shown to correlate with surface adsorption. The rotational conformations of attached polymer chains can be influenced by variables such as molecular weight and solvent quality. A range of conformers has been observed, including chain extended "train" conformations (i.e. as planar zigzag rotational isomers), and coiled "loops" with inter-dispersed sites of attachment (2). On the other hand, the influence of chain configuration or tacticity (i.e. stereochemical isomeric sequences) on adsorption has not been as well documented. Given that certain rotational conformations may tend to be favored upon adsorption depending on the solvent medium, it follows that stereochemical sequencing (configuration) will also influence adsorption since the energetic favorability of rotational conformers will differ for isotactic or syndiotactic sequences (3).

Konstadinidis et al. (4) have shown that in the case of atactic poly(methylmethacrylate) (PMMA), specific adsorption interactions with aluminum oxide occur via surface hydrolysis of ester groups with resultant carboxylate formation. Moreover, they have concluded from IR and solid state NMR experiments that a gauche to trans rotational conformational change occurs upon adsorption, and that this phenomenon is most pronounced among the meso sequences of atactic and isotactic triads.

Other researchers have also found that isotactic PMMA sequences seem to preferentially adsorb onto surfaces such as silica (5), and that this phenomenon can be influenced by the choice of solvent (6). This further suggests that polymer tacticity, as well as chain conformation, can influence surface adsorption. With these findings in mind, the objective of this study was to illustrate the effect of PMMA tacticity on aluminum oxide powder dispersion stability through simple sedimentation experiments in a common solvent system. X-ray photoelectron spectroscopy (XPS or ESCA) was also used to characterize the surface composition of the PMMA/alumina powders.

EXPERIMENTAL

Vehicle solutions containing 5% (all concentrations by weight) atactic, syndiotactic, and isotactic PMMA (M_w = 100,000 from Polysciences) were prepared at 25°C using a 50/50 blend of HPLC grade acetone and toluene from Fisher. Slurries containing 43% alumina were then prepared by mixing the polymer vehicles and a pure solvent control vehicle with a non-porous grade of Alcoa alumina powder (Al_2O_3, approximately 5μm average particle diameter, $0.8 m^2/g$). Aliquots of the slurries were then weighed into 10 ml graduated cylinders after 24 hours of agitation in a shaker bath at both 25°C and 45°C. Equilibrium sediment densities at both temperatures were recorded as a percentage of the theoretical density ($3.98 g/cm^3$ for alumina) after 24 hours of gravity settling with an error of approximately 3% in all cases. The clear supernatants were then removed from samples at 45°C, and pure solvent was added with subsequent re-agitation and subsequent settling. After this process was repeated six times to remove excess (non-adsorbed) polymer, sediment densities were recorded, and then the powder was allowed to dry under a hood at 25°C for 1 week prior to performing the ESCA analyses.

ESCA spectra were obtained with a Kratos XSAM 800 photoelectron spectrometer equipped with a Kratos DS800 Control and Data System (Version V). All spectra were acquired using a non-monochromatic Mg K_a X-ray source (1253.6 eV), with the anode operated at 15 kV and 12 mA. The hemispherical electron energy analyzer was operated in the high resolution, low magnification, fixed retarding ratio (retarding ratio = 53) mode. The normal analyzer/sample geometry of the spectrometer has an electron take-off angle of 90°. The instrument typically operates at pressures below 5×10^{-9} torr in the analysis chamber. The powder samples were mounted on standard Kratos specimen holders with double-sided tape.

ESCA peak areas for quantitative calculations were determined with standard Kratos software. In all the computations, the spectral background was assumed to be linear over the peak widths. The relative elemental sensitivity factors used for the quantitative determinations were: C 1s, 0.697; O 1s, 1.052; and Al 2p, 0.555. The photoelectron sensitivity factors were calculated for the Kratos instrument using the procedure described by Hanke et al. (7). The reported atomic concentrations were determined with a precision of ± 8% relative standard deviation or better.

RESULTS AND DISCUSSION

The settling behavior of inorganic slurries has often been used to provide an indication of relative dispersion stability (1,8). Slurries with well-dispersed particles will produce well-packed sediments having higher sediment densities. Conversely, poorly stabilized slurries are characterized by the existence of floc structures which lead to inefficient packing and low densities. Thus, the settling behavior of a slurry is sensitive to processes which minimize particle/particle floc interactions. These processes can involve competitive interactions between solvent, polymer, and particle surfaces.

In a low dielectric solvent medium with a homopolymer like PMMA, a certain degree of polymer surface adsorption is expected, where the percent of segment attachment will depend on the nature of all other competitive processes. The portions of the PMMA chains that are not directly attached to the particle surfaces will extend into the solvent medium in the form of either "loops" or "tails" to provide some degree of steric stabilization (9). The slurries which are more efficiently stabilized would be expected to exhibit higher sediment densities.

Table 1 shows the sediment density results for the various samples. The control sample with no polymer (only solvent) exhibits a low sediment density, while samples with PMMA exhibit higher densities. This indicates that the solvent affinity is lower than the polymer affinity for the alumina surface sites (1,10).

TABLE 1: Al_2O_3 Sedimentation Density vs. PMMA Tacticity

Sample	T(°C)	% of Theor. ρ Density	% of Theor. ρ after supernatant decanting
Solvent Control	25	16	---
	45	18	---
Syndiotactic	25	25	---
	45	25	39
Atactic	25	41	---
	45	39	45
Isotactic	25	45	---
	45	45	50

In the presence of polymer, the sediment density is sensitive to tacticity but not to temperature. Given that a change in temperature, and hence a change in polymer solubility (11) has no apparent effect on the trend, it appears that the adsorbed polymer/particle interactions are more significant than polymer/solvent interactions at the temperatures studied. Given that atactic PMMA is primarily composed of syndiotactic sequences (11), it appears that sedimentation density and dispersion stability increase as the level of syndiotacticity decreases. This result implies that the isotactic polymer may allow for more efficient adsorption onto the alumina powder surface.

This trend is supported by atomic percent composition from the ESCA analyses as shown in Table 2, where the percent carbon level generally increases, and the percent aluminum level decreases as the isotactic character is increased.

TABLE 2: ESCA Analyses of Decanted and "Washed" Al2O3 Powders vs. PMMA Tacticity, Relative Surface Concentrations (Atomic Percent)

Sample	C	O	Al
Control powder, no polymer	35	37	28
Syndiotactic	43	32	25
Atactic	45	31	24
Isotactic	52	27	21

Also as shown in Table 1, the sediment densities increase after six cycles of supernatant decanting and resettling. This could be a result of either a time dependence for achieving equilibrium surface coverage (12), of a lower concentration of free polymer (which reduces the chance for bridging flocculation) (2,6), or of the fractionation of isotactic rich polymer chains through adsorption (5). Regardless of the exact reason for this phenomenon, the trend remains unchanged.

Since the characteristic ratio of isotactic PMMA chains are generally higher than the ratios for the atactic or syndiotactic configurations (11), it follows that the more extended conformation of isotactic sequences in solution may facilitate the adsorption of acrylate groups with a smaller loss of conformational entropy, and hence with a more negative free energy of adsorption (with all enthalpic considerations being similar). This explanation seems reasonable in light of recent studies which suggest that meso sequences undergo a conformational change from gauche to trans upon adsorption (4). Although further work is needed to test this concept, our present results support the idea that isotactic PMMA adsorbs more favorably onto alumina, and therefore it can provide a more efficient barrier to particle flocculation.

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