

# Competitive Adsorption Phenomena in Nonaqueous Tape Casting Suspensions

Kim Blackman, Rita M. Slilaty,\* and Jennifer A. Lewis\*

Department of Materials Science and Engineering and the Beckman Institute of Advanced Science and Technology, University of Illinois, Urbana, Illinois 61801

**Competitive adsorption phenomena in alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>)–polyvinyl butyral (PVB)–Menhaden fish oil (MFO) suspensions are studied using diffuse reflectance Fourier transform infrared spectroscopy and thermogravimetric analysis. PVB and MFO commonly serve as binder and dispersant species, respectively, in nonaqueous tape casting systems. Adsorption isotherm measurements reveal that both PVB and MFO have an affinity for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surfaces, with corresponding plateau coverages of 3.4 and 2.3 mg/m<sup>2</sup>, respectively. Sequential competitive adsorption of these species occurred during two-stage milling. MFO was fully adsorbed onto  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder in the absence of PVB during first-stage milling. PVB was then introduced to the system during second-stage milling and found to displace preadsorbed MFO species from such surfaces. At the culmination of milling, PVB composed 25–35 wt% of the adsorbed organic layer. Complete displacement of MFO was not observed, which limited PVB adsorption on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.**

## I. Introduction

THE tape casting process produces thin ceramic layers, which serve as basic building blocks in multilayer ceramic packages and capacitors,<sup>1–3</sup> and have potential use in laminated structural ceramics, solid oxide fuel cells, and sensor/actuator applications. Commercial casting suspensions are complex, consisting of single or multiple ceramic phases and several organic additives in a multicomponent solvent system. In the adsorbed state, organic dispersants promote suspension stability via steric stabilization.<sup>4</sup> Polymeric species serve as rheological modifiers and also provide green strength to as-cast layers. Such constituents can either be nonadsorbed, i.e., “free” in solution, or adsorbed onto the ceramic particle surfaces. Before casting, suspensions typically undergo a two-stage milling process.<sup>1</sup> In the first stage, ceramic powder is milled with the dispersant/solvent system. Here, powder agglomerates are reduced, and the dispersant adsorbs onto the ceramic particle surfaces. In the second stage, polymeric species are added in solution, and the suspension is milled to promote homogeneous mixing. Because of the competitive adsorption phenomena, the final distribution of organic additives in such suspensions may deviate significantly from their aforementioned states.

The competition between adsorption of different organic additives on ceramic powder surfaces has received scant attention, even though the distribution of such species strongly influences suspension stability and rheological properties and, hence, the properties of as-formed components.<sup>5–11</sup> It is anticipated that

competitive adsorption phenomena affect the uniformity, solids content, and thickness of tape-cast ceramic layers.<sup>12–14</sup> Related work on aqueous systems has demonstrated that polymer adsorption influences suspension viscosity,<sup>5,15</sup> compaction behavior of spray-dried ceramic powders,<sup>16,17</sup> polymer migration during drying,<sup>5,18,19</sup> and strength of as-formed green bodies.<sup>20</sup> As an example, Hidber and co-workers<sup>5</sup> studied the competitive adsorption between polyvinyl alcohol (PVA) and citric acid on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder, and found that the presence of adsorbed citric acid dramatically reduced PVA adsorption. Components derived from such systems exhibited microstructural inhomogeneities stemming from segregation of nonadsorbed PVA at the drying front.<sup>5</sup> More recently, Guo and Lewis<sup>21</sup> observed similar microstructural inhomogeneities due to segregation of low molecular weight soluble species (e.g., salt) during drying of aqueous SiO<sub>2</sub> suspensions.

In this paper, competitive adsorption of Menhaden fish oil (MFO) and polyvinyl butyral (PVB) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is studied by diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and thermogravimetric analysis (TGA) during milling of nonaqueous tape casting suspensions. Both MFO and PVB have an affinity for hydroxyl groups present on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surfaces. Such species sequentially adsorbed during a two-stage milling process. The dispersant, MFO, was adsorbed onto  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder in the absence of PVB during first-stage milling. PVB species were then introduced to the suspension during second-stage milling and found to partially displace preadsorbed fish oil species from such surfaces. At the culmination of the milling process, PVB composed ~25–35 wt% of the adsorbed layer. These results highlight the potential importance of competitive adsorption phenomena in colloidal processing of ceramic films and bulk forms.

## II. Experimental Procedure

### (1) Materials System

The materials system used in this study represents a simplified version of commercial casting formulations and consists of single-ceramic, polymeric, and dispersant constituents in a two-component solvent system.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder (AKP-50, Sumitomo, Ltd., Sumitomo, Japan) serves as the ceramic phase. AKP-50 powder has a mean size of 0.2  $\mu$ m, as determined by sedimentation analysis (X-Ray Sedigraph, Model 5000E, Micromeritics, Inc., Norcross, GA) and a specific surface area of 11.2 m<sup>2</sup>/g, as determined by BET analysis (ASAP, Model 2400, Micromeritics). PVB (B79 and B76, Monsanto Chemical Co., St. Louis, MO) serves as the binder phase. PVB is commercially prepared by an acid-catalyzed butyraldehyde condensation reaction with PVA, which is almost fully hydrolyzed. Because of incomplete conversion, the resulting polymer is actually a terpolymer of PVB, PVA, and polyvinyl acetate. The chemical structure of PVB is shown in Fig. 1. The chemical compositions of PVB B79 and B76 are nearly identical, with A = 70.8 mol%, B = 27.2 mol%, and C = 2.0 mol%. Their average molecular weights are reported to be 65 000 g/mol and 105 000 g/mol for B79 and B76, respectively.<sup>22</sup> MFO is a complex mixture of triglycerides of saturated and unsaturated fatty acids, as shown in Fig. 2.<sup>23,24</sup> Calvert *et al.*<sup>23</sup> report that MFO contains roughly equal amounts of saturated, monosaturated, and

L. Bergstrom—contributing editor

Manuscript No. 188142. Received November 17, 2000; approved April 9, 2001. Supported by the National Science Foundation (NSF), through Grant Nos. DDM 93–13126 and DMR 94–53446.

Partially supported through an NSF SURGE Fellowship awarded to K. Blackman by the College of Engineering, University of Illinois, Urbana, IL.

\*Member, American Ceramic Society.

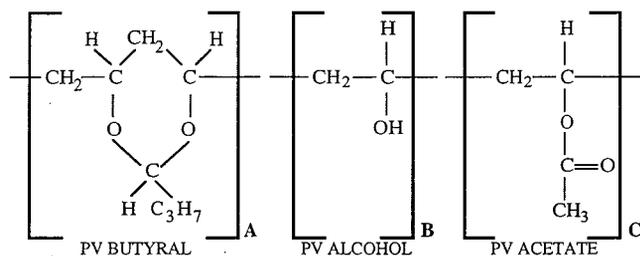


Fig. 1. Chemical structure of PVB.

penta- or hexa-unsaturated acids. To improve dispersant behavior, the starting oil is modified by an oxidation process conducted at  $\sim 90^\circ\text{C}$ . Dispersant-grade MFO (Werner G. Smith, Inc., Cleveland, OH) has an average molecular weight between 2000 and 3000 g/mol and a higher viscosity than the starting oil due to cross-linking of multiple triglyceride units during oxidation. The resulting oil is believed to contain approximately one acid group per six triglyceride units, with such groups located at chain ends.<sup>23</sup>

## (2) Adsorption Isotherms

Adsorption isotherm measurements were conducted on  $\text{Al}_2\text{O}_3$ -PVB (B76 and B79) and  $\text{Al}_2\text{O}_3$ -MFO suspensions with volumetric ratios of  $\text{Al}_2\text{O}_3$ /organic additive varying between 40/1 and 1/1 to determine the plateau coverage of these individual species on  $\alpha$ - $\text{Al}_2\text{O}_3$  powder. Stock solutions were prepared by first dissolving an appropriate amount of the organic additive in a 1/1 mixture by weight of methyl ethyl ketone (MEK)/toluene.  $\alpha$ - $\text{Al}_2\text{O}_3$  powder (10 vol%) was then added, and the suspensions were ball-milled for 24 h. A 5 mL aliquot was removed from each ball-milled suspension and centrifuged at 10 000 rpm. The supernatant was then decanted, and the sedimented powder was washed by redispersion in 50 mL of fresh solvent for 12 h. The suspensions were re-centrifuged and washed five additional times before drying the powder sediment. TGA (Model High Res-2950, TA Instruments, Newark, DE) was conducted on the dried powders. Samples (50 mg) were heated in air at  $10^\circ\text{C}/\text{min}$  to  $100^\circ\text{C}$ , held at  $100^\circ\text{C}$  for 1 h, heated to  $1000^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , and then cooled to room temperature.

## (3) Competitive Adsorption during Second-Stage Milling

Competitive adsorption experiments were conducted on tape casting suspensions to determine the compositional evolution of the adsorbed organic layer (adlayer) during milling. These suspensions contained 10 vol%  $\alpha$ - $\text{Al}_2\text{O}_3$  powder, 8 vol% PVB (B79 or B76), and 4 vol% MFO in the appropriate solvent mixture. Suspensions were formulated so that excess PVB and MFO species (greater than their respective plateau coverages) were present in solution, and were prepared by first dissolving MFO in a 1/1 by weight mixture of MEK/toluene.  $\alpha$ - $\text{Al}_2\text{O}_3$  powder was then slowly added to the MFO solution, and the suspension was milled for 24 h. At the end of first-stage milling, a 5 mL aliquot of suspension was extracted from the mill. A PVB stock solution (in 1/1 MEK/toluene) was then added to the mill, and second-stage milling was conducted for  $\leq 100$  h. To avoid complications arising from the creation of "fresh"  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces during second-stage

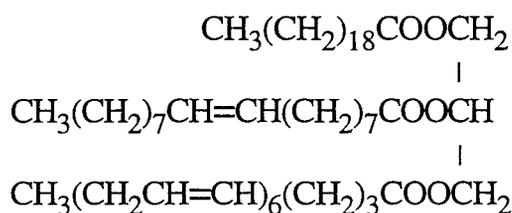


Fig. 2. Chemical structure of triglyceride units present in MFO.

milling, analogous suspensions were also fast-rolled in the absence of milling media for the same periods of time. A representative portion of each suspension was extracted at intermittent times during second-stage milling or rolling. The extracted samples were washed following the procedure described earlier. Nitrogen gas adsorption measurements (Model ASAP 2400, Micromeritics) were conducted on each dried powder sample to determine their specific surface area. The remaining samples were stored in a desiccator before further analysis.

DRIFTS and TGA analyses were conducted on the dried powders to evaluate their adlayer composition and mass, respectively. DRIFTS samples were prepared by mixing the dried powders with KBr at a weight ratio of 5/95 using an agate mortar and pestle. The samples were studied using a spectrometer (Model Magna IR 550, Nicolet Instruments Corp., Madison, WI) equipped with a triglycerine sulfate (TGS) detector and mounted with a diffuse reflectance cell (Model Collector<sup>TM</sup>, Spectra-Tech, Inc., Shelton, CT) in the optics chamber. The chamber was purged with filtered air, which eliminated  $\text{H}_2\text{O}(g)$  and  $\text{CO}_2(g)$  from the inlet stream. Each spectrum was acquired at a resolution of  $2\text{ cm}^{-1}$  and represented an average of 128 scans. The as-collected spectra were converted to Kubelka-Munk units to yield the desired direct relationship between functional group concentration and corresponding peak intensity.<sup>25,26</sup> TGA samples were heated following the thermal profile outlined earlier.

Control samples of known adlayer composition were also analyzed by DRIFTS. Samples were prepared by blending together two  $\alpha$ - $\text{Al}_2\text{O}_3$  powders: one with adsorbed MFO ( $2.3\text{ mg}/\text{m}^2$ ), and the other with adsorbed PVB ( $3.4\text{ mg}/\text{m}^2$ ). Such powders were blended together in appropriate weight ratios so that the adsorbed layer content varied between 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 of MFO/PVB by weight, and then mixed with KBr and analyzed following the procedure described above. These control samples facilitated the analysis of adlayer composition in the milled and rolled samples where sequential competitive adsorption of both additives occurred.

## III. Results and Discussion

### (1) Adsorption of PVB and MFO on $\alpha$ - $\text{Al}_2\text{O}_3$

The respective adsorption isotherms of PVB B76, PVB B79, and MFO on the  $\alpha$ - $\text{Al}_2\text{O}_3$  powder are shown in Fig. 3. Plateau coverage of PVB on  $\alpha$ - $\text{Al}_2\text{O}_3$  occurred at  $3.46\text{ mg PVB}/\text{m}^2\text{ Al}_2\text{O}_3$ , which corresponded to a weight ratio of  $45\text{ mg PVB}/\text{g}$  of  $\text{Al}_2\text{O}_3$

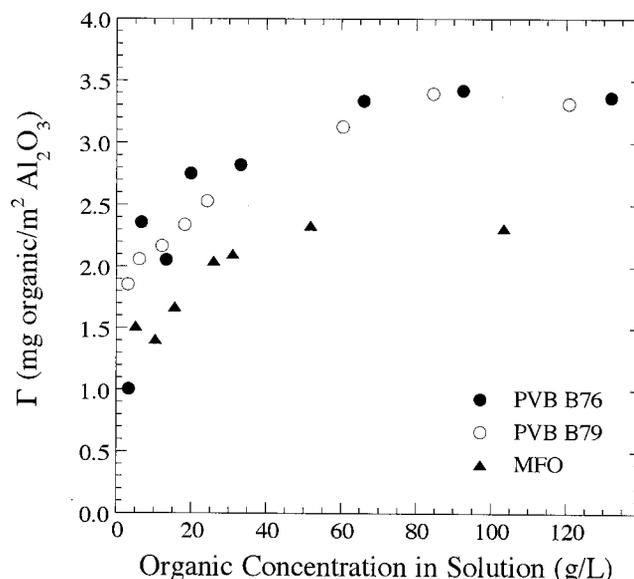
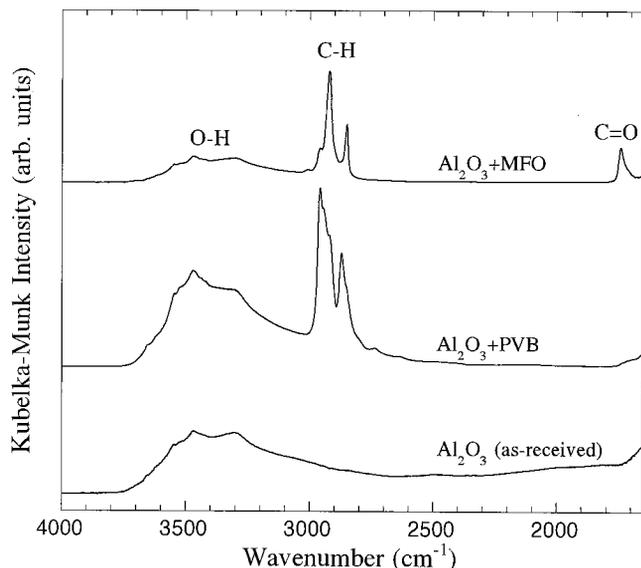


Fig. 3. Adsorption isotherms ( $\Gamma$ ) of PVB B79, PVB B76, and MFO on  $\alpha$ - $\text{Al}_2\text{O}_3$  powder in a 1/1 MEK/toluene solvent system.



**Fig. 4.** DRIFTS spectra of as-received  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ - $\text{Al}_2\text{O}_3$  powder with adsorbed layer of PVB or MFO, respectively.

powder. Interestingly, the plateau coverage of PVB B79 and B76 appeared to be identical, even though their average molecular weights differed by almost a factor of two. Similar trends were reported by Howard *et al.*<sup>27</sup> for adsorption of PVB of differing chain lengths onto  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces. The relative insensitivity of adlayer mass to PVB chain length likely stemmed from the broad molecular weight distribution of these commercially prepared polymers. Plateau coverage of MFO on  $\alpha$ - $\text{Al}_2\text{O}_3$  occurred at 2.31 mg fish oil/m<sup>2</sup>  $\text{Al}_2\text{O}_3$ , which corresponded to a weight ratio of 30 mg fish oil/g of  $\text{Al}_2\text{O}_3$  powder.

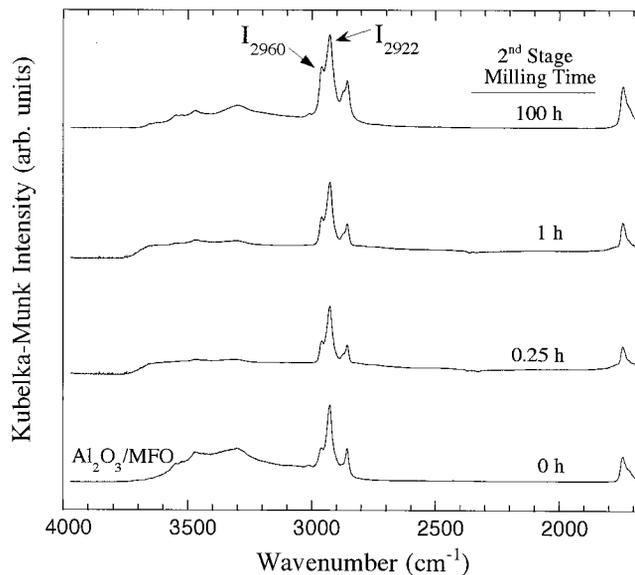
DRIFTS analysis of as-received  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  powder with plateau coverages of adsorbed PVB B79, PVB B76, and MFO are shown in Fig. 4. As-received  $\text{Al}_2\text{O}_3$  powder had DRIFTS peaks between 3200–3600  $\text{cm}^{-1}$  corresponding to surface hydroxyl groups, and a strong absorption edge below 1500  $\text{cm}^{-1}$ . Additional DRIFTS peaks were observed at 2960, 2922, and 2873  $\text{cm}^{-1}$  for powders with adsorbed PVB, which corresponded to aliphatic C–H stretching. In comparison, powders with adsorbed MFO had these same peaks (i.e., 2960, 2922, and 2873  $\text{cm}^{-1}$ ) as well as a peak at 1744  $\text{cm}^{-1}$ , which corresponded to C=O stretching.

The interaction of PVB with  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces has been studied previously by Sacks and Scheiffel<sup>28</sup> and Howard *et al.*<sup>27</sup> Both studies found evidence indicating that hydroxyl side groups on PVB chains interact strongly with surface hydroxyl groups on oxide powders via hydrogen bonding. Howard *et al.*<sup>27</sup> also suggest that strong interactions may occur between residual acetate groups on PVB chains and oxide surfaces. Given the chemical composition of PVB studied here, it is expected that hydrogen bonding between hydroxyl side groups and the hydroxylated oxide surface would be the predominate interaction promoting its adsorption onto  $\alpha$ - $\text{Al}_2\text{O}_3$ .

The interaction of MFO with  $\alpha$ - $\text{Al}_2\text{O}_3$  powder suspended in toluene has been studied in detail by Calvert *et al.*<sup>23</sup> The carboxylic acid groups present in MFO anchor strongly to  $\alpha$ - $\text{Al}_2\text{O}_3$  surface via interaction with surface hydroxyl sites. Calvert *et al.*<sup>23</sup> have estimated the area occupied per adsorbed fish oil molecule to be roughly 0.85  $\text{nm}^2$ . Assuming this cross-sectional area and an average molecular weight of 2500 g/mol for MFO, one finds ~50% of the  $\alpha$ - $\text{Al}_2\text{O}_3$  powder surface is covered by such species at the end of first-stage milling.

## (2) Competitive Adsorption of PVB and MFO on $\alpha$ - $\text{Al}_2\text{O}_3$ during Second-Stage Milling

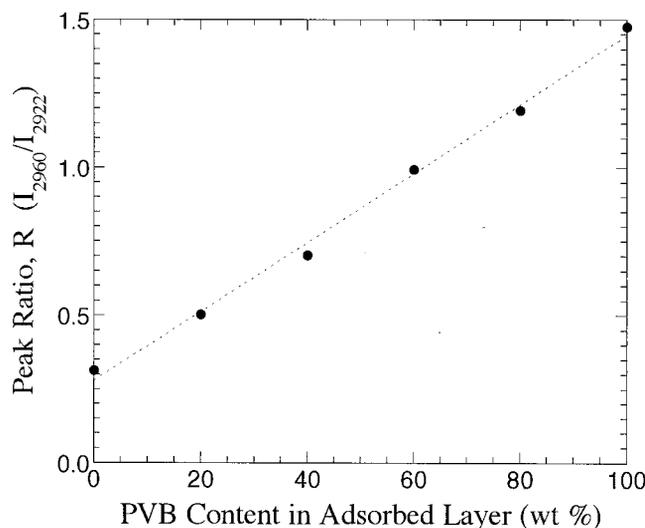
DRIFTS spectra obtained from  $\alpha$ - $\text{Al}_2\text{O}_3$  powders with preadsorbed MFO milled in the presence of PVB for various times are



**Fig. 5.** DRIFTS spectra of milled  $\alpha$ - $\text{Al}_2\text{O}_3$  powder with preadsorbed MFO layer as function of second-stage milling time. (Note: Samples were milled in presence of PVB.)

shown in Fig. 5. The lower curve corresponds to the DRIFTS spectra obtained on powders that have not been second-stage milled ( $t = 0$  min) and is analogous to that in the spectra shown in Fig. 4 for  $\text{Al}_2\text{O}_3$ /MFO (only). Note, such samples have a characteristic maximum peak at 2922  $\text{cm}^{-1}$ , with intensity  $I_{2922}$ . In contrast, a characteristic maximum peak at 2960  $\text{cm}^{-1}$ , with intensity  $I_{2960}$ , is observed for  $\text{Al}_2\text{O}_3$ /PVB (only), as shown in Fig. 4. The DRIFTS peak intensities (in Kubelka–Munk units) are directly proportional to the concentration of adsorbed organic species. The peak intensity ratio,  $R (= I_{2960}/I_{2922})$ , increases as a function of second-stage milling (or rolling) time, indicating increasing PVB adsorption on the  $\alpha$ - $\text{Al}_2\text{O}_3$  powder.

To determine the compositional evolution of the adsorbed organic layer during second-stage milling, the observed peak intensity ratio,  $R$ , for a given sample was compared with values obtained from adsorption standards. As described earlier, standards consisting of  $\text{Al}_2\text{O}_3$ /MFO (only) and  $\text{Al}_2\text{O}_3$ /PVB (only) powders were blended together to produce different organic layers



**Fig. 6.**  $R$  as function of PVB content in adsorbed organic layers present on blended  $\alpha$ - $\text{Al}_2\text{O}_3$ /MFO and  $\alpha$ - $\text{Al}_2\text{O}_3$ /PVB powder standards, where  $R = I_{2960}/I_{2922}$ .

of known composition and analyzed by DRIFTS. A plot of the  $R$  as a function of PVB content in the adsorbed organic layer for these standard samples is shown in Fig. 6. The value of  $R$  was found to increase linearly with increasing PVB content. Using this relationship, the amount of PVB adsorbed on the  $\alpha$ - $\text{Al}_2\text{O}_3$  powder during second-stage milling (or rolling) was determined, as shown in Figs. 7(a) and (b) for PVB B79 and B76, respectively. At short times ( $t < 6.3$  h), the amount of PVB adsorbed increased rapidly, followed by an asymptotic approach to plateau values at longer times ( $t > 20$  h). The inset plots in Fig. 7 depict the square root of time ( $t^{1/2}$ ) dependence of adlayer composition in the short-time regime. Here, the PVB content in the adsorbed organic layer increased linearly with  $t^{1/2}$  for the rolled samples. This trend was not observed for the milled powders, where PVB adsorption occurred to a slightly greater extent. Such differences likely arose from complications due to changes in the specific surface area of the  $\alpha$ - $\text{Al}_2\text{O}_3$  powders with increased milling time, as shown in

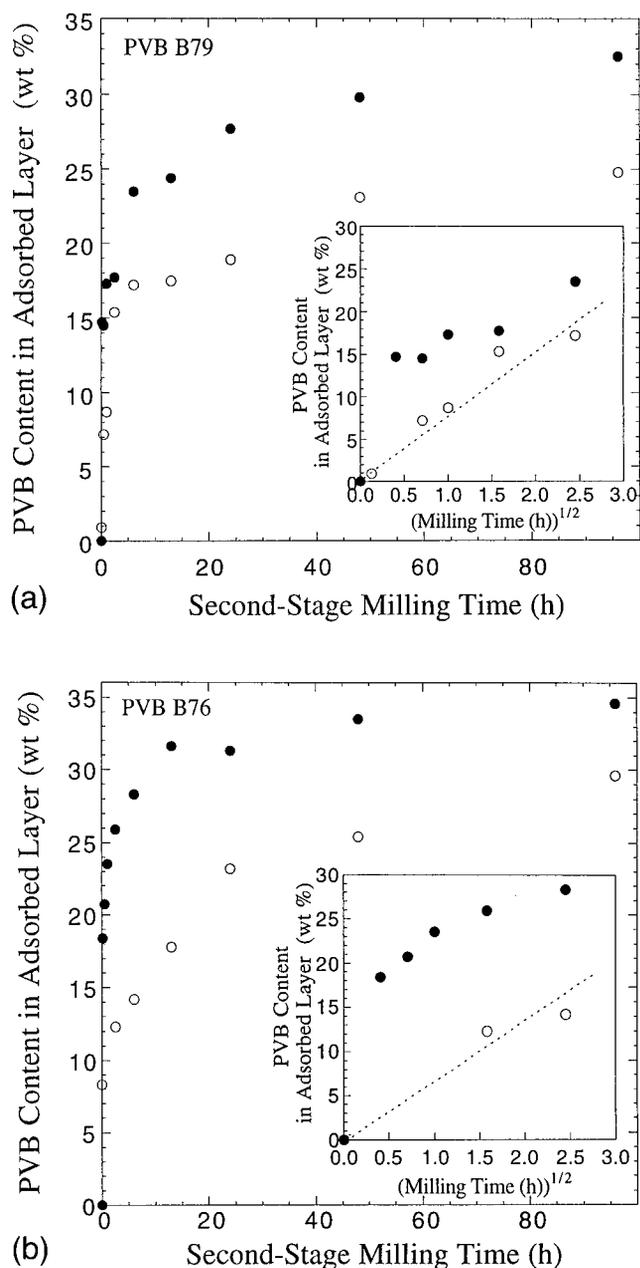


Fig. 7. PVB content in adsorbed organic layers of milled  $\alpha$ - $\text{Al}_2\text{O}_3$  powder with preadsorbed MFO layer as function of second-stage milling time. Samples were milled in presence of (a) PVB B79 and (b) PVB B76. (Note: (●) denote milled samples, and (○) denote rolled samples.)

Table I. Milling Effects on Specific Surface Area of  $\text{Al}_2\text{O}_3$  Powder<sup>†</sup>

Sample	Specific surface area ( $\text{m}^2/\text{g}$ )
As-received	11.23
Premilled for 24 h, second-stage-milled for 1 h	13.13
Premilled for 24 h, second-stage-milled for 24 h	13.22
Premilled for 24 h, second-stage-milled for 48 h	13.40
Premilled for 24 h, second-stage-milled for 100 h	13.79

<sup>†</sup>Sample is AKP-50  $\text{Al}_2\text{O}_3$ .

Table I. Note, these complications were avoided by rolling samples in the absence of milling media, which exhibited a constant specific surface area of  $\sim 13 \text{ m}^2/\text{g}$  during this process.

To evaluate whether PVB chains actually displace preadsorbed MFO species on  $\alpha$ - $\text{Al}_2\text{O}_3$  or simply attach at different surface sites (i.e., coadsorb), TGA analysis was conducted on the milled (or rolled) powders. The total organic layer mass was plotted in Fig. 8(a) and (b) as a function of second-stage milling (or rolling) time for PVB B79 and B76, respectively. These data were normalized by powder surface area measured for a given set of conditions, as discussed above. The dashed lines in Fig. 8 depict the calculated values of adlayer mass at  $t = 100$  h for coadsorption and competitive adsorption of PVB on  $\alpha$ - $\text{Al}_2\text{O}_3$  powder. These respective values were estimated based on the averaged organic layer composition at the culmination of second-stage milling and rolling processes (refer to Fig. 7). The final mass of the adsorbed organic layer, as determined by TGA, exhibited good agreement with the mass calculated assuming competitive adsorption of PVB (via MFO displacement) on the milled and rolled  $\alpha$ - $\text{Al}_2\text{O}_3$  powders. For PVB B79, the experimental values were slightly below this estimated mass; whereas, for B76, the experimental values slightly exceeded the estimated mass. However, it should be noted that these experimental values were far below the adlayer masses estimated for coadsorption of both MFO and PVB species, in both the milled and rolled powders.

Adsorption of organic species involves a complex interplay of several processes: diffusion from the bulk solution to the solid/liquid interface, attachment (or detachment) to the surface, and rearrangement into an equilibrium conformation.<sup>29–34</sup> Diffusion is a relatively rapid process that scales inversely with the molecular weight of the organic species. The  $t^{1/2}$  dependence of the adlayer composition in the short-time regime of second-stage rolling ( $t < 6.3$  h) suggests that the initial displacement of MFO by PVB is diffusion-controlled (refer to inset plots in Fig. 7). In this regime, a preadsorbed MFO layer exists on the  $\alpha$ - $\text{Al}_2\text{O}_3$  surface. Thus, the rate-limiting step in this process could be diffusion of PVB from the bulk solution to the solid surface, diffusion of PVB through the adsorbed MFO layer, or diffusion of MFO from the surface to the bulk solution. Given the large molecular weight differences between PVB and MFO, this latter process is unlikely to be rate-limiting. Adsorption and desorption processes scale with the number of surface-segment contacts and can occur over long time scales for organic species (e.g., polymers), which contain multiple adsorbing groups. In this case, the surface-segment bonds depend on surface affinity, and many “bonds” must be either formed or broken for polymer adsorption or desorption, respectively, to occur.<sup>30,33</sup> At longer times, adsorbed species alter their configuration on solid surfaces to adopt an equilibrium structure. This process, known as relaxation, is also expected to occur slowly for species adsorbed at multiple surface sites, because chains must reconfigure to their equilibrium structure by another segment-by-segment process.<sup>34</sup>

Competitive adsorption phenomena occur when multiple organic species, each with an affinity for the solid surface(s), exist in solution or suspension.<sup>29–47</sup> The degree of competition between such species depends on many factors, including their molecular weight, chemical structure (i.e., affinity for the solid surface), and solid-surface geometry. In the tape casting suspensions studied here, such phenomena could be driven either by molecular weight

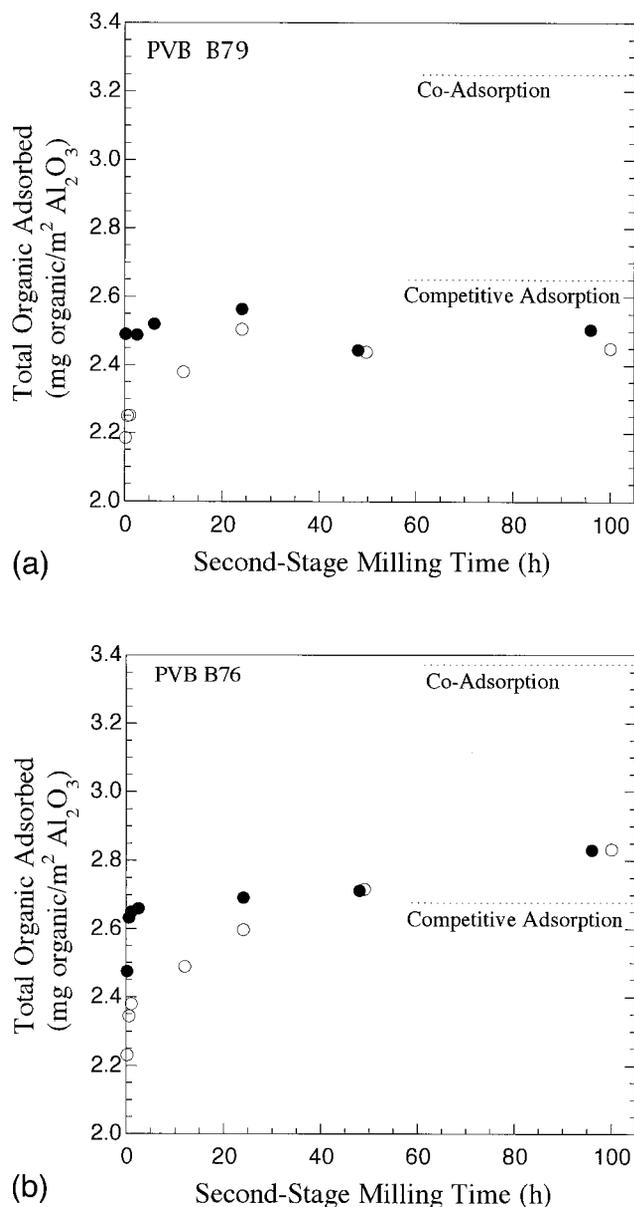


Fig. 8. Total adsorbed organic layer mass on milled  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder with preadsorbed MFO layer as function of second-stage milling time. Samples were milled in presence of (a) PVB B79 and (b) PVB B76. (---) represent estimated average plateau values for competitive adsorption and coadsorption of PVB, respectively. (Note: (●) denote milled samples, and (○) denote rolled samples.)

or chemical differences between PVB and MFO. In the absence of chemical (or surface affinity) differences between competing organic species, it is well known that higher molecular weight species preferentially adsorb onto solid surfaces. Such size-driven competitive adsorption processes have been studied previously for polymers with broad molecular weight distributions.<sup>30,34,36,38,40,41</sup>

In these experiments, short chains were found to adsorb initially, because they could diffuse more quickly to the solid/liquid interface. However, such species are ultimately displaced from solid surface(s) by the adsorption of longer chains. Preferential adsorption of higher molecular weight species is thermodynamically favored due to entropic considerations. In fact, Scheutjens and Fleer<sup>48</sup> have shown that when the molecular weight varies by more than a factor of 2, longer chain species completely displace short chains from solid surfaces. Size-driven competitive adsorption does not always prevail, however, as evidenced by the results obtained in the present study. Given the dramatic difference in molecular weight between MFO and PVB, one would expect

PVB to completely displace preadsorbed MFO species during second-stage milling, if size-driven effects were the only driving force.

Dijt *et al.*<sup>37</sup> have shown that preferential adsorption arising from segmental adsorption energy differences dominates over chain-length differences. Hidber *et al.*<sup>5</sup> found similar effects in their study of competitive adsorption behavior in aqueous Al<sub>2</sub>O<sub>3</sub>-PVA-citric acid suspensions. They found that the adsorption of PVA (MW  $\approx$  22 000 g/mol) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> decreased over 75%, from 0.044 to 0.01 mg/m<sup>2</sup>, in the presence of more strongly adsorbing, lower molecular weight citric acid. In the present study of nonaqueous Al<sub>2</sub>O<sub>3</sub>-PVB-MFO suspensions, the presence of preadsorbed MFO species reduced PVB adsorption on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by a comparable amount. Thus, one concludes that MFO has a stronger affinity for these solid oxide surfaces, so that it is not completely displaced when milled in the presence of PVB.

#### IV. Conclusions

Competitive adsorption phenomena were studied during milling of nonaqueous Al<sub>2</sub>O<sub>3</sub>-PVB-MFO suspensions. Such suspensions are representative of those used to fabricate tape-cast ceramic layers. First, the adsorption behavior of these organic additives was studied independently. Adsorption isotherm measurements revealed that both species had an affinity for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder surfaces. Their respective plateau coverages on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> occurred at 3.46 mg PVB/m<sup>2</sup> Al<sub>2</sub>O<sub>3</sub> and 2.31 mg fish oil/m<sup>2</sup> Al<sub>2</sub>O<sub>3</sub>. In the first milling stage, MFO was allowed to adsorb onto  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder in the absence of PVB. During the second milling stage, PVB was found to partially displace preadsorbed MFO species on such surfaces. At the culmination of the milling process, PVB composed  $\sim$ 25–35 wt% of the adsorbed organic layer. Because the distribution of organic additives in tape casting suspensions may affect suspension viscosity, binder migration during drying, and strength of tape-cast ceramic layers, these observations suggest that competitive adsorption phenomena could significantly influence the processing of tape-cast ceramic layers. Such phenomena are driven by differences in chemical functionality and/or molecular weight, and can be expected to occur in suspensions containing either multiple organic processing aids (each of which have an affinity for ceramic powder surfaces) or single polymeric additives of broad molecular weight distribution. To minimize property variability in as-formed ceramic films and bulk shapes, one must carefully consider these effects when designing suspension formulations and appropriate processing conditions.

#### Acknowledgments

The authors gratefully acknowledge the experimental assistance of P. Desai and A. Ogden.

#### References

- R. E. Mistler, "Tape Casting: The Basic Process for Meeting the Needs of the Electronic Industry," *Am. Ceram. Soc. Bull.*, **69** [6] 1022–26 (1990).
- W. Young, "Multilayer Ceramic Technology"; pp. 403–22 in *Ceramic Materials for Electronics*. Edited by R. Buchanan. Marcel Dekker, New York, 1986.
- R. R. Tummala, "Ceramic Packaging"; pp. 455–521 in *Microelectronics Packaging Handbook*. Edited by R. R. Tummala and E. J. Rymaszewski. Van Nostrand Reinhold, New York, 1989.
- D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*. Academic Press, London, U.K., 1983.
- P. C. Hidber, T. J. Graule, and L. J. Gauckler, "Competitive Adsorption of Citric Acid and Polyvinyl alcohol onto Alumina and Its Influence on the Binder Migration during Drying," *J. Am. Ceram. Soc.*, **78** [7] 1775–80 (1995).
- J. R. Morris and W. R. Cannon, "Rheology and Component Interactions in Tape Casting Slurries"; pp. 135–42 in *Defect Properties and Processing of High Technology Nonmetallic Materials*, Materials Research Society Symposium Proceedings, Vol. 60. Edited by Y. Chen, W. D. Kingery, and R. J. Stokes. Materials Research Society, Pittsburgh, PA, 1986.
- R. Mereno, "The Role of Slip Additives in Tape Casting Technology, Part 2: Binders and Plasticizers," *Am. Ceram. Soc. Bull.*, **71** [11] 1647–57 (1992).
- R. M. Silitay, "The Effects of Suspension Stability and Rheology on the Microstructure of As-Cast Alumina-Poly(vinyl butyral) Tapes"; M. S. Thesis. University of Illinois, Urbana, IL, 1994.

- <sup>9</sup>L. Braun, J. R. Morris Jr., and W. R. Cannon, "Viscosity of Tape Casting Slips," *Am. Ceram. Soc. Bull.*, **64** [5] 727–29 (1985).
- <sup>10</sup>V. L. Richards II, "Adsorption of Dispersants on Zirconia Powder in Tape Casting Slip Compositions," *J. Am. Ceram. Soc.*, **72** [2] 325–27 (1989).
- <sup>11</sup>J. A. Lewis, "Colloidal Processing of Ceramics," *J. Am. Ceram. Soc.*, **83** [10] 2341–59 (2000).
- <sup>12</sup>Y. T. Chou, Y. T. Ko, and M. F. Yan, "Fluid Flow Model for Ceramic Tape Casting," *J. Am. Ceram. Soc.*, **70** [10] C280–C281 (1987).
- <sup>13</sup>R. Pitchumani and V. M. Karbhari, "Generalized Fluid Flow Model for Ceramic Tape Casting," *J. Am. Ceram. Soc.*, **78** [9] 2497–503 (1995).
- <sup>14</sup>J. A. Lewis, K. A. Blackman, A. L. Ogdan, J. Payne, and L. Francis, "Drying of Tape-Cast Ceramic Layers," *J. Am. Ceram. Soc.*, **79** [12] 3225–34 (1996).
- <sup>15</sup>W. J. Walker, J. S. Reed, and S. K. Verma, "Polyethylene Glycol Binders for Advanced Ceramics" (Paper No. 52-EP-92) and "Rheology and Spray Drying of Polyethylene Glycol-Based Alumina Slurries" (Paper No. 53-EP-92); presented at the Annual Meeting of the American Ceramic Society, Minneapolis, MN, April 12–16, 1992.
- <sup>16</sup>R. G. Frey and J. W. Holloran, "Compaction Behavior of Spray-Dried Alumina," *J. Am. Ceram. Soc.*, **67** [3] 199–203 (1984).
- <sup>17</sup>C. W. Nies and G. L. Messing, "Binder Hardness and Plasticity in Granule Compaction"; pp 58–66 in *Forming of Ceramics*, Advances in Ceramics, Vol. 9. Edited by J. A. Mangels. American Ceramic Society, Columbus, OH, 1984.
- <sup>18</sup>Y. Zhang, M. Kawasaki, K. Ando, Z. Kato, N. Uchida, and K. Uematsu, "Surface Segregation of PVA during Drying of a PVA–Water–Al<sub>2</sub>O<sub>3</sub> Slurry," *J. Ceram. Soc. Jpn., Int. Ed.*, **100** [8] 1055–58 (1992).
- <sup>19</sup>Y. Zhang, X. Tang, N. Uchida, and K. Uematsu, "Mathematical Simulation for Segregation of PVA during Drying," *J. Ceram. Soc. Jpn., Int. Ed.*, **101** [2] 177–80 (1993).
- <sup>20</sup>K. Kendall, N. McN. Alford, and J. D. Birchall, "The Strength of Green Bodies"; pp 255–65 in *Special Ceramics 8*, British Ceramic Society Proceedings, Vol. 37. Edited by S. P. Howlett and D. Taylor. Institute of Ceramics, Stoke-on-Trent, U.K, 1986.
- <sup>21</sup>J. Guo and J. A. Lewis, "Aggregation Effects on Compressive Flow Properties and Drying Behavior of Colloidal Silica Suspensions," *J. Am. Ceram. Soc.*, **82** [9] 2345–58 (1999).
- <sup>22</sup>Butvar Resins Product Literature, No. 8084A. Monsanto Chemical Co., St. Louis, MO.
- <sup>23</sup>P. D. Calvert, E. S. Tormey, and R. L. Pober, "Fish Oil and Triglycerides as Dispersants for Alumina," *Am. Ceram. Soc. Bull.*, **65** [4] 669–72 (1986).
- <sup>24</sup>R. Moreno and G. Cordoba, "Oil Dispersion of Alumina for Tape Casting," *Am. Ceram. Soc. Bull.*, **74** [7] 69–74 (1995).
- <sup>25</sup>P. Kubelka, "New Contributions to the Optics of Intensely Light-Scattering Materials, Part I," *J. Opt. Soc. Am.*, **38**, 448–57 (1948).
- <sup>26</sup>M. P. Fuller and P. R. Griffiths, "Diffuse Reflectance Measurements by Infrared Fourier Transform Spectroscopy," *Anal. Chem.*, **50** [13] 1906–10 (1978).
- <sup>27</sup>K. E. Howard, C. D. E. Lakeman, and D. A. Payne, "Surface Chemistry of Various Polyvinyl butyral Polymers Adsorbed onto Alumina," *J. Am. Ceram. Soc.*, **73** [8] 2543–46 (1990).
- <sup>28</sup>M. D. Sacks and G. W. Scheiffele, "Polymer Adsorption and Particulate Dispersion in Nonaqueous Al<sub>2</sub>O<sub>3</sub> Suspensions Containing Polyvinyl butyral Resins," *Adv. Ceram.*, **19**, 175–84 (1986).
- <sup>29</sup>H. E. Johnson and S. Granick, "Exchange Kinetics between the Adsorbed State and Free Solution: Poly(methyl methacrylate) in Carbon Tetrachloride," *Macromolecules*, **23** [13] 3367–74 (1990).
- <sup>30</sup>P. Frantz and S. Granick, "Exchange Kinetics of Adsorbed Polymer and the Achievement of Conformational Equilibrium," *Macromolecules*, **27**, 2553–58 (1994).
- <sup>31</sup>J. C. Dijt, M. A. Cohen Stuart, J. E. Hofman, and G. J. Fleer, "Kinetics of Polymer Adsorption in Stagnation Point Flow," *Colloids Surf.*, **51**, 141–58 (1990).
- <sup>32</sup>M. Kawaguchi, S. Anada, K. Nishikawa, and N. Kurata, "Effect of Surface Geometry on Polymer Adsorption. 2. Individual Adsorption and Competitive Adsorption," *Macromolecules*, **25** [5] 1588–93 (1992).
- <sup>33</sup>J. C. Dijt, M. A. Cohen Stuart, and G. J. Fleer, "Kinetics of Adsorption and Desorption of Polystyrene on Silica from Decalin," *Macromolecules*, **27** [12] 3207–18 (1994).
- <sup>34</sup>P. Frantz and S. Granick, "Kinetics of Polymer Adsorption and Desorption," *Phys. Rev. Lett.*, **66** [7] 899–902 (1991).
- <sup>35</sup>D. J. Kuzmenka and S. Granick, "Kinetics of Polymer Adsorption Measured in Situ at the Solid–Liquid Interface: Utility of the Infrared Total Internal Reflection Method," *Colloids Surf.*, **31**, 105–116 (1988).
- <sup>36</sup>G. K. Rowe and S. E. Creager, "Chain Length and Solvent Effects on Competitive Self-Assembly of Ferrocenylhexanethiol and 1-Alkanethiols onto Gold," *Langmuir*, **10** [4] 1186–92 (1994).
- <sup>37</sup>J. C. Dijt, M. A. Cohen Stuart, and G. J. Fleer, "Surface Exchange Kinetics of Chemically Different Polymers," *Macromolecules*, **27** [12] 3229–37 (1994).
- <sup>38</sup>J. C. Dijt, M. A. Cohen Stuart, and G. J. Fleer, "Competitive Adsorption Kinetics of Polymers Differing in Length Only," *Macromolecules*, **27** [12] 3219–28 (1994).
- <sup>39</sup>H. E. Johnson, S. J. Clarson, and S. Granick, "Overshoots as Polymers Adsorb," *Polymer*, **34** [9] 1960–62 (1993).
- <sup>40</sup>P. Frantz, D. C. Leonhardt, and S. Granick, "Enthalpic Effects in Competitive Polymer Adsorption: Adsorption Isotope Effect and Chain End Effect," *Macromolecules*, **24** [8] 1868–75 (1991).
- <sup>41</sup>C. Vander Linden and R. Van Leemput, "Adsorption Studies of Polystyrene on Silica. 2. Polydisperse Adsorbants," *J. Colloid Interface Sci.*, **67** [1] 63–69 (1978).
- <sup>42</sup>K. Furusawa, K. Yamashita, and K. Konno, "Adsorption of Monodisperse Polystyrene onto Porous Glass. 1. Preference Adsorption and Displacement of High-Molecular-Weight Species," *J. Colloid Interface Sci.*, **86** [1] 35–42 (1980).
- <sup>43</sup>K. Furusawa and K. Yamamoto, "Adsorption of Monodisperse Polystyrene onto Porous Glass," *J. Colloid Interface Sci.*, **96** [1] 268–74 (1983).
- <sup>44</sup>M. Kawaguchi, Y. Sakata, S. Anada, T. Kato, and A. Takahashi, "Kinetics of Competitive Adsorption of Polystyrene Chains at a Porous Silica Surface," *Langmuir*, **10** [2] 538–41 (1994).
- <sup>45</sup>R. Csempesz, S. Rohrer, and P. Kovacs, "Interfacial Behavior of Binary Polymer Mixtures II. Competitive Polymer Adsorption and its Effect on the Stability of Colloidal Dispersions," *Colloids Surf.*, **24** [2–3] 101–17 (1987).
- <sup>46</sup>C. Ligoure and L. Leibler, "Decoration of Rough Surfaces by Chain Grafting," *Macromolecules*, **23** [23] 5044–46 (1990).
- <sup>47</sup>M. Singh, M. Tirrell, and P. Bates, "Adsorption of End-Functionalized Polystyrene on Model Textured Surfaces," *Macromolecules*, **27** [9] 2586–94 (1994).
- <sup>48</sup>J. M. H. M. Scheutjens and G. J. Fleer, *The Effect of Polymers on Dispersion Properties*. Edited by Th. F. Thadros. Academic Press, New York, 1982. □