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Chain Conformation of Adsorbed Ethylene Random Copolymers

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ABSTRACT: The structures formed by the adsorption of poly(ethylene-*co*-acrylic acid) (PEA), poly(ethylene-*co*-vinyl alcohol) (EVOH), poly(ethylene-*co*-vinyl acetate) (EVA), and polyethylene (PE) on metal oxide powders were characterized by solid-state NMR spectroscopy and FTIR-PAS. The effect of the copolymer loading and the polar group density on the chain conformation and mobility were examined. In the case of the strongest polar group−substrate interactions, the chain conformation is determined by the sticker group density rather than the coverage until all the binding sites have been occupied. As the binding strength decreases, this trend diminishes, and there is a corresponding increase in the chain order as reflected by the ^{13}C chemical shifts of the ethylene segments. The chain conformation of the most weakly bound copolymer (EVA on alumina) shows no dependence on either the sticker group content or the coverage, similar to the homopolymer, PE. Some surface hydrolysis of EVA and of the residual ester groups of EVOH is also detected.

1. Introduction

Polymer adhesion is widely studied due to its relevance in industrial applications. Composite manufacturing and durability, adhesion promoters for polymer coatings on metals, paper and laminates, as well as protective coatings and photoresists are a few examples of areas where knowledge of polymer adhesion is important. The fundamental understanding of the behavior of polymer chains near the solid surface is of importance since the structure and strength of polymer−solid interfaces are intimately related.[1] It is well-known that the adhesion of a polymer to a surface can be enhanced by incorporating certain functional groups into the polymer. Most research has been limited to determining the effect of these modifications on the material properties. Recently, it has been suggested that the interaction of polymer sticker groups and substrate receptor group is the main factor controlling the strength of the polymer−solid interface.[2] The surface bond strength in turn determines the configuration of the adsorbed polymer. Strong equilibrium binding is expected to produce a compact layer of trains whereas weaker binding allows the formation of a more diffuse layer of loops and tails. Nonequilibrium strong binding will also give rise to loops and tails of unreacted polymer chains extending away from the surface.[3] The formation of such structures ultimately determines the adhesive and cohesive strengths of a polymer coating on a solid surface.

Copolymers of polyethylene-containing polar groups are commonly used as adhesion promoters between metal surfaces and polyethylene coatings. In previous work, Nasreddine et al.[4] studied poly(ethylene-*co*-acrylic acid) (PEA) random copolymers adsorbed onto zirconia by solid-state NMR and FTIR. The PEA/zirconia system was chosen because it is a convenient system that displays strong polymer adsorption. A connection between the chain conformation of polyethylene segments as determined by ^{13}C chemical shifts and the interaction of the acrylic acid with the surface as determined by FTIR was established. Solid-state 2D wide-line separation (WISE) and ^{1}H spin diffusion NMR experiments were used to determine chain motion and morphology of bulk and adsorbed copolymers. Results showed that the polymer conformation depended on sticker density and not on coverage. Also, the adsorbed copolymers with a low density of sticker groups had an ordered, less mobile component that was attributed to partially folded loops and not trains. [4]

In other relevant studies, Hjertberg et al.[5] showed that the adhesion between alumina and polyethylene increased with the content of butyl acrylate and vinyl acetate as comonomers. Ulrén et al.[6] looked at the effect of carboxylic acid, ester, and silane functional groups in ethylene copolymers on the adhesion with aluminum. The interface was studied by FTIR, and the adhesion mechanism for each functional group was evaluated. They were able to determine that the strength of the interfacial interactions depended on acidity/basicity and the concentration of the functional group. Cosgrove et al.[7] studied the adsorption of random copolymers of poly(ethylene-*co*-vinyl acetate) on modified silica surfaces by NMR, SANS, and MC. The solution-state NMR measurements showed that there was a direct correlation between the adsorbed amount and the bound fraction. Finally, Brogly and co-workers published a series of papers using surface IR methods to study the interaction of random copolymers of EVA with alumina and determined that the polymer interacted via a Lewis acid−base interaction.[8]

The goals of the present paper are to study the effect of sticker group density and binding strength on chain conformation and dynamics of adsorbed ethylene copolymers by using a number of random copolymers at various weight percents. Since the key parameter is interfacial sticker group density rather than bulk polymer sticker group density, the extent of binding was monitored by vibrational spectroscopy. In order of increasing binding strength, the polymers used were polyethylene (PE), poly(ethylene-*co*-vinyl acetate) (EVA), poly(ethylene-*co*-vinyl alcohol) (EVOH), and poly(ethylene-*co*-acrylic acid) (PEA).[5] The effect of the substrate on chain conformation and dynamics was studied by

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Table 1. Information on PEA, EVA, and EVOH

	PEA 5%	PEA 15%	EVA 25%	EVA 12%	EVOH 15%
M_n			16000[9]	37000[9]	
M_w	7900[4]	1300[4]			
crystallinity (%)	24	8	8	19	14
polydispersity	1.8	1.1	2.5	6	
av no. of methylene groups between sticker groups	~100	~30	~15	~37	~12

varying the surface area and basicity of the metal oxide substrates. FTIR-PAS and TGA were used to characterize the polymer−substrate interactions and the surface coverage, respectively. Solid-state ^{13}C CP-MAS NMR was employed to obtain the conformation of adsorbed polymers from the transoid and gauchoid components of the polyethylene segments. Finally, variable temperature and NMR relaxation measurements were also carried out to obtain dynamic information; the presence of loops, trains, and tails was assigned on the basis of the chain mobility.

2. Experimental Section

2.1. Materials. Random copolymers of poly(ethylene-*co*-acrylic acid) (PEA) were obtained from Scientific Polymer Products Inc. Two copolymers were used that had 5 and 15 wt % acrylic acid and are denoted PEA 5% and PEA 15% throughout this article. Random copolymers of poly(ethylene-*co*-vinyl alcohol) (EVOH) were obtained from Scientific Polymer Products Inc. The two copolymers that were used had 15 and 25 wt % vinyl alcohol and are denoted EVOH 15% and EVOH 25%. Two poly(ethylene-*co*-vinyl acetate) (EVA) random copolymers were obtained from Aldrich Chemical Co. Inc. having vinyl acetate contents of 12 and 25 wt %, respectively. These two polymers are denoted EVA 12% and EVA 25% herein. Polyethylene (PE) was also obtained from Aldrich Chemical Co. Inc. M_N, M_W, crystallinity, and polydispersity values for the copolymers are listed in Table 1. The metal oxide surfaces, powdered aluminum oxide C (Al_2O_3) and zirconia (ZrO_2), were supplied by Degussa. Alumina had a reported average particle size of 13 nm and a BET surface area of 100 ± 15 m^2/g, while zirconia had a reported average particle size of 30 nm and a BET surface area of 40 ± 10 m^2/g. All chemicals were used as received.

As can be seen in Table 1, EVA is approximately 10 times the molecular weight of PEA. For both EVA and PEA the crystallinity is higher for the lower weight percent polymer. An average number of carbons between binding groups was estimated to see if loops could be formed, with PEA 5% having approximately 100 methylenes between binding groups and 15% EVOH having approximately 12 methylenes between binding groups.

2.2. Sample Preparation. For each copolymer, 10 solutions were prepared by dissolving 30, 60, 90, 120, 180, 240, 300, 600, 900, and 1200 mg of copolymer in 50 mL of warm xylene. A second solution was prepared by dispersing 2 g of alumina in 250 mL of xylene with 15 min of sonication. The alumina and copolymer solutions were added and allowed to reflux for 24 h. The adsorbed copolymer was washed six times by redispersing in 40 mL of xylene under heating. After the final washing the adsorbed copolymer was filtered and dried under vacuum. Thermal gravimetric analysis (TGA) determined the weight percent of copolymer adsorbed on alumina. Samples were prepared in the same manner as stated above when zirconia was the substrate with the exception that zirconia was heated at 400 °C for 5 h before use.

2.3. Solid-State ^{13}C CP-MAS NMR. All solid-state ^{13}C NMR spectra (75.34 MHz) were recorded on a Chemagnetics CMX-300 NMR spectrometer with a 7.5 mm PENCIL probe. Samples were spun at a rate of 4 kHz. The ^{13}C CP-MAS spectra were obtained with a pulse delay of 1 s, 4000 scans, a pulse width of 4 μs, and a contact time of 1 ms.

Two pulse sequences were used to determine the various T_1 values for the ethylene region of the ^{13}C spectra. The Torchia pulse sequence[10] was used for longer T_1 values, while the inversion recovery pulse sequence was used for shorter T_1 values. Torchia spectra were collected with the following parameters: a pulse delay of 1 s, 640 scans, a pulse width of 4.25 μs, and a contact time of 1 ms. The relaxation times were 1, 5, 8, 13, and 20 s. Inversion recovery spectra were obtained under the following conditions: a pulse delay of 4 s, 1600 scans, and a pulse width of 4.25 μs.

2.4. FTIR-PAS. A Fourier transform Mattson Research series 1 spectrometer equipped with a photoacoustic cell (MTEC model 300) was used to collect all IR spectra. The spectra were collected with a 4.0 cm^{-1} nominal resolution.

2.5. Thermal Gravimetric Analysis (TGA). All samples were heated to 600 °C in a nitrogen environment at a rate of 10 °C/min, and then they were held at 600 °C in an oxygen environment for 10 min. This process allowed the amount of organic material attached to the metal oxide surface to be determined. All samples were run on the TGA Q500 from TA Instruments.

3. Results and Discussion

3.1. Effect of Substrate: PEA on Alumina. Studies of the adsorption of carboxylic acids on metal oxides show that they bind much more strongly to zirconia as compared to alumina.[11] The adsorption of PEA on alumina was chosen as a starting point since previous work on PEA on zirconia showed distinctive trends as far as coverage and polar group density were concerned. Therefore, to see the effect of binding strength, the substrate was changed while using the same polymer. Alumina and zirconia contain both acid and base sites which are important for catalytic and adsorption processes. The isoelectric points, a rough measure of the basicity of the metal oxide, were reported to be 9 and 8.2 for alumina oxide C and VP zirconium oxide, respectively.[12] Strong Lewis acid sites can be exposed to the surface layer by oxygen and hydroxyl ion vacancies and Lewis base sites arise from surface hydroxyls and adsorbed molecular water.[13] Characterization of the surface acid−base properties of γ-aluminum oxide C showed the presence of octahedrally and tetrahedrally coordinated Al^{3+} sites, Lewis base sites (OH^-), and H-bond donor sites (partially positively charged surface OH groups) which are either bridging or multicentered groups.[14] Infrared studies of zirconia have shown the presence of terminal and bridging hydroxyl groups. A surface study of the VP zirconium concluded that it is a weakly acidic oxide with Lewis acid sites (Zr^{4+}) but no Brönsted acid sites.[15] Weak Lewis base sites (OH^-) are also present as demonstrated by the formation of hydrogen carbonates from adsorbed CO_2. However, the exact densities of these acid/base surface sites have not been reported for either oxide.

For PEA 5% on alumina, samples were prepared with loadings from 1.6 to 23 wt % of copolymer adsorbed on the surface. The ^{13}C CP-MAS NMR spectra for PEA 5% on alumina, shown in Figure 1, have two distinct regions: one at low loadings (1.6−9 wt %) and the other at high loadings (10−23 wt %). The low loadings exhibit resonances in the methylene region at 33 and 31 ppm due to the backbone methylene carbons, which are of similar relative intensities. Above the 10 wt %, the peak at 33 ppm increases in intensity. In the bulk polymer these peaks were assigned to chains in the crystalline and amorphous regions, respectively. When considering the adsorbed copolymers, the resonance at 33 ppm is better described as originating from chain segments

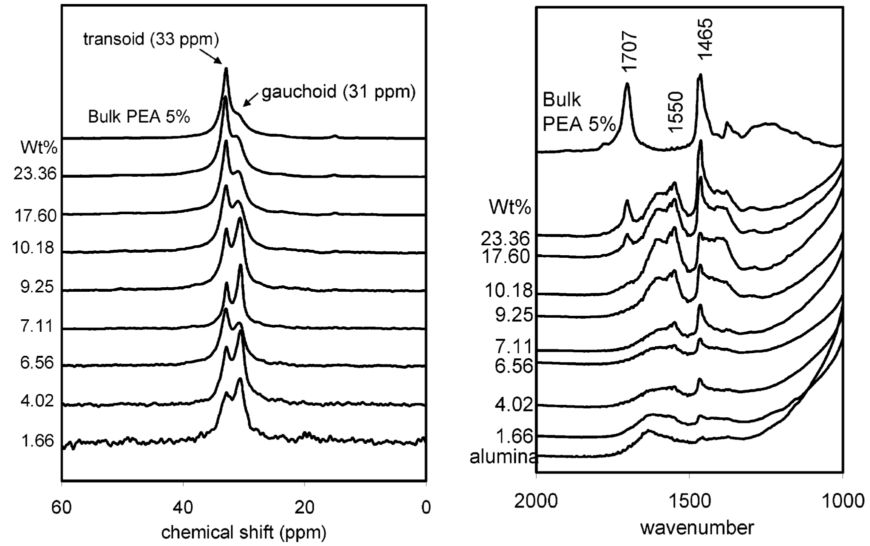

Figure 1. ^{13}C CP-MAS NMR spectra and FTIR-PAS spectra for PEA 5% on alumina.

with a high trans content (transoid) and the 31 ppm resonance arises from conformationally disordered chain segments with a higher population of gauche defects (gauchoid). This distinction is important because long-range order, crystallinity, does not occur in polymers adsorbed on heterogeneous surfaces. The ^{13}C NMR spectra were acquired using $^{1}H-^{13}C$ cross-polarization (CP) which is not a quantitative method since it is sensitive to differences in mobility and type of carbon (number of nearby protons). For the qualitative comparisons presented here, it is assumed that the CP relaxation parameters for the transoid and gauchoid peaks do not vary much with coverage.

For the lower loadings, all the carboxylic acid groups are bound to the surface as indicated by the lack of a free acid C=O band at ~1700 cm^{-1} in the FTIR-PAS spectra along with the appearance of new bands in the carboxylate region. The bands at 1550 and 1465 cm^{-1} are assigned to the asymmetric and symmetric −C−O stretches of surface-bound carboxylate groups. The band at 1465 cm^{-1} overlaps with the $-CH_2-$ stretch at 1460 cm^{-1}. A broad band at 1523 cm^{-1} was also reported for PEA spin-coated on hydrated aluminum. This band was assigned to carboxylate species, which form when the PEA comes into contact with the pseudoboehmite film produced by the hydration of the aluminum foil.[16] An earlier study of spin-coated and hot-pressed PEA films on oxidized aluminum surfaces suggested that PEA primarily interacts with the surface by Lewis acid/base interactions.[6] The IR spectra in Figure 1 all have a broad band at approximately 1610 cm^{-1} arising from the alumina. This band is also seen when the alumina was treated as described in the Experimental Section but without any polymer added. The FTIR methylene crystalline bands (i.e., CH_2 rocking modes) at 710−730 cm^{-1}, which are sensitive to chain conformation, were not detected because the metal oxide fingerprint region below 1100 cm^{-1} masks any polymer signal in this region. Likewise, no information was extracted from the very broad OH stretching modes of alumina at ~3500 cm^{-1}, which did not show any significant changes in the presence of adsorbed polymer.

At a loading of 17.60 wt %, a distinct peak at 1707 cm^{-1} appears in the FTIR-PAS spectrum due to unbound carboxylic acid groups. On zirconia powder, these bands for unbound acid groups appeared at much lower loadings due to the lower surface area of this substrate.[4] At the 10.18 wt % loading of PEA 5% on alumina, the transoid component becomes more intense than the gauchoid peak in the ^{13}C CP-MAS NMR spectra, indicating an increase in the chain order coinciding with the presence of unbound acid groups. However, this change in the chain conformation with the appearance of unbound acid groups was much more evident for PEA on zirconia.[4]

In the case of the adsorbed copolymer with a higher density of sticker groups, PEA 15%, the ^{13}C CP-MAS NMR also shows that there is very little change in the NMR spectra until most of the binding sites are occupied as signaled by the appearance of a FTIR band for unbound acid groups (Figure 2a). Unlike the PEA 5% adsorbed on alumina, the ^{13}C CP-MAS NMR spectra of adsorbed PEA 15% contain only the 31 ppm component for low loadings (2.5−10 wt %). The 33 ppm transoid component does not appear until the 13.7 wt % loading, coinciding with the appearance of the 1705 cm^{-1} free acid peak in the FTIR spectra (Figure 3a). Unlike the PEA 5%, the PEA 15% ^{13}C CP-MAS NMR spectra do not approach the bulk copolymer spectrum at the highest loadings, and the chain order is still low (a small transoid component). Although there is a significant population of free acid groups at the highest loading, the band at 1554 cm^{-1} for surface-bound carboxylate groups is still intense relative to the free acid band at 1705 cm^{-1}. In the case of similar loadings of PEA 15% on zirconia powder, the NMR spectra did approach that of the bulk, but the amount of bound groups as compared to unbound groups was also smaller, indicating a larger proportion of the polymer is not in direct contact with the surface for this lower surface area substrate.[4] The relative proportion of bound and unbound groups is such that crystallization of PEA 15% is still hindered at the highest loading measured. The key finding is that despite the weaker binding of PEA on alumina as compared to zirconia, the same trend is seen as with the PEA/ZrO_2 system: the conformation depends on the sticker group content rather than the coverage. The only difference is that the bulklike PEA 15% spectra are not seen at the highest loadings due to the much higher surface area of the alumina (100 m^2/g) as compared to the zirconia (40 m^2/g).

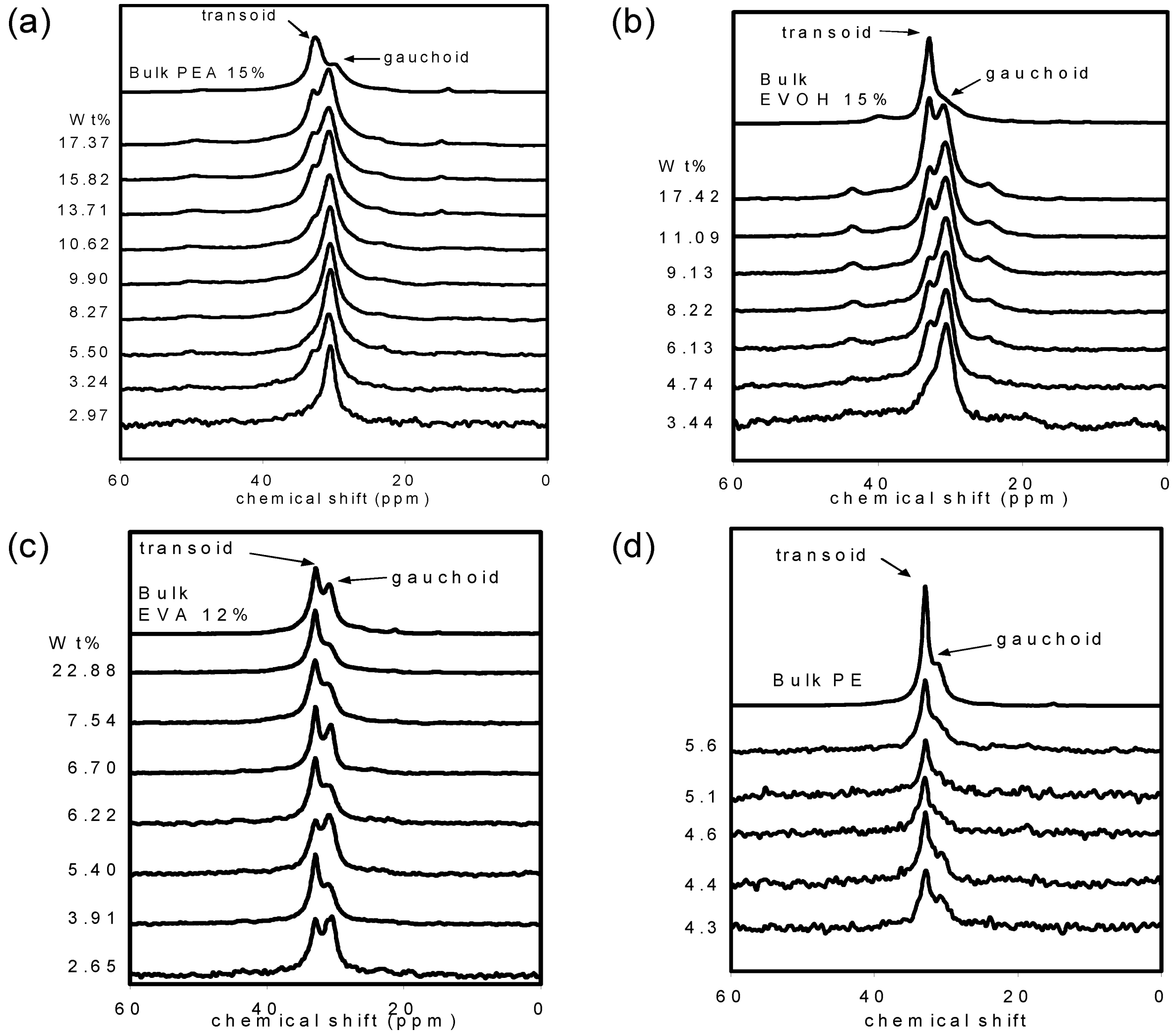

Figure 2. ^{13}C CP-MAS NMR spectra of (a) PEA 15%, (b) EVOH 15%, (c) EVA 12%, and (d) PE on alumina.

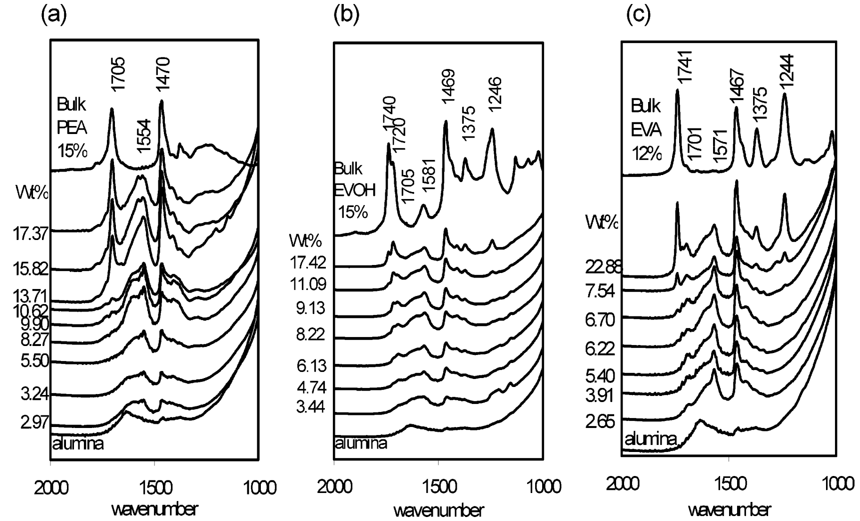

Figure 3. FTIR-PAS spectra of (a) PEA 15%, (b) EVOH 15%, and (c) EVA 12% on alumina.

3.2. Effect of Weaker Binding Groups (EVOH, EVA, and PE on Alumina). 3.2.1. Chain Conformation: Solid-State ^{13}C NMR. Ethylene copolymers with other polar functional groups (OH, OC=OCH$_3$), as well as polyethylene, were examined next to see whether the trend in chain conformation with loading as noted above persists for much weaker polymer/substrate binding. Figure 2 compares the ^{13}C CP-MAS NMR spectra of PEA, EVOH, EVA, and PE adsorbed on alumina. The polar group contents of these copolymers are similar with relatively short ethylene segments of 30, 12, and 37 CH$_2$ groups between the CO$_2$H, OH, and OC=OCH$_3$ sticker groups of PEA 15%, EVOH 15%, and EVA 12% (Table 1). The trend in the trans/gauche populations of the ethylene segments of EVA 12% on alumina greatly differs from that observed for PEA 15% on the same substrate. The lowest loading of EVA 12% on alumina shows a strong transoid component at 33 ppm, whereas the ethylene segments of adsorbed PEA 15% are disordered with a single gauchoid peak at 31 ppm. Unlike PEA, the relative intensities of the 33 and 30 ppm components of adsorbed EVA 12% do not show a smooth trend with loading but are bulklike at the highest loadings.

The ^{13}C CP-MAS spectra of EVOH 15% on alumina (Figure 2b) show a general trend that is intermediate between EVA 12% and PEA 15%. A transoid component at 33 ppm appears at much lower loadings as compared to PEA 15% but is not present at the lowest loadings, unlike EVA 12%. However, at the highest loading the transoid component dominates unlike the adsorbed PEA 15%. The ^{13}C CP-MAS spectra of PE on alumina (Figure 2d) display a dominant transoid component at 33 ppm for all loadings. Only a minimal amount of polyethylene actually adheres to the alumina substrate, which is expected due to the lack of polar sticker groups. Most of the PE was removed during the washing steps, and a maximum loading of only 5.6 wt % was obtained. Literature precedence gives an explanation for the observed trends. Hjertberg[5] did studies of copolymers adsorbed on thin films; the order of binding strength that he noted was carboxylic acid > hydroxyl > acetate. The main conclusion that can be obtained from Figure 2 is that there is more conformational order with weaker binding strength. The picture that comes to mind is that of PEA binding so strongly that it sticks randomly and irreversibly to the surface during the adsorption process, so that until all the sites are occupied, the ethylene segments will be conformationally disordered, whereas for EVA the binding is sufficiently weak that the polymer chain can partially detach from the surface during the adsorption process and thus reach a more ordered chain conformation even at low loadings.

The competition between adsorption and self-association/crystallization of EVA/EVOH as compared to PEA should also be considered. In general, these ethylene copolymers display low crystallinities, which decrease with increasing polar group content. However, the 8% crystallinity of bulk PEA15% is significantly lower that EVA 12% (19% crystallinity). In both copolymers, the polar groups are excluded from the crystals formed by the ethylene chains. However, the disruptive effect on crystallization is greater in the case of PEA due to the hydrogen-bonding interactions among the carboxylic acid groups, which are extensively dimerized. A FTIR study of ethylene copolymers concluded that whereas the restrained effect of the vinyl acetate groups in EVA is not strong enough to affect the crystalline behavior of the PE segments, the hydrogen bonds among the carboxylic acid groups of PEA play a cross-linking role which prevents the PE segments from adopting the stable orthorhombic form.[17] Studies of the phase structure of EVA found that not only the degree of crystallinity but also the relative contents of two crystalline phases (monoclinic and orthorhombic) vary with VA content.[18] The stronger tendency of PEA to adsorb plus the more favorable crystallization of EVA can both play a role in the higher degree of order observed for adsorbed EVA vs PEA. However, surface IR and AFM studies of EVA thin films spin-coated on alumina detected very low crystallinity, attributed to the effect of the chain conformation at the interface. [8f] To further investigate this, DCS scans were run on bulk and adsorbed EVA 12%. The T_g of bulk EVA, a semicrystalline polymer, was difficult to detect; therefore, it was not surprising that the T_g was not seen for adsorbed EVA. A melting transition was only detected for the highest loading, but it was very broad and it was not possible within experimental error to determine whether it was significantly shifted from the bulk value.

3.2.2. Surface Binding: FTIR-PAS. The FTIR-PAS spectra of adsorbed PEA 15% in Figure 3a correlates well with the NMR data in that the chain conformation changes with the appearance at ~13.7 wt % of a free acid peak at 1705 cm^{-1}. The FTIR-PAS spectra of the lowest loadings of EVA 12% (Figure 3c) are characterized by the lack of a free acetate C=O band at ~1740 cm^{-1} along with the appearance of new bands in the carboxylate region. These spectra differ from previous surface IR studies of EVA films deposited on planar alumina substrates.[8] Brogly reported a splitting of the acetate C=O stretch band due to a Lewis acid–base interaction of the acetate groups with the alumina hydroxyl groups. The splitting was as large as 16 cm^{-1} when the EVA was bound to a weakly hydroxylated aluminum substrate. The absence of this splitting in the FTIR-PAS spectra of EVA adsorbed on powdered alumina may be due to the limited resolution or the different selection rules for surface IR. The acetate peak at 1740 cm^{-1} was only present at coverages above 7 wt %. Instead, a strong broad carboxylate band at 1571 cm^{-1} appears which is assigned to partial hydrolysis of the EVA in the presence of alumina along with heating; the products of this reaction would be EVOH and acetic acid. This assumption is supported by studies of the adsorption of acetic acid on alumina, which show a FTIR band at 1570 cm^{-1}.[19]

The absence and occurrence of hydrolysis when EVA is deposited on aluminum by spin-coating vs adsorption from solution was also reported for PMMA on the native metal oxide surfaces.[3] The lack of hydolysis of the spin-coated PMMA was attributed to the rapid removal of solvent and rapid vitrification of the polymer during the spin-coating process such that most of the PMMA segments are immobilized into positions where they cannot react with the surface. Presumably, a similar process occurs for EVA when it is spin-coated rather than adsorbed onto alumina.

The FTIR-PAS spectra of EVOH 15% on alumina, shown in Figure 3b, are complicated by incomplete hydrolysis of the initial polymer (which is commercially produced via hydrolysis of EVA) along with further hydrolysis occurring upon adsorption. The extent of hydrolysis of EVOH 15% was determined from solution ^{1}H NMR.[20] The ^{1}H NMR spectra showed that EVOH 15% contained approximately 22% unhydrolyzed starting material, while EVOH 25% was approximately 12% unhydrolyzed. In the FTIR-PAS spectra of adsorbed EVOH 15%, the band at 1740 cm^{-1} is due to residual acetate groups, the band at 1720 cm^{-1} is due to the presence of ketones,[21] and the band at 1581 cm^{-1} is due to adsorbed acetic acid as in the case of EVA adsorbed on alumina. At low loadings, adsorbed EVOH has bands at 1705 and 1720 cm^{-1}, and the relative intensities of these two bands change as the loadings increase. At the highest loadings, there is no longer a band at 1705 cm^{-1}, assigned to acetic acid, but there are ketone and acetate bands at 1720 and 1740 cm^{-1}.

Apart from the complication of the IR spectra due to partial hydrolysis, it is not possible to correlate the

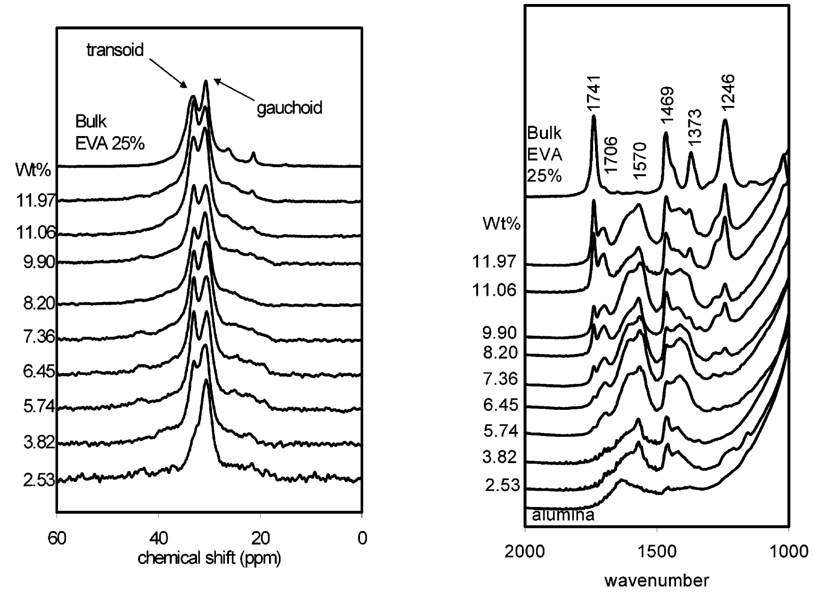

Figure 4. ^{13}C CP-MAS NMR spectra and FTIR-PAS spectra of EVA 25% adsorbed on alumina.

occupation of the binding sites with the chain conformation for either EVA or EVOH. In the case of EVOH, the broad hydroxyl band cannot be used to determine binding and for EVA; no splitting of the acetate band was detected. However, the fact that the initial EVOH bulk polymer was incompletely hydrolyzed was useful for confirming that some hydrolysis of EVA as well as further hydrolysis of EVOH occurs upon adsorption. Although the extent of this hydrolysis cannot be easily measured from the IR bands, it appears that most of the EVA and EVOH is hydrolyzed at low coverages since no acetate bands are present.

Despite the FTIR evidence for extensive hydrolysis, which would convert EVA to EVOH, the trend in the chain conformation of EVA with loading is significantly different from EVOH. In the case of the hydrolysis and subsequent chemisorption of PMMA on metal oxides, Tannenbaum and co-workers argue that the adsorption process occurs via a two-step mechanism in which the first step of hydrolysis is a necessary but insufficient condition for anchoring the polymer to the surface.[3] The efficiency of the second step is dependent on the interfacial chemistry possible for a particular polymer/metal oxide pair as well as the conformation, flexibility, and molecular weight of the polymer.

3.3. Effect of Increasing Sticker Group Density. The NMR and FTIR-PAS spectra of EVA 12% were compared to those of EVA 25% to study the effect of increasing the sticker group content for weak polymer/metal oxide binding. The ^{13}C CP-MAS NMR (Figure 4) shows that despite the high polar group content, there is still a significant transoid component. With the exception of the lowest loading, the chain conformation of the adsorbed polymer is not significantly perturbed from that of the bulk polymer as seen by the relative intensities of the transoid and gauchoid peaks. Figure 4 illustrates that there is little dependence on coverage, indicating that the weaker binding polymer can rearrange on the surface during the adsorption process. The IR spectra of EVA 25% on alumina are very similar to those of EVA 12%, with the appearance of the bands due to partial hydrolysis, and once again no splitting of the acetate band at 1740 cm^{-1} is seen. The ^{13}C CP-MAS NMR and FTIR-PAS spectra for EVOH 25% on alumina, not shown, show that the trans/gauche populations, as well as intensities of the FTIR bands with coverage, follow the same trends as for EVOH 15%.

3.4. Effect of Increased Substrate Binding Strength (EVA/Zirconia and EVOH/Zirconia). Samples where the ethylene copolymers were adsorbed onto a more basic metal oxide (ZrO_2) were examined next to see whether the trend in chain conformation persists. The ^{13}C CP-MAS NMR spectra for EVA 12% on zirconia (Figure 5) show the same trends as for EVA 12% on alumina. There is a transoid component for all loadings, which dominates over the gauchoid component.

The FTIR-PAS spectra (Figure 6) for EVA 12% adsorbed on zirconia show all the acetic acid groups are bound to the surface in the samples with the lowest copolymer loadings as indicated by the lack of a free acetate C═O band at ~1740 cm^{-1}. The bands in the carboxylate region are due to adsorbed CO_2, which overlap with the bands arising from the hydrolyzed EVA. The FTIR-PAS spectrum of zirconia contains a broad peak at 3500 cm^{-1} due to the surface hydroxyls, two weak peaks at 1630 and 1460 cm^{-1}, and a large fingerprint below 900 cm^{-1}.

EVA 12% was compared to EVA 25% to study the effect of increasing the sticker group content. The ^{13}C CP-MAS NMR of EVA 25% on zirconia (Figure 5) shows that there is a transoid component at all loadings, but it is minimal at low loadings as compared to the same copolymer on alumina. This difference may be due to the stronger binding strength of the zirconia substrate, which is usually viewed as being more basic than alumina.[22] The IR spectra of EVA 25% on zirconia in Figure 6 are very similar to that of EVA 12%, with the bands due to partial hydrolysis, and no splitting is seen at 1740 cm^{-1}. The ^{13}C CP-MAS and FTIR-PAS spectra of EVOH 15% on zirconia, not shown, showed the same trend as on alumina.

3.5. Relaxation and Variable Temperature Studies. Variable temperature and relaxation studies were performed to explore the possible chain configurations that give rise to the high degree of conformational order seen for EVA on alumina. The ^{13}C CP-MAS NMR showed a transoid peak for all coverages for both EVA

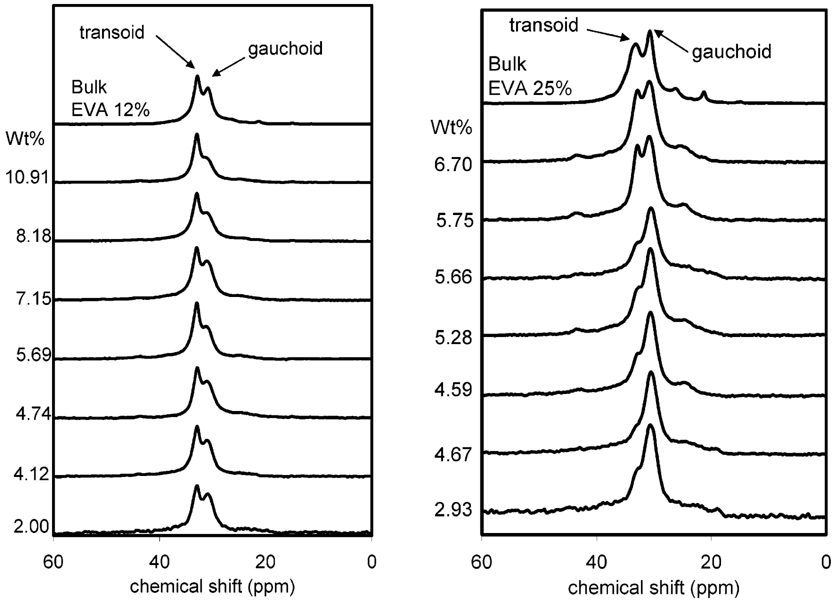

Figure 5. ^{13}C CP-MAS NMR spectra for 12% and 25% EVA on zirconia.

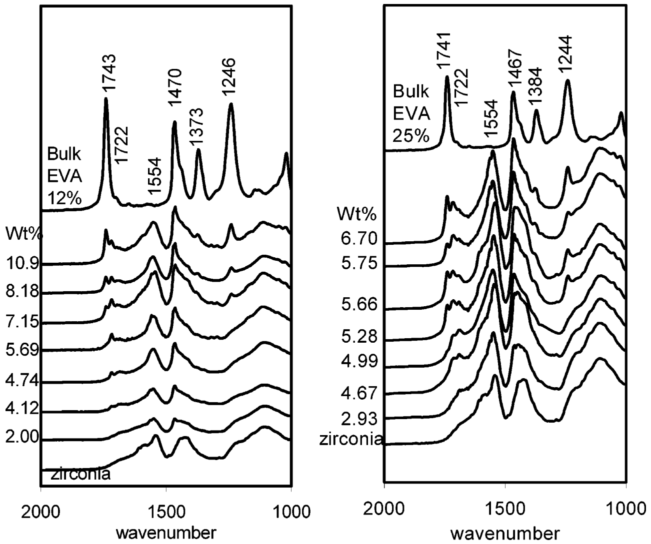

Figure 6. FTIR-PAS spectra for 12% and 25% EVA on zirconia.

Table 2. Carbon T_1 (s) for Bulk and Adsorbed EVA 12% and 25% on Alumina

sample	33 ppm	31 ppm
EVA 12%	3.35, 67.11	0.294
23 wt % EVA 12%	3.25, 59.22	0.396
4 wt % EVA 12%	2.74, 56.18	0.419
EVA 25%	1.47, 19.38	0.295
12 wt % EVA 25%	3.02, 52.35	0.401
6.5 wt % EVA 25%	4.38, 76.9	0.395

copolymers. This component could be the result of folded loops as proposed for the PEA/ZrO$_2$ system or the presence of trains lying flat on the surface. A folded loop is a loop that contains segments of an all-trans conformation of carbons atoms as shown schematically elsewhere.[4] ^{13}C NMR relaxation measurements were carried out using two pulse sequences. The Torchia pulse sequence was used to measure the longitudinal relaxation time (T_1) of the rigid component at 33 ppm, while the inversion recovery pulse sequence was used to examine the amorphous component at 31 ppm, which has a much shorter spin−lattice relaxation time. In previous work, Zhang et al.[18] used solid-state NMR to look at a series of ethylene−vinyl acetate copolymers. It was observed that the crystalline region of all samples had a biexponential ^{13}C NMR spin−lattice relaxation behavior. The longer ^{13}C spin−lattice relaxation time was ascribed to the internal part of the crystalline region, whereas the component with shorter T_1 was accredited to the interfacial region between the amorphous and crystalline domains. The authors also noted that the crystallinity decreased with increasing vinyl acetate content.

The relaxation results in Table 2 show that the T_1 values for the amorphous peak do not change from bulk to adsorbed polymer. The 33 ppm data was fit to a biexponential curve, yielding two T_1 values. For EVA 12% there was little change from bulk to adsorbed polymer. For EVA 25% there was an increase in T_1 from bulk to adsorbed polymer. Since variable temperature measurements showed that EVA 25% is on the slow side of the T_1 vs correlation time curve, the ordered component of the adsorbed polymer is less mobile than the bulk state. This contrasts with previous relaxation studies of PEA adsorbed on ZrO$_2$, which showed an enhanced mobility of the 33 ppm component which arises from a folded loop structure.[4]

The possible sources for the ordered component of adsorbed EVA and EVOH can be considered. The 33 ppm transoid peak of the adsorbed polymer could arise from (i) a self-associated, crystallized polymer which is not interacting with the surface—the 33 ppm component would arise from the crystalline regions in this case; (ii) a folded loop structure such as proposed for PEA 5% adsorbed on zirconia;[4] and (iii) flat, extended trains lying on the surface.

We suggest that the trans component of adsorbed EVA and EVOH arises from train configurations based on the following experimental data:

1. EVA and EVOH have a significant population of all-trans conformations of the polyethylene segments at low coverages where all the polymer chains are more likely to be in direct contact with the surface.

2. At low coverages, no free acetate groups are detected for adsorbed EVA, yet large carboxylate bands

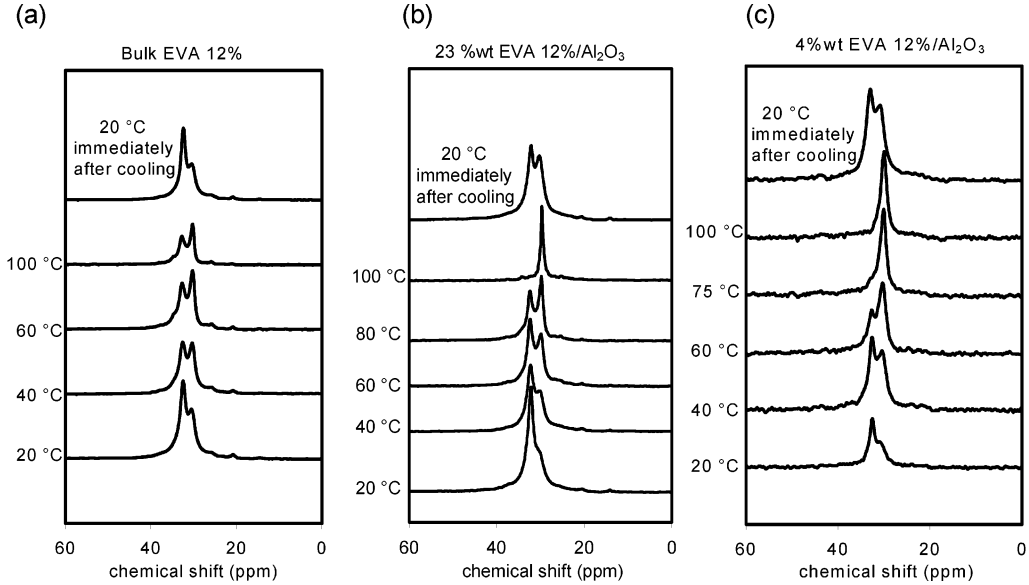

Figure 7. VT ^{13}C CP-MAS NMR spectra for (a) EVA 12%, (b) 23 wt % EVA 12%, and (c) 4 wt % EVA 12% on alumina.

are present which are attributed to adsorbed acetic acid. The polymer has interacted sufficiently with the surface for significant hydrolysis to occur.

3. Adsorbed EVA showed reduced chain mobility for the transoid component, which is opposite to what was observed for PEA/ZrO_2 (folded loops).

In theory, the hydrolyzed polymer could only be self-associated and not interacting with the surface. However, most of the nonadsorbed polymer should have been removed by the extensive washing steps. Furthermore, studies of spin-coated EVA films by Brogly and coworkers strongly support the formation of train configurations. Their detailed surface IR studies of EVA films concluded that at the interface the EVA chains lie parallel to the alumina surface, which in turn hinders the crystallization of the polymer chains not in direct contact with the substrate.[8f]

Thermal stability studies (Figure 7) were also carried out in order to gain insight into the nature of the ordered component. When the bulk polymer was heated to 100 °C and then cooled to room temperature, it was slightly more ordered then the original polymer. At 100 °C there is still a transoid component at 33 ppm arising from the crystalline regions of the bulk copolymer. For both high and low loadings, the adsorbed copolymer is totally disordered at 100 °C, but given enough time, within a few days, the polymer returns to its initial configuration. The loss of the transoid component occurs at a lower temperature (below 75 °C) for the lower loading (4 wt %) as compared to the higher loading (23 wt %), which still has a transoid component at 80 °C. This behavior was also observed for 5% PEA/ZrO_2; however, the chain conformation returned to the original state immediately upon cooling.[23] In this case the ordered component arises from folded loops which unfold with heating and then return to the original configuration since the loops are irreversibly pinned via strong zirconium carboxylate linkages. In the case of EVA, the ethylene segments between sticker groups are too short to form folded loops unless some of the acetate groups are not bound to the surface. However, the FTIR spectra show otherwise, and this along with the reduced mobility indicates that the 33 ppm component arises from train configurations. Thus, for complete disordering to occur, the polar groups must detach with heating. Unfortunately, there is no IR signature for polymer—surface interactions that would allow direct observation of detachment of EVA as heating occurs. In the case of PEA on ZrO_2, it was possible to show directly that the Zr—carboxylate surface bond remains completely immobile and intact during the chain disordering process through VT NMR studies of long chain fatty acids adsorbed on ZrO_2 which were ^{13}C-labeled at the C=O group. Presumably, the acetate groups of EVA interact via ionic or hydrogen bonds which are weak enough to be overcome by the thermal energy unlike the stronger Al or Zr carboxylate linkages of adsorbed PEA.

4. Conclusions

The chain conformation of adsorbed ethylene copolymers is strongly dependent on the binding strength of the polar sticker groups with the substrate. In the case of PEA on zirconia, the chain conformation was previously found to be strongly dictated by the polar group content rather than coverage. This behavior persisted for PEA adsorbed on alumina, a more weakly binding substrate as compared to zirconia. The dependence of the conformation on sticker group density decreases with binding strength. A strong transoid component of the ethylene segments of EVA with a large acetate content was observed. This ordered component showed little dependence on coverage. Apparently, the chain conformation is not affected by irreversible binding during the adsorption process for this particular polymer/substrate pair. Instead, the binding is weak enough to allow detachment and the formation of an ordered component. Relaxation measurements, as well as the absence of an FTIR band for free acetate groups for low coverage samples, indicate that the trans component of EVA arises from chains lying flat on the surface. This trans component disappears completely with heating, which is only possible if the polar groups can detach. EVOH showed a trend intermediate between PEA and EVA, in agreement with the order of the binding strength, carboxylic acid > hydroxyl > acetate. The FTIR spectra reveal some hydrolysis of EVA occurs upon adsorption, but the extent of this surface reaction is insufficient to significantly perturb the distinct trend of an increasing chain order with decreasing binding strength.

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