Adsorption of Ethylene–Vinyl Acetate Copolymer on Silica Surface

Masami KAWAGUCHI, Akihiro INOUE, and Akira TAKAHASHI

*Department of Industrial Chemistry, Faculty of Engineering,
Mie University, Kamihama-cho, Tsu, Mie 514, Japan*

(Received February 17, 1983)

ABSTRACT: Adsorption of ethylene–vinyl acetate copolymers (vinyl acetate content (mol%) *ca.* 60) onto a nonporous silica (Aerosil 130) from trichloroethylene solutions at 25°C was studied by IR spectroscopy and differential refractometry. The observed IR frequency shift of the silanol groups was attributed to hydrogen bonding between ester carbonyl groups in the copolymer and the silanol groups. The adsorbance, A , was determined by a differential refractometer, while the fraction of silanol groups occupied, θ , and the fraction of the adsorbed ester carbonyl groups, p , were determined by IR spectroscopy. The three important quantities A , θ , and p reached plateau values at extremely low polymer concentrations. The value of A for the copolymer in the plateau region somewhat increased with increasing molecular weight. The plateau values of both p and θ were nearly independent of molecular weight.

KEY WORDS Adsorption / Ethylene–Vinyl Acetate Copolymer / Silica / IR Spectroscopy / Frequency Shift / Adsorbance / Silanol Group / Ester Carbonyl Group /

When functional groups of a polymer interact with silanol groups on a silica surface, frequency shifts of the IR bands for the silanol and functional groups occur. Since Fontana and Thomas¹ first applied the IR spectroscopy to poly(lauryl methacrylate) adsorbed on a silica surface, this method has been extensively used for studying various problems of polymer adsorption.^{2–17} Most papers, however, have been concerned only with the determination of the fraction of adsorbed polymer segments, by using IR frequency shift of the functional groups of the polymer.

In our previous papers, the adsorption of polystyrene,¹⁵ polybutadiene,¹⁶ poly(4-vinylpyridine),¹⁷ and styrene–butadiene copolymer¹⁸ onto the silica surface was studied using IR spectroscopy along with a UV spectrometer and differential refractometer to determine the polymer concentration in the supernatant. The three important quantities, *i.e.*, the fraction θ of silanol groups occupied by the functional groups, the fraction p of the polymer segment adsorbed directly on the silanol groups, and the surface excess Γ were determined. Here Γ is defined by

$$\Gamma = (AN_A/n_{\text{OH}}M_u) \quad (1)$$

where A is the adsorbance per unit area, N_A , Avogadro's constant, n_{OH} , the number of silanol groups per unit area, and M_u , the molecular weight of a monomer unit. For the adsorption of polystyrene, the frequency shift of the IR band of the silanol groups was attributed to the interaction between phenyl groups in the polymer and the silanol groups; for the adsorption of polybutadiene, the shift was attributed to the interaction between double bonds in the polymer and the silanol groups; and for the adsorption of poly(4-vinylpyridine), it was attributed to the interaction between pyridine groups in the polymer and the silanol groups.

With the expectation that the ester carbonyl groups should strongly interact with the silanol groups by hydrogen bonding, Thies and Botham^{5,6} studied by IR spectroscopy the adsorption of poly(vinyl acetate) and three ethylene–vinyl acetate copolymers with a vinyl acetate content of 20.4, 28.8, and 44.2 wt% from trichloroethylene solutions onto a silica surface. They measured the adsorbance and the fraction p of adsorbed carbonyl groups in

the polymers. However, the samples used were unfractionated and hence polydisperse with regard to molecular weight. The aim of this paper is to offer experimental data on A , θ , and p for fractionated ethylene-vinyl acetate copolymer samples. The adsorption of ethylene-vinyl acetate copolymer with a vinyl acetate content of 60 mol% was measured using an IR spectrometer and a differential refractometer as a function of molecular weight. The measured values of A , θ , and p were compared with the data for vinyl acetate homopolymer.

EXPERIMENTAL

Materials

An ethylene-vinyl acetate (EVA) copolymer, supplied from Kuraray Co. (Kurashiki, Okayama JAPAN), was precipitated by the dropwise addition of its methanol solution into a large volume of vigorously stirred water. The resulting precipitate was soaked in water and dried in a vacuum. This purified EVA copolymer was dissolved in acetone and separated into the fractions using *n*-hexane as the precipitant at 25°C. Each fraction was freeze-dried from a benzene solution. The number average molecular weights of the fractions were determined by a 502 High Speed Membrane Osmometer (Hewlett Packard) in toluene at 30°C. The content of the vinyl acetate units in the fractionated samples was determined by NMR measurement. The NMR spectra of 10% solutions of five fractions in CDCl_3 were obtained using a JEOL-C-60 NL NMR spectrometer and TMS as the internal standard. The characteristics of the fractions are given in Table I.

Spectroquality trichloroethylene (Dojin Chemical Co.) was distilled before use. Spectroquality ethyl acetate (Merck) was used without purification.

The nonporous Aerosil 130 silica supplied by Degussa A. G. (West Germany) was used as the adsorbent after being cleaned by the procedure described in previous papers.¹⁵⁻¹⁷ The surface concentration of silanol groups was determined to be three silanol groups per 100 Å². According to the manufacturer, the particle diameter was 160 Å with a surface area of 141 m² g⁻¹.

Adsorption of Polymers onto the Silica

Twenty ml of a polymer trichloroethylene solution of known concentration were mixed with the silica (0.16 g) in a stoppered centrifuge tube and the

Table I. Characteristics of EVA copolymers

Sample	Vinyl acetate mole fraction	$M_n \times 10^{-3}$
EVA-1	0.605	648
EVA-2	0.607	310
EVA-3	0.602	185
EVA-4	0.610	124
EVA-5	0.611	69.7

mixture was gently stirred by a magnetic chip for 20 h at 25°C. The silica suspensions were centrifuged at 5,000 *g* for 10 min to sediment the silica, and the supernatant was carefully decanted. The polymer concentration in the supernatant, *i.e.*, the equilibrium bulk concentration, C_p , was determined as follows: Following the evaporation of trichloroethylene, the residue was dried in vacuum, then dissolved in a definite amount methanol, and C_p was measured by a Wood differential refractometer (Model RF-60) at a wavelength of 633 nm. The adsorbance (g cm^{-2}), A , was determined from the difference between the amount of initially added polymer and that of the polymer in the supernatant, and also from the amount of the silica added.

The sedimented silica was subjected to IR measurement according to the same method as that described previously.¹⁵⁻¹⁷

RESULTS AND DISCUSSION

Adsorbance

The adsorption isotherms of the EVA fraction are shown in Figure 1. Initially, the isotherms rose steeply with increasing C_p and reached a plateau region. The complete adsorbance data are summarized in Table II.

In Figure 2, the adsorbance at the highest C_p is plotted against the molecular weight. For comparison, the adsorbance of vinyl acetate homopolymer at the plateau region is also illustrated in the figure.¹⁹ The plateau values of A for the EVA copolymers somewhat increase with increasing molecular weight, while for the vinyl acetate homopolymer, a stronger molecular weight dependence of the plateau A was observed. However, the plateau adsorbance of the EVA copolymers is larger than that of vinyl acetate homopolymer. This may be explained as a result of the fact that the ethyl-

Adsorption of EVA Copolymer

Table II. Adsorption data for EVA copolymers on Aerosil 130

Sample	$C_p \times 10^2$ g ml ⁻¹	$A \times 10^7$ g cm ⁻²	$A_{VA} \times 10^7$ g cm ⁻²	θ	p	Γ	p_{TOT}	Γ_{TOT}
EVA-1	0.383	1.0 ₄	0.85 ₈	0.59 ₇	0.27 ₀	2.0 ₀	0.22 ₃	3.3 ₁
	0.280	1.0 ₆	0.87 ₄	0.55 ₃	0.27 ₂	2.0 ₄	0.22 ₄	3.3 ₇
	0	0.88 ₇	0.73 ₂	0.55 ₈	0.29 ₄	1.7 ₁	0.24 ₂	2.8 ₂
	0	0.17 ₇	0.14 ₆	0.27 ₄	0.98 ₇	0.34 ₀	0.81 ₄	0.56 ₃
	0	0.035 ₅	0.029 ₃	0.16 ₄	1.0	0.06 ₈	0.82 ₅	0.11 ₃
EVA-2	0.388	0.99 ₃	0.82 ₀	0.56 ₃	0.28 ₆	1.9 ₁	0.23 ₆	3.1 ₅
	0.293	0.94 ₉	0.78 ₄	0.54 ₄	0.28 ₆	1.8 ₃	0.23 ₆	3.0 ₁
	0	0.88 ₇	0.73 ₃	0.54 ₁	0.26 ₅	1.7 ₁	0.21 ₉	2.8 ₂
	0	0.17 ₇	0.14 ₆	0.21 ₀	0.59 ₁	0.34 ₀	0.48 ₈	0.56 ₂
	0	0.035 ₅	0.029 ₃	0.08 ₀	1.0	0.06 ₈	0.82 ₆	0.11 ₃
EVA-3	0.384	1.0 ₃	0.84 ₈	0.57 ₅	0.25 ₅	1.9 ₈	0.21 ₀	3.2 ₈
	0.286	1.0 ₁	0.83 ₁	0.56 ₁	0.26 ₉	1.9 ₄	0.22 ₁	3.2 ₂
	0.004	0.85 ₁	0.70 ₀	0.56 ₂	0.26 ₃	1.6 ₃	0.21 ₇	2.7 ₁
	0	0.17 ₇	0.14 ₆	0.23 ₇	0.67 ₁	0.34 ₀	0.55 ₂	0.56 ₄
	0	0.035 ₅	0.029 ₃	0.16 ₆	1.0	0.06 ₈	0.82 ₃	0.11 ₃
EVA-4	0.396	0.91 ₆	0.75 ₈	0.60 ₄	0.24 ₇	1.7 ₇	0.20 ₄	2.9 ₀
	0.297	0.91 ₃	0.75 ₆	0.58 ₆	0.24 ₈	1.7 ₆	0.20 ₄	2.8 ₉
	0	0.88 ₇	0.73 ₄	0.60 ₉	0.31 ₂	1.7 ₁	0.25 ₈	2.8 ₁
	0	0.17 ₇	0.14 ₇	0.28 ₁	0.85 ₈	0.34 ₂	0.71 ₀	0.56 ₀
	0	0.035 ₅	0.029 ₄	0.10 ₀	1.0	0.06 ₈	0.82 ₈	0.11 ₂
EVA-5	0.398	0.90 ₄	0.74 ₉	0.54 ₃	0.23 ₀	1.7 ₅	0.19 ₀	2.8 ₆
	0.301	0.87 ₈	0.72 ₇	0.59 ₁	0.27 ₂	1.6 ₉	0.22 ₅	2.7 ₈
	0	0.88 ₇	0.73 ₄	0.60 ₂	0.27 ₁	1.7 ₁	0.22 ₅	2.8 ₁
	0	0.17 ₇	0.14 ₇	0.30 ₁	0.70 ₃	0.34 ₂	0.58 ₄	0.56 ₀
	0	0.035 ₅	0.029 ₄	0.15 ₅	1.0	0.06 ₈	0.82 ₉	0.11 ₂

Figure 1. Adsorption isotherms of ethylene-vinyl acetate copolymers onto Aerosil-130 silica: ○, EVA-5; ○-, EVA-4; -○, EVA-3; ○, EVA-2; ○, EVA-1.

Figure 2. Molecular weight dependence of adsorbance: ○, EVA copolymer; ●, vinyl acetate homopolymer.

ene units in the EVA copolymer protrude into the bulk solution, leading to the formation of loops larger than those in the case of the vinyl acetate homopolymer, since the polar vinyl acetate comonomer in the EVA copolymer more strongly interacts with the silanol groups than the nonpolar ethylene comonomer. The theoretically calculat-

ed adsorption energies, ϵ_0 , of an ethylene unit and a vinyl acetate unit are $\epsilon_0 \leq kT^{20}$ and $\epsilon_0 \geq 5kT^{21}$ respectively. Furthermore, the IR frequency shift of the silanol groups due to the interaction of only the vinyl acetate units with the silanol group can be observed. It is assumed that the ethylene units do not interact with the silanol groups. The

larger adsorbance of the EVA copolymer than that of the vinyl acetate homopolymer is in good agreement with the experimental results obtained in benzene solutions by Mizutani, Hara, and Imoto,^{22,23} who, however, measured only the adsorbance.

Fraction of Surface Silanol Groups Occupied, θ

Figure 3 illustrates the differential IR spectrum between the supernatant polymer solution and the silica on which EVA was adsorbed. For comparison, the spectrum of the silica adsorbed by vinyl acetate homopolymer is also presented in Figure 3. Both spectra show two characteristics bands: one located at 3660 cm^{-1} due to isolated silanol groups and another at 3375 cm^{-1} due to hydrogen bonding between the silanol and carbonyl groups of the adsorbed polymers. Thus, both the number of free silanol groups and that of the occupied silanol groups can be determined if the extinction coefficients for the respective absorption bands are known.

For free silanol groups on the silica immersed in trichloroethylene (Figure 3), the extinction coefficient at 3660 cm^{-1} was determined to be $114.6\text{ l mol}^{-1}\text{ cm}^{-1}$.

The IR spectrum of the silica immersed in an ethyl acetate trichloroethylene solution is also displayed in Figure 3. Ethyl acetate is considered to be a model compound for the vinyl acetate monomer unit. An absorption was observed at 3375 cm^{-1} possibly due to hydrogen bonding between the silanol and ester carbonyl groups in the ethyl acetate. The peak position agreed well with that due to the hydrogen bonding between the silanol group and the vinyl acetate units in the polymer. The extinction coefficient at 3375 cm^{-1} was determined to be $47.66\text{ l mol}^{-1}\text{ cm}^{-1}$.

n-Hexane may be regarded as a homology of the ethylene unit. The IR spectra of silica dispersed in trichloroethylene containing various portions of *n*-hexane were examined by IR spectroscopy. However, the results were the same as those in trichloroethylene, indicating that the ethylene units do not interact with the silanol groups.

The value of θ occupied by vinyl acetate units can be calculated from

$$\theta = S_{3,375} / (S_{3,375} + S_{3,660}) \quad (2)$$

where $S_{3,375}$ and $S_{3,660}$ are the number of silanol

Figure 3. Infrared spectra of Aerosil-130 silica immersed in trichloroethylene: —, none; ---, in the presence of ethyl acetate; ·····, in the presence of EVA copolymer; — · —, in the presence of vinyl acetate homopolymer.

Figure 4. Plots of θ vs. equilibrium polymer concentration of EVA copolymer: Symbols are the same as in Figure 1.

groups adsorbed by vinyl acetate units in the polymer and that of the free silanol groups, respectively. The values of θ for the copolymers calculated from eq 3 are plotted against C_p in Figure 4.

The value of θ for each sample steeply increases with increasing C_p and levels off. In general, the total fraction of surface sites occupied by a copolymer is given by the sum of the fractions of surface sites occupied by each comonomer in the copolymer. However, in our case, the total fraction of silanol groups occupied by the EVA copolymer corresponds to the fraction of the silanol groups occupied by vinyl acetate units, since the ethylene units do not interact with the surface silanol groups. The plateau values of θ are plotted against the molecular weight in Figure 5, where the θ values for

Figure 5. Molecular weight dependence of θ . Symbols are the same as in Figure 2.

the vinyl acetate homopolymer are also illustrated. These θ values are almost independent of both molecular weight and composition of the polymer.

Fraction p of Adsorbed Segments

The fraction p of the polymer segments attached directly to the silica surface can be calculated from the equation derived by Fontana and Thomas¹:

$$p = \frac{\text{wt of attached polymer segments}}{\text{wt of total adsorbed polymer segments}} \quad (3)$$

For EVA copolymers, since only vinyl acetate units interact with silanol groups, we define the following two: One is p , the number of vinyl acetate units attached to the silanol groups relative to the total vinyl acetate units in the copolymer, and another is p_{TOT} , the number of vinyl acetate units attached relative to the total number of segments (vinyl acetate + ethylene).

The value of p_{TOT} is calculated from p by

$$p_{\text{TOT}} = p w_{\text{VA}} \quad (4)$$

where w_{VA} is the weight fraction of vinyl acetate units in an EVA copolymer. The values of p and p_{TOT} are summarized in Table II.

The values of p are plotted against C_p in Figure 6. As seen from Figure 6, for a given molecular weight, p , is large at lower C_p and almost 1 indicating a flattened adsorbed conformation, and decreases to a constant value at higher C_p , indicating the formation of loops and tails. The p values at the highest C_p are plotted against the molecular weight together with the plateau p for vinyl acetate homopolymer in Figure 7. The p value of EVA copolymer is independent of molecular weight within experimental error and nearly equal to that for vinyl acetate homopolymer.

Botham and Thies⁶ measured p_{TOT} for the EVA copolymers of different vinyl acetate content as a

Figure 6. Plots of p vs. equilibrium polymer concentration of EVA copolymer: Symbols are the same as in Figure 1.

Figure 7. Molecular weight dependence of p . Symbols are the same as in Figure 2.

Figure 8. Plots of p and p_{TOT} vs. vinyl acetate mole fraction: $\bullet$, p ; $\circ$, p_{TOT} .

function of copolymer concentration, and reported that p_{TOT} at the highest EVA concentration increased with increasing vinyl acetate content. Since the vinyl acetate content in the three EVA copolymers is available, we can convert p_{TOT} to p using eq 5.

In Figure 8, p_{TOT} and p are plotted against the vinyl acetate mole fraction. The p_{TOT} and p values for an EVA copolymer with 60 mol% vinyl acetate content correspond to average values at the highest C_p . For comparison, the average value of p for a vinyl acetate homopolymer, for which $p = p_{\text{TOT}}$, is also shown. The p_{TOT} value increases with increasing vinyl acetate mole fraction, while the p value is nearly independent of vinyl acetate content. This

latter finding seems to be striking, but at present, no explanation can be offered for it.

Surface Excess

The surface excess, *i.e.*, the total number of segments adsorbed per surface site, is an important quantity defined by eq 1. The surface excess, Γ_A , of unit *A* in a copolymer is expressed by an analogous equation

$$\Gamma_A = \frac{A_A N_A}{n_{OH} M_{u,A}} \quad (5)$$

where A_A is the adsorbance of unit *A* and $M_{u,A}$ is the molecular weight of an *A* comonomer unit. For EVA copolymers the surface excess, Γ , of vinyl acetate units can be calculated by substituting the adsorbance of vinyl acetate units and the molecular weight of the vinyl acetate comonomer into eq 6. The calculated values of Γ are presented in Table II.

The total surface excess, Γ_{TOT} , is calculated from eq 1. The M_u in this study is an average molecular weight of an ethylene-vinyl acetate copolymer unit defined as

$$M_u = M_{u,VA} m_{VA} + M_{u,E}(1 - m_{VA}) \quad (6)$$

where m_{VA} is the vinyl acetate mole fraction in the EVA copolymer and $M_{u,VA}$ and $M_{u,E}$ are the molecular weights of the vinyl acetate and ethylene comonomers, respectively. The Γ_{TOT} values listed in Table II are larger than the Γ values. The difference between Γ_{TOT} and Γ may be ascribed to the effect of the ethylene units.

Acknowledgement. The authors are indebted to Drs. M. Ueda and I. Tanaka of Kuraray Co. for supplying the ethylene-vinyl acetate copolymer sample.

REFERENCES

1. B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).
2. C. Thies, P. Peyser, and R. Ullman, "The Determination of Polymer Structure at a Liquid-Solid Interface by Infrared Analysis, in Proceedings of the 4th International Congress on Surface Active Substrates," Vol. II, Gordon and Breach, Science Publishers, New York, N. Y., 1967, p 1041.
3. P. Peyser, D. J. Tutas, and R. R. Stromberg, *J. Polym. Sci., A-1*, **5**, 651 (1967).
4. C. Thies, *J. Phys. Chem.*, **70**, 3783 (1966).
5. C. Thies, *Macromolecules*, **1**, 335 (1968).
6. R. Botham and C. Thies, *J. Polym. Sci., C*, **30**, 369 (1970).
7. G. R. Joppien, *Makromol. Chem.*, **175**, 1931 (1974).
8. G. R. Joppien, *Makromol. Chem.*, **176**, 1129 (1975).
9. E. Diets, *Makromol. Chem.*, **177**, 2113 (1976).
10. J. C. Day and I. D. Robb, *Polymer*, **21**, 408 (1980).
11. M. Korn and E. Killmann, *J. Colloid Interface Sci.*, **76**, 19 (1980).
12. K. I. Brebner, R. S. Chahal, and L. E. St-Pierre, *Polymer*, **21**, 533 (1980).
13. K. I. Brebner, G. R. Brown, R. S. Chahal, and L. E. St-Pierre, *Polymer*, **22**, 56 (1981).
14. C. V. Linden and R. V. Leemput, *J. Colloid Interface Sci.*, **67**, 48 (1978).
15. M. Kawaguchi, K. Hayakawa, and A. Takahashi, *Polym. J.*, **12**, 265 (1980).
16. M. Kawaguchi, T. Sano, and A. Takahashi, *Polym. J.*, **13**, 1019 (1981).
17. M. Kawaguchi, K. Kamiya, and A. Takahashi, *Polym. J.*, **14**, 563 (1982).
18. M. Kawaguchi, M. Aoki, and A. Takahashi, *Macromolecules*, **16**, 635 (1983).
19. Unpublished data.
20. H. L. Frisch, *J. Phys. Chem.*, **59**, 633 (1955).
21. W. I. Higuchi, *J. Phys. Chem.*, **65**, 487 (1961).
22. K. Mizuhara, K. Hara, and I. Imoto, *Kolloid Z. Z. Polym.*, **229**, 17 (1969).
23. K. Hara and T. Imoto, *Kolloid Z. Z. Polym.*, **237**, 297 (1970).