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Studies on polymer-metal interfaces
Part 1. Comparison of adsorption behavior between oxygen and nitrogen functionality in model copolymers onto metal surfaces

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Abstract

The effect of oxygen or nitrogen containing functionality in model copolymers on the interfacial characteristics between the copolymers and metals was examined by adhesion strength and infrared spectroscopy. The adhesion strength with both copper and aluminum increased with increasing the vinyl pyridine (VP) content in poly (styrene-*co*-vinyl pyridine) copolymers (SVP). The adhesion strength between poly (styrene-*co*-acrylic acid) copolymers (SAA) and both metals increased at lower acrylic acid (AA) contents in the copolymers, but the adhesion strength remained almost unchanged at higher AA contents due to competition between interaction of free carboxylic acid with metal and self-association of acrylic acid units in the copolymer through dimerization of carboxylic acids. From the reflection-absorption infrared (RAIR) spectroscopy, it is concluded that the enhancement of adhesion strength by the incorporation of comonomers is caused by specific interaction between the copolymers and metals and orientation behavior of carbonyl groups in AA units and pyridine rings in VP units to the metal surfaces. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene-acrylic acid copolymer; Styrene-vinyl pyridine copolymer; Copper

1. Introduction

Understanding of adsorption behavior of polymers onto metal surfaces is important in applications such as adhesive bonding, corrosion protection, colloid stabilization and many other areas [1]. Accordingly, there has been considerable interest in the characterization of the structure and properties of polymer-metal interface.

It has been reported that nitrogen-containing polymers can form a complex with metal, which may significantly enhance the adhesive strength between polymer and metal [2,3]. Among many nitrogen containing functional groups, the interfacial activity of 2-vinylpyridine (2VP) and 4-vinyl pyridine(4VP) with metal surface has extensively been investigated by several workers [4–11]. Xue and his coworkers [4,5] studied the surface geometry and orientation of poly(4-vinyl pyridine) on silver surface by observing the change in relative intensity of the out-of-plane ring deformation to the in-plane ring stretching vibration bands in surface-enhanced Raman scattering (SERS) spectra. They found that the pyridine ring lies flat on metal surface with a π-bonded geometry at ambient temperature, while upon heating the ring stands up to form an N-bonded geometry. Tsai et al. [7] analyzed the conformation of poly (2-vinyl pyridine-*b*-styrene) (2VP/S) block copolymers adsorbed onto silver surface by SERS. They reported that the 2VP block was preferentially adsorbed onto silver surface and that the 2VP layers were enriched by σ-bonding through the pyridine nitrogen atoms with a vertical conformation to the metal surface in the interfacial region.

In the early 1980’s, Burkstrand [12] reported that the interfacial adhesive strength between polymer and metal was significantly enhanced through metal-oxygen-polymer complex formation when metal atoms were vapor-deposited on oxygen-containing polymers. As an example of oxygen containing functionality, the ability of polyacid to function as an adhesive at an ionic interface was investigated by using Fourier transform infrared (FTIR) spectroscopy technique [13]. The effects of carboxylic acid groups in the pendant of poly (acrylic acid) on ionic reactions and adsorption onto metal oxide surfaces are also of primary interest in understanding the fundamental adhesion mechanisms between polar metal oxide surfaces and functional polyacid macromolecules. Sugama et al. [14] investigated the nature of the adhesion mechanisms and how they affect the

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Table 1
Characteristics of copolymers

Designation	Comonomer content (mol%)	T_g(°C)	M_n(g/mol)	M_wM_n
S4VP10	9.1	109	0.23[a]	—
S4VP30	27.9	117	0.39[a]	—
S4VP50	52.0	126	0.48[a]	—
S4VP70	68.3	137	0.34[a]	—
S2VP10	10.6	105	17 500	1.32
S2VP30	31.7	104	36 000	1.37
S2VP50	53.0	102	39 800	1.69
S2VP70	67.2	103	77 000	1.74
SAA10	10.8	111	230 000	1.86
SAA30	28.2	122	114 300	2.63
SAA60	62.0	137	250 000	2.03

[a] Intrinsic viscosity (dl/g).

interactions between the functional polyacids and the metal surfaces. They concluded that good bonding can be attributed to the following factors: (i) mechanical interlocking associated with the surface topography by metals, (ii) surface wettability of metal by the polymers, (iii) strong chemisorption, and (iv) the type and degree of polymer-metal interfacial interaction.

Although many researchers have reported about the interfacial activity of oxygen or nitrogen containing functional groups upon metal surface as mentioned above, any experimental attempt to directly compare the effect of the two functionalities containing oxygen and nitrogen atoms on the adhesion strength with metal is still lacking. Therefore it is our primary object to compare the interfacial activity of two representative oxygen and nitrogen functionalities in terms of adhesive strength, specific interaction and orientation behavior at the interface. For the purpose, poly (styrene-*co*-acrylic acid) (SAA), poly (styrene-*co*-4-vinyl pyridine) (S4VP) and poly (styrene-*co*-2-vinyl pyridine) (S2VP) random copolymers are used as representatives for oxygen and nitrogen containing model polymers.

2. Experimental

2.1. Synthesis of Copolymers

The styrene-4-vinylpyridine (S4VP), styrene-2-vinylpyridine (S2VP) and styrene-acrylic acid (SAA) random copolymers were synthesized in a sealed glass ampoule by bulk free radical copolymerization at 60°C, using 2,2-azobisisobutyronitrile (AIBN) as an initiator. All the copolymers are assumed to be random copolymers, because the values of $r_1 r_2$ lie between 0 and 1, where the monomer reactivity ratios (r_i) are given as [15–17]: $r_S = 0.52$, $r_{4VP} = 0.69$; $r_S = 0.5$, $r_{2VP} = 1.27$; $r_S = 0.15$, $r_{AA} = 0.25$. The content of VP and AA comonomers was varied over 10 ∽ 70 mol%, and the comonomer content was determined by the titration method [15,18]. The copolymer composition and other characteristics are listed in Table 1. It is noteworthy that the glass transition temperature (T_g) of S2VP copolymer remains almost unchanged, while the T_g of S4VP copolymer increases with increasing the 4VP content as shown in Table 1. This is because the T_g's of polystyrene, poly (2-vinyl pyridine) and poly (4-vinyl pyridine) homopolymers are 100°C, 104°C and 142°C, respectively [19,20].

2.2. Preparation of Metal Substrates

Metal substrates for reflection-absorption infrared (RAIR) spectroscopy were prepared as follows [21]. Copper and aluminum plates with a thickness of 1.5 mm were mechanically polished with a series of dry silicon carbide abrasive papers ranging from 220 to 1000 grit. After the surface was grounded, wet polishing was performed using 0.3 and 0.05 μm alumina powder in Microcloths (Buehler Inc.) with deionized water as a lubricant. The resulting mirrors were ultrasonically rinsed in deionized water and dried by blowing with nitrogen gas. Substrates for adhesion test were prepared as follows. Sheets of copper and aluminum with a size of $100 \times 25 \times 2\ \text{mm}^3$ were mechanically polished as described above. The grounded metal sheets were etched by 20% hydrochloric acid solution for 1 min to remove the surface oxide layer. The resulting plates were washed with ethanol for copper and with acetone for aluminum followed by rinsing the plates with deionized water, and then dried by blowing with nitrogen gas.

2.3. Adhesion Strength Measurement

Test specimens were prepared by applying a film of 10% polymer solution onto one metal plate, and another plate was placed onto the film with a lap area of $25 \times 15\ \text{mm}^2$. The assembly was tightly clamped. The adhesion strength was measured by the lap shear test (ASTM D1092-72) at a pull rate of 10 mm/min, using a universal tensile machine (LLOYD, LR 10K). The lap shear strength was calculated by dividing the strength by the lap area. Five specimens for each polymer were tested, and the average was reported.

2.4. Infrared Spectroscopy

The bulk spectra of polymers were recorded on a FTIR, Perkin–Elmer 1760X) at a resolution of $4\ \text{cm}^{-1}$, and 32 scans were collected. The RAIR spectroscopy was used to analyze the structure of polymer/metal interface. The RAIR spectra were obtained using a Bomem MB-100 spectrometer at a resolution of $4\ \text{cm}^{-1}$ with 100 scans. A Graseby Spec P/N 19650 monolayer/grazing angle accessory was used. The angle of incidence was 78°, and freshly polished copper and aluminum substrates were used to obtain the reference spectrum.

3. Results and Discussion

Fig. 1 shows the adhesion strength between copper substrate and SAA, S2VP or S4VP copolymers as a function

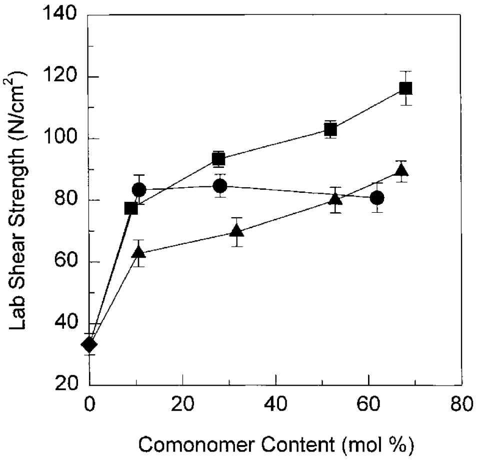

Fig. 1. Lab shear strength between copper/SAA (●), copper/S2VP (▲) and copper/S4VP (■) as an function of comonomer content.

of comonomer content. The adhesion strength increases with increasing the 2VP and 4VP comonomer content in copolymers. When the adhesion strength of S4VP is compared with that of S2VP, it is revealed that the 4VP is more effective in enhancing the adhesion to the copper substrate. Another interesting feature to note is that the adhesion strength of the SAA copolymers to the copper substrate is higher than those of S4VP and S2VP at low AA content, while the adhesion strength does not increase with increases in the AA content in the copolymer. When the AA content is high, the AA units in the copolymer may self-associate through dimerization of carboxylic acid groups, which prevents the interaction with metal. Consequently, there exists a competition between interaction of AA with metal and self-associations of AA's, and as a result, the adhesion strength remains unchanged as the AA content in the copolymer increases.

A similar behavior can be seen in Fig. 2 for aluminum substrate. As compared with the copper substrate, the adhesion strength between S2VP copolymers and aluminum substrate does not increase significantly with the comonomer content. When the absolute value of adhesion strength with the copper substrate (Fig. 1) is compared with that of the aluminum substrate (Fig. 2), the adhesion strength between the copolymers and the copper substrate is higher than the aluminum substrate.

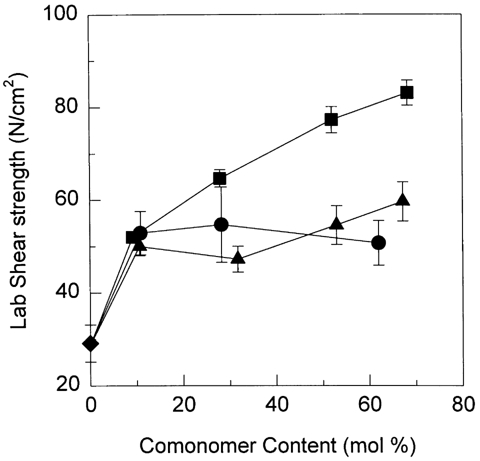

Fig. 2. Lab shear strength between aluminum/SAA (●), aluminum/S2VP (▲) and aluminum/S4VP (■) as a function of comonomer content.

In order to investigate the nature of the adhesion between the copolymers and metal substrates, the transmission IR spectroscopy and RAIR spectroscopy were used. Fig. 3 shows the transmission IR spectrum of SAA10 and RAIR spectra obtained from SAA10 adsorbed onto copper and aluminum substrate from 2% solution in THF. In Fig. 3(a), the SAA10 copolymer has absorption bands at 1744.4 cm^{-1} and 1704 cm^{-1}, which correspond to C=O stretching of free carboxylic acid groups and of dimerized carboxylic acid groups, respectively [18]. When the SAA10 is adsorbed onto copper, the band at 1744.4 cm^{-1} shifts to 1731 cm^{-1} as shown in Fig. 3b while the band at 1704 cm^{-1} remains unchanged. Therefore, the band at 1731 cm^{-1} can be assigned to C=O stretching of the free carboxylic groups which interact specifically with copper surface. Moreover, the intensity of this new peak becomes stronger as compared with the intensity of the acid dimer band at 1704 cm^{-1}. Since the RAIR spectroscopy is very sensitive to preferential orientation of functional groups at the surface of a metal, i.e. vibrational modes having transition moments perpendicular to the surface of the substrate appear with much greater intensity than do vibrations having transition moments parallel to the surface [22,23], the difference between the transmission and the RAIR spectrum may come from the orientation difference of functional groups. This type of analysis has also been used by several workers to reveal the orientation behavior of polymers on metal surfaces [24–34]. From the enhancement of C=O band of free carboxylic acid in RAIR spectra, it is concluded that the SAA10 is adsorbed onto metal surface with an edge-on configuration in which the carbonyl bond is approximately perpendicular to the copper surface. When the SAA10 is adsorbed onto aluminum, the band at 1744.4 cm^{-1}, shifts to 1735 cm^{-1}, but the intensity does not increase significantly as compared to the case of copper substrate, as shown in Fig. 3(c) This result indicates that under the same condition the carbonyl groups are more oriented in a vertical direction to the copper surface than to the aluminum one, which may explain larger adhesion strength of the SAA10 with copper substrate than with aluminum substrate.

The transmission IR spectrum of SAA30 and RAIR spectra of the SAA30 adsorbed onto the two metal substrates are shown in Fig. 4. When Fig. 4(a) is compared with Fig. 3(a), the relative intensity of dimerized carboxylic acid in SAA30 at 1704 cm^{-1} as compared to that of free carboxylic acid at 1745 cm^{-1} is larger than in the case of the SAA10, indicating that carboxylic acid groups in the SAA30 are more likely to form dimers than in the SAA10. The band at 1745 cm^{-1} caused by free carboxylic acid groups shifts to

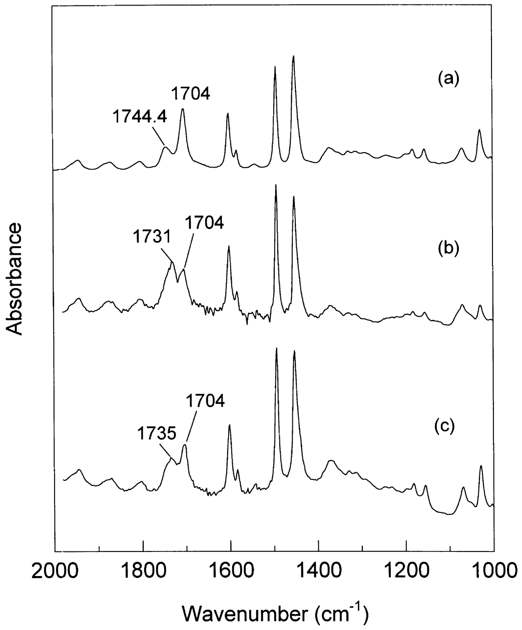

Fig. 3. Transmission IR spectrum of SAA10 (a), RAIR spectrum of SAA10 adsorbed on copper from 2% solution in THF (b) and RAIR spectrum of SAA10 adsorbed on aluminum from 2% solution in THF (c).

lower frequency and its intensity in RAIR spectrum significantly increases for the copper substrate. It is shown that the relative intensity of free carboxylic acids, interacted with metal surface, to the intensity of dimerized carboxylic acids in SAA30 is very much comparable to that in SAA10, when Fig. 3(b) is compared with Fig. 4(b). This result is in good agreement with the adhesion strength (Fig. 1). In other words, the adhesion strength remains almost constant when the AA content in copolymers increases from 10% to 30%. Fig. 4 also shows that the carbonyl groups in the SAA30 are more oriented in a vertical direction to the copper surface than to the aluminum surface. When the AA content in SAA copolymer increases further to 60%, the transmission spectrum of the SAA60 (Fig. 5a) shows that the band of free carboxylic acid groups becomes very weak, but the band shifts to lower frequency and its intensity still increases although the increase is not large, when the SAA60 is adsorbed onto the metal surface (Fig. 5b and 5c). This phenomenon is directly related to the relatively weak adhesion strength between SAA60 and metal substrate as compared with SAA copolymers having lower AA content. It should be noted that the formation and diffusion of metal oxides in the polymer are important for adhesion [35]. Sugama et al. [14] reported that the metal carboxylate was formed between poly (acrylic acid) and metal oxide by observing the absorption bands at 1550 cm^{-1} and 1400 cm^{-1} in IR spectra which can be assigned to the asymmetrical and symmetrical stretching vibrations of carboxylic anions, COO^{-}, respectively. However, such an interfacial reaction between SAA and metal atoms seems not to occur in our case because an absorption band around 1550 cm^{-1} and 1400 cm^{-1} is not observed, as shown in Fig. 5b and 5c.

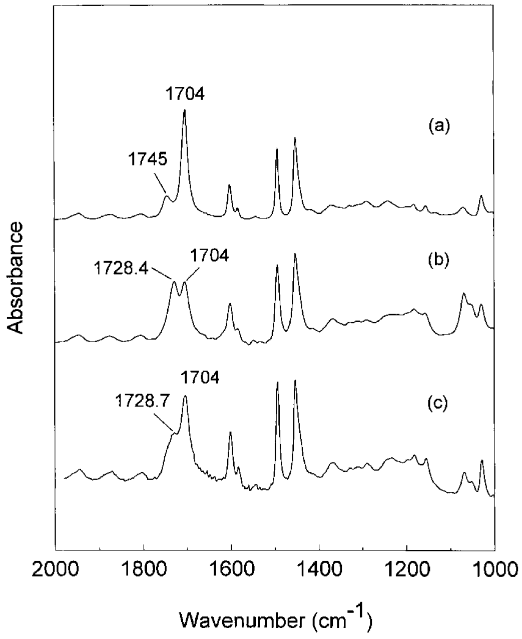

Fig. 4. Transmission IR spectrum of SAA30 (a), RAIR spectrum of SAA30 adsorbed on copper from 2% solution in THF (b) and RAIR spectrum of SAA30 adsorbed on aluminum from 2% solution in THF (c).

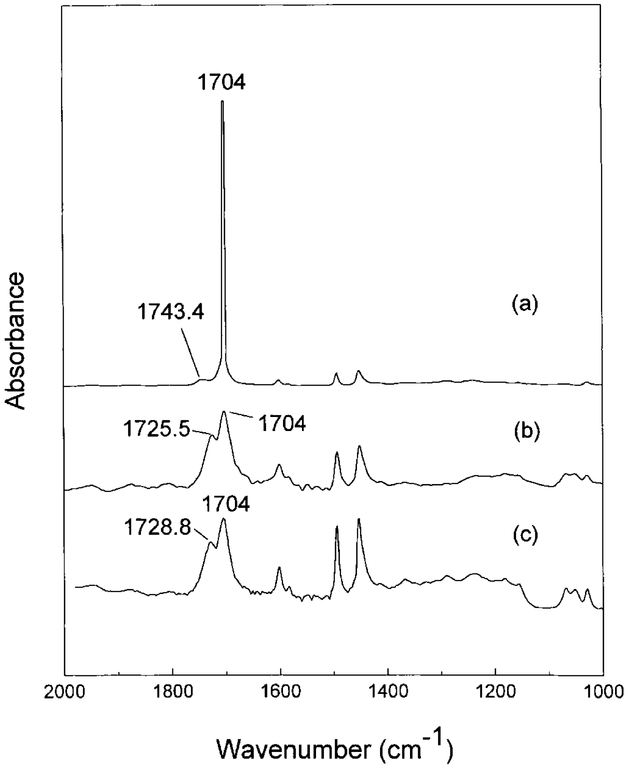

Fig. 5. Transmission IR spectrum of SAA60 (a), RAIR spectrum of SAA60 adsorbed on copper from 2% solution in THF (b) and RAIR spectrum of SAA60 adsorbed on aluminum from 2% solution in THF (c).

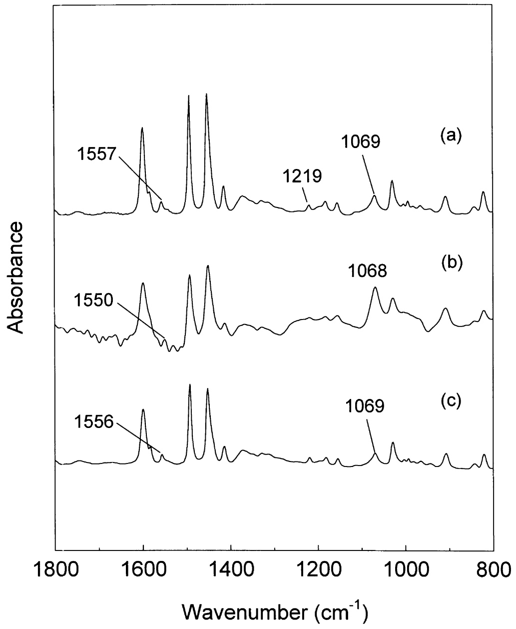

Fig. 6. Transmission IR spectrum of S4VP10 (a), RAIR spectrum of S4VP10 adsorbed on copper from 2% solution in THF (b) and RAIR spectrum of S4VP10 adsorbed on aluminum from 2% solution in THF (c).

The transmission IR spectrum of S4VP10 and RAIR spectra of S4VP10 obtained from 2% solution in THF onto copper and aluminum substrate are shown in Fig. 6. In the transmission IR spectrum [Fig. 6(a)], the bands at 1219 cm^{-1} and 1069 cm^{-1} are assigned to in-plane ring bending modes of pyridine ring [7,36,37]. When the transmission IR spectrum is compared with the RAIR spectra, some differences are observed: The band near 1069 cm^{-1} associated with the in-plane ring bending modes of S4VP10 in bulk increases in intensity when the copolymer is adsorbed onto copper substrate, as can be seen in Fig. 6(b). It has been observed that in the RAIR spectrum, the intensity of in-plane modes of the rings is enhanced more strongly than that of out-of-plane modes when the rings have a vertical orientation to the copper surface, whereas the intensity of out-of-plane mode is more strongly enhanced when the molecules are adsorbed parallel to the surface [22,36]. Therefore, an increase of the intensity near 1069 cm^{-1} in the RAIR spectra indicates that the 4VP unit in S4VP is adsorbed on the metal surface nearly in a vertical direction. However the increase of the intensity near 1069 cm^{-1} is not significant when the copolymer is adsorbed onto the aluminum substrate. This result is consistent with the results of adhesion strength. Another feature to note from Fig. 6 is that the 1557 cm^{-1} band in bulk spectrum of the S4VP10 due to C=N stretching shifts to a lower frequency of 1550 cm^{-1} when adsorbed on copper (Fig. 6b) whereas the band does not shift significantly for aluminum substrate (Fig. 6c). This also indicates that the 4VP groups interact more strongly with copper substrate than with aluminum substrate.

4. Conclusions

Interfacial characteristics between three model copolymers containing oxygen and nitrogen functionality and two selected metal substrates were compared. The adhesion strength with both the copper and aluminum substrate increased with increasing the 2VP and 4VP content in S2VP and S4VP copolymers, and the effect was more prominent for the copper substrate. The adhesion strength between SAA and both metals did not increase with increasing the AA content in SAA copolymer due to competing reaction between interaction of free carboxylic acid with metal and self-association of AA units through dimerization of carboxylic acid groups. At low AA contents, the SAA shows higher adhesion strength than S2VP and S4VP, but the situation was reversed at higher comonomer contents. For all the three kinds of copolymers studied, the adhesion strength was higher for the copper substrate than for the aluminum substrate. It is revealed from RAIR spectroscopy that the enhancement of adhesion strength is closely related to the orientation behavior of the functional groups in comonomer units to the metal surface. From observation of the frequency shift and the intensity increment at 1744.4 cm^{-1} in RAIR spectroscopy of SAA copolymers, it is concluded that the free carboxylic groups interact specifically with copper and that the carbonyl groups are oriented in a perpendicular direction to the metal surface. The selective increase in intensity of in-plane ring mode of S4VP copolymers is also observed in RAIR spectroscopy when the copolymer is adsorbed onto metal, which is responsible for the increase in adhesion strength. In summary, there exists a close relationship between the adhesion strength and the orientation behavior of functional groups in copolymers when the copolymers are adsorbed onto metal surfaces.

Acknowledgements

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