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A study on interfacial mechanisms and structure of poly(ethylene-co-methacrylic acid)/copper with reflection–absorption infrared spectroscopy

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Abstract The interfacial mechanism and structure of poly(ethylene-co-methacrylic acid)/copper were investigated using reflection-absorption infrared spectroscopy (RAIR). Based on IR spectrum of EMAA/copper, a strong absorption peak appearing at approximate 1,600 cm^{-1} is attributed to the asymmetric stretching vibration of COO^{-} ($\upsilon\mathrm{COO}_{\mathrm{as}}^{-}$) and a relatively weak absorption band at 1,375 cm^{-1} is assigned to the symmetric stretching vibration of COO^{-} ($\upsilon\mathrm{COO}_{\mathrm{s}}^{-}$). Therefore, it can be determined that copper interacts with EMAA through a strong ionic interaction and carboxylate structure is formed in the interfacial regions. And, according to the band intensities of carboxylate stretching modes and different sensitivities of RAIR to perpendicular and parallel transition moments, it can be concluded that EMAA is absorbed onto a copper substrate with a configuration in which the twofold axis of the $C_{2\upsilon}$ point group for carboxylate group inclines certain degree from the normal to the surface. In addition, the interfacial carboxylate structure of EMAA/copper is confirmed to be a monodentate one through calculating the difference ($\Delta\upsilon$)between the asymmetric carboxylate stretch ($\upsilon\mathrm{COO}_{\mathrm{as}}^{-}$) and the symmetric stretch ($\upsilon\mathrm{COO}_{\mathrm{s}}^{-}$).

Introduction

Adsorption of polymer molecules to metal substrates is of major importance in many areas including microelectronics, adhesion, corrosion protection and colloid stabilization [1–3]. The adsorption behavior of polymers containing oxygen-functionality onto metal surfaces has been extensively investigated using an array of surface analysis techniques, such as reflection-absorption infrared spectroscopy (RAIR), x-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS). Polymers containing oxygen-functionality, in particular, those with reactive carboxylic acid groups have attracted much attention because of their importance to understand the fundamental adhesion mechanisms between polymer and metal and many significant results have been reported [3–19].

In past a few years, many researches about the interface between polymer and metal have concentrated on the exploration regarding interfacial mechanisms and structures. Boerio et al. [12] investigated myristic acid adsorbed from dilute solutions in nitrobenzene onto metal surfaces and concluded that the acid was adsorbed onto aluminum with a vertical conformation by analyzing the data of reflection–adsorption infrared spectroscopy. Chollet et al. [13] determined the molecular orientation in films of stearamide formed on aluminum by the Langmuir–Blodgett

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technique and found that the plane of molecules made an angle of nearly 67°with the surface of metal substrate. Pyromellitic dianhydride-oxydianiline (PMDA-ODA)-derived polyamic acid-metal interactions were delineated by Linde with grazing incidence infrared spectroscopy on mirror surfaces [14]. The ability of poly (acrylic acid) (PAA) to function as an adhesive at an interface between PAA/oxidized metal surfaces was investigated by Sugama et al. and they suggested acid-base surface interaction mechanisms and salt-bridge intermolecular reaction mechanisms [15]. Alexander et al. [16] investigated the interfacial interaction between plasma-polymerized acrylic acid and an oxidized aluminum surface using XPS, FTIR, and they concluded that the interface formation occurred via an acid-base interaction between PAA and aluminum. Leadley and Watts [17] used XPS to examine the interaction of poly (acrylic acid) with oxidized metal substrates and proposed three types of interfacial acid-base interactions. And they pointed out that the interfacial mechanisms had strong dependence on the acid-base natures of oxidized metal surface. Hidetoshi Yamabe [18] researched the stabilization of poly (acrylic acid)/metal interface and demonstrated the strong ionic interaction takes place between the surface of Cu and the carboxyl group by analyzing the shifts of binding energy of O1s spectra. And, the presence of $COOM^+$ (M: Fe, Cu, Al) ions was detected using static secondary ion mass spectroscopy (SSIMS), which is the evidence and associated with strong interactions of carboxyl groups with the metal oxide surface.

Although many researches are concerned with the interfacial mechanisms and structures between polymer and metal, the elements that determine the nature of interfacial mechanisms and the details of interfacial mechanisms resulting in the formation of different structures remained to be clarified. In the present study, poly (ethylene-co-methacrylic acid) (EMAA) was adopted as a model copolymer to investigate the mechanisms and structures of interfaces between poly (ethylene-co-methacrylic acid) and metal. Copper that presents technology importance in many applications was used in this research to give further insight into the interfacial mechanism and structure.

Experimental section

Materials

Poly(ethylene-co-methacrylic acid), i.e. Nucrel®, used in this study is a commercial copolymer provided by Dupont company and the specific physical and chemical properties of this copolymer are listed in Table 1.

Table 1 The physical and chemical properties of Poly (ethylene-co-methacrylic acid)

Properties	Test methods	Values
Methacrylic acid, %	Provided by Dupont	10.0
Melt Index, g/10 min	ASTM D-1238 (Condition 190°C/2.16 kg)	500
Density, kg/m^3	ASTM D-792	930
Tensile strength, MPa	ASTM D-638	10.3
Elongation, %	ASTM D-638	500 ± 50
Flexural modulus, MPa	ASTM D-790	64.8
Hardness, Shore D	ASTM D-2240	42
Vicat softening Temperature, °C	ASTM D-1525	65
Notched Izod, J/m	ASTM D-256	No Break

Preparation of metal substrates

The copper plates used in this study are all commercial level products and their purities are 99.9%. The preparation of metal substrates for RAIR measurements was processed according to the following method. The metal plates with a thickness of 1.5 mm were mechanically polished with a series of dry silicon carbide abrasive papers ranging from 320 to 2,000 grit. Then, wet polishing was performed using 0.05 μm alumina powder in Microcloths with deionized water as a lubricant. The surface roughness of resultant metal planes is 0.02 μm. Copper plates were rinsed by alcohol and acetone respectively. After the former wash, the resulting mirrors were rinsed with deionized water and dried in a vacuum for later uses.

Infrared spectroscopy

The spectra information of the bulk was recorded on a Fourier transform infrared spectrometer (FTIR, Perkin-Elmer 1760x) at a resolution of 4 cm^{-1}, and 32 scans were collected. Preparation of samples for RAIR spectroscopy was carried out according to the following method, i.e. dipping the prepared metal substrates into 1% polymer solutions for 6 h. The solvent is xylene for Poly (ethylene-co-methacrylic acid). Then, the samples were withdrawn and dried in a vacuum for another 8 h in order to evaporate the remaining solvent. The RAIR spectra of polymer/metal interfaces were obtained using a Bomem MB-100 spectrometer at a resolution of 4 cm^{-1} with 100 scans. A Graseby Spec P/N 19650 monolayer/grazing angle accessory was used and the incidence angle was 78^0.

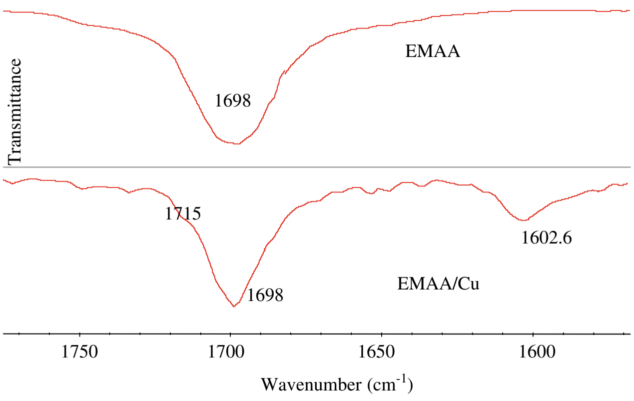

Fig. 1 Transmission IR spectrum of EMAA and RAIR spectra of EMAA/Cu

Result and discussion

In order to explore the interfacial mechanisms and the structures of interfaces between polymer and metal, transmission IR and RAIR spectroscopy were used for the bulk and the interface respectively, as shown in Fig. 1. It can be seen that the spectrum of EMAA displays a strong characteristic absorption bands at about 1,698 cm^{-1}, which is assigned to C = O stretching vibration of dimerized carboxylic acid groups in EMAA [19–21]. On the basis of strong intensity of C = O stretching of dimerized carboxyl, it can be concluded that the self-association of methacrylic acid units through dimerization is the predominant form of carboxylic groups in EMAA. For EMAA/copper, the spectrum presents two new absorption bands. The weak peak at 1,715 cm^{-1} results from the redistribution of C = O stretching of methacrylic acid segments of EMAA [21]. The strong characteristic peak at 1,602 cm^{-1} is assigned to the asymmetric stretching vibration of COO^{-} (υCOO^{-}_{as}) [22], which is an indication of the formation of carboxylate structures in the interface regions.

For the sake of clarity, the spectrum of pure EMAA was subtracted from that of EMAA/Cu to amplify the difference between EMAA and EMAA/metal systems, and the resultant spectrum is listed in Fig. 2.

From Fig. 2., a down characteristic peak appears at 1,698 cm^{-1} is in EMAA/copper, indicating less carboxylic groups exist in the form of self-association through hydrogen bonds compared with pure EMAA due to certain interaction between polymer and metal. From the spectrum of EMAA/Cu, a intense upward absorption peak appearing at approximate 1,600 cm^{-1} is attributed to the asymmetric stretching vibration of COO^{-} (υCOO^{-}_{as}) and a relatively weak up characteristic band at 1,375 cm^{-1} is assigned to the symmetric stretching vibration of COO^{-} (υCOO^{-}_{s}). The two characteristic adsorption bands are both associated with ion interactions between EMAA and the copper surface.

Generally, to COO^{-} anion, it exhibits the resonance structure rather than the characteristic peak of dissociative carbonyl. The bond length of C–O single bond in normal COO^{-} is 0.136 nm and C = O bond length is 0.123 nm, while the bond lengths are both 0.127 nm in complete resonance structure. Therefore, both carbon–oxygen in COO^{-} can be assumed equivalent. Then, the point group for carboxylate group is $C_{2\upsilon}$, as shown in Fig. 3. The symmetric stretch transition moment is along the bisector of each oxygen–carbon–oxygen group and the asymmetric stretch moment is perpendicular to the symmetric stretch moment, i.e., the transition moments for the symmetric and asymmetric stretching modes are parallel to and perpendicular to the twofold axis, respectively.

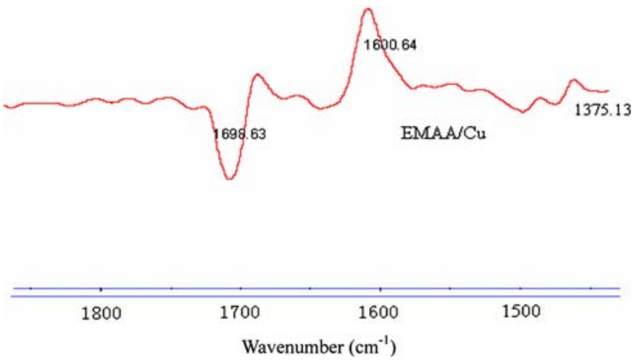

Fig. 2 The RAIR spectra of EMAA/Cu (obtained by subtracting the spectrum of EMAA from the original spectrum of EMAA/Cu)

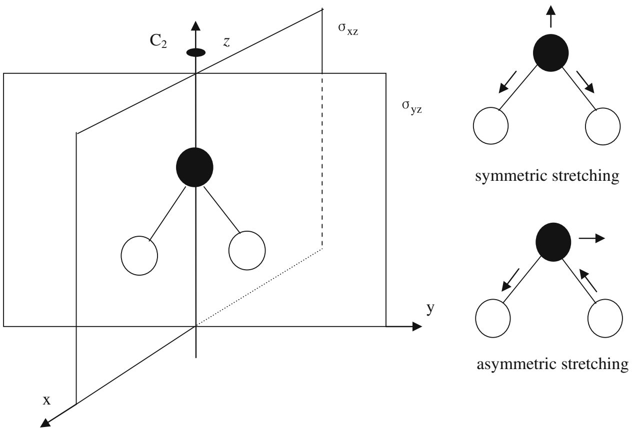

Fig. 3 The symmetry characteristics of carboxylate group and two stretching vibrations (Black ball: Carbon; White ball: Oxygen)

Because RAIR spectroscopy is more sensitive to preferential orientation of functional groups at the surface of a metal, namely, vibrational modes with transition moments perpendicular to the surface of the substrate appear with much stronger intensity than do vibrations with transition moments parallel to the surface. Therefore, if the twofold axis of the $C_{2\upsilon}$ point group is completely vertical to the surface, the adsorption peak of symmetric carboxylate stretching vibration (υCOO_s^-) at 1,375 cm^{-1} will be much stronger than asymmetric carboxylate stretching vibration (υCOO_{as}^-) near 1,600 cm^{-1}. However, in the present study, the intensity of symmetric carboxylate stretching mode is much weaker than that of asymmetric carboxylate vibration. Therefore, it can be concluded that the twofold axis of the $C_{2\upsilon}$ point group inclines certain degree from the normal to the surface rather than completely vertical to the surface. And the specific obliquity can be calculated employing quantitative absorption-reflection thickness infrared (QUARTIR) [9]. The orientation of carboxylate for EMAA/copper is different from the general result concerning small molecular organic acid absorbed on mirror metal substrates. To small molecular acids, they are often absorbed onto metal substrates with a configuration in which the carboxyl is approximately vertical to the metal surface [12].

In addition, the compositions of metal surfaces under the atmosphere contribute to the understanding about probable interfacial structures. The isoelectric point of surface (IEPS) of a hydrated metal oxide surface is considered as its acid-base character [23]. The IEPS can be estimated as the pH of an aqueous solution in which the solid surface exists in a state of electrical neutrality. A low IEPS value indicates an acidic surface while a high IEPS suggests a basic one. Copper oxidizes rapidly in air [24, 25] and the air-passivated copper surface consists of CuO and Cu $(OH)_2$ [17]. These surface compounds, including CuO and Cu $(OH)_2$, can be considered as several basic substances in view of chemical reactivity during the interaction in that the IEPS values for CuO and Cu $(OH)_2$ are 9.5 and 9.4 [26]. Therefore, it is reasonable to expect the formation of certain carboxylate according to the nature of compositions of copper surface as well as the effective evidence coming from IR spectra.

It is well known that a carboxylate ion can coordinate to metals in a number of ways and three basic possibilities are monodentate, chelating and bridging bidentate structures [27], as shown in Fig. 4. It is an interesting exploration to identify the carboxylate structure in the interface regions between polymer and metal. The difference ($\Delta\upsilon$) between the asymmetric carboxylate stretch (υCOO_{as}^-) and the symmetric stretch (υCOO_s^-) has been applied to assign the type of bonding from a survey of coordination compounds formed between the metal and the carboxylateion [16, 27]. Hu et al. [27] have applied this method to the interaction of PAA with the surface of metal oxide powders and they found $\Delta\upsilon$is small for a bidentate chelating structure, intermediate for the bidentate bridging and large for the monodentate structure. An RAIR spectrum of EMAA/Cu obtained at a wider frequency region is presented in Fig. 5.

Compared with the spectra shown in Fig. 1 and 2, the spectrum of Fig. 5 reveals more characteristic absorption bands because of the adoption of a greater frequency area. Similarly, the peak at 1,715 cm^{-1} comes from the retribution of the C = O stretching of methacrylic acid segments of EMAA. The absorption bands appearing at 1,698 cm^{-1} and 1,467 cm^{-1} are attributed to the C = O stretching vibration of dimerized carboxylic acid groups and the stretching vibration of C–H respectively. Obviously, the spectrum takes on two characteristic carboxylate peaks including the peak

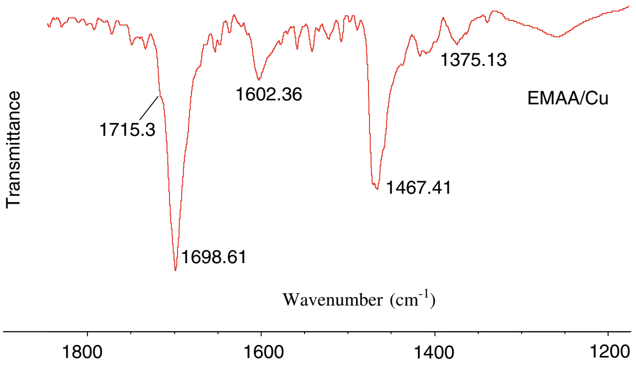

Fig. 5 RAIR spectrum of the EMAA/Cu system

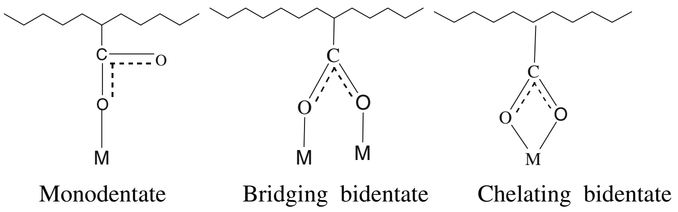

Fig. 4 Three basic carboxylate structures that can form between carboxylate ion and metal (M means a metal atom)

Table 2 $\Delta\upsilon$ values for various metal salts of PAA and their structures

$\Delta\upsilon$ (cm^{-1})	Carboxylate	Structure
128	Na(OH)-PAA	Bidentate
231	MgO-PAA	monodentate
228	CuO-PAA	monodentate
227	CaO-PAA	monodentate
244	ZnO-PAA	monodentate

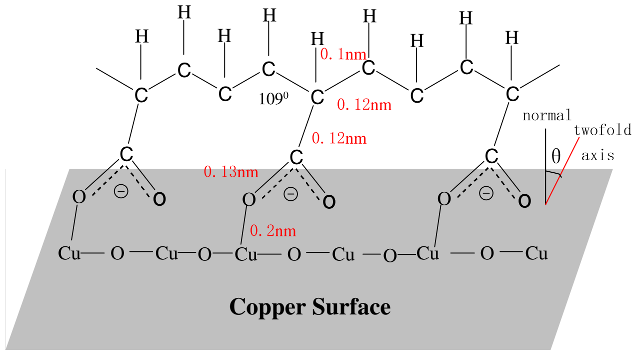

Fig. 6 The interfacial structure of the interface between EMAA and copper

at 1,602 cm^{-1} (υCOO_{as}^{-}) and that at 1,375 cm^{-1} (υCOO_{s}^{-}).

As mentioned previously, since $\Delta\upsilon = (\upsilon COO_{as}^{-})-(\upsilon COO_{s}^{-})$, thus, for EMAA/Cu, $\Delta\upsilon = 227\ cm^{-1}$. Hu et al. have provided some $\Delta\upsilon$values for a bidentate structure and a selection of monodentate salts, and the specific $\Delta\upsilon$values are listed in Table 2.

Comparing our value of $\Delta\upsilon = 227\ cm^{-1}$ with those for carboxylates with monodentate structures, it can be concluded that the interface between EMAA and copper has a monodentate structure. Considering the orientation of carboxylate structure revealed by RAIR spectra, a conceivable interface structure could be proposed and illustrated in Fig. 6. According to the data of bond length and bond angle, the thickness of a monolayer is estimated to be approximate 0.6 nm from the standpoint of theory.

Conclusions

The interfacial mechanisms and structures of poly(ethylene-co-methacrylic acid)/copper were investigated using reflection–absorption infrared spectroscopy (RAIR). For EMAA/copper, the IR spectrum shows that two new absorption peaks attributed to the asymmetric stretching vibration of COO^{-}(υCOO_{as}^{-}) and symmetric stretching vibration of COO^{-}(υCOO_{s}^{-}) appear at 1,602 cm^{-1} and 1,735 cm^{-1} respectively, which reveals that copper interacts with EMAA through strong ionic interactions and the carboxylate structure is formed in the interfacial regions between EMAA and copper. Based on the result of RAIR, utilizing its different sensitivities to perpendicular transition moments and parallel transition moments, it can be concluded that EMAA is absorbed onto copper substrates with a configuration in which the twofold axis of carboxylate inclines certain degree from the normal to metal surface. In addition, the interfacial carboxylate structure of EMAA/copper is confirmed to be a monodentate one by virtue of calculating the difference ($\Delta\upsilon$)between the asymmetric carboxylate stretch (υCOO_{as}^{-}) and the symmetric stretch (υCOO_{s}^{-}).

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