Surface-enhanced Raman scattering used as an *in situ* analytical method for studies of polymer–metal interface

G. Xue*, Y. Lu and G. Shi
Department of Chemistry, The Coordination Chemistry State Key Laboratory, Nanjing University, Nanjing 210008, People's Republic of China

(Received 6 July 1993; revised 10 November 1993)

Physicochemical phenomena at the polymer–metal interface have been observed by the use of surface-enhanced Raman scattering (SERS). SERS spectra are compared with the infra-red reflection-absorption spectra for coatings of polymer on metals. Results show that SERS is an effective *in situ* analytical technique which is highly informative in that the authentic adsorption state and the microstructure of the first monolayer near the metal surface can be revealed with much less interference from the polymer bulk.

(Keywords: polymer–metal interface; adsorption; catalysis)

INTRODUCTION

Polymer–metal composites, which include engineering materials, adhesives and coatings, are of great interest in both science and technology. An understanding of the role of the physical chemistry of the polymer–metal interface is critical to the control of the final properties of the composites. However, direct measurements of the interfacial structure has long been a difficulty. Polymers adsorbed from a solution usually form multilayers on a solid surface. A 'very thin layer' of polymer formed on a metal is usually at least tens or hundreds of angstroms thick. Seen as a macroscopic film, the surface is entirely covered with polymer. However, in terms of the microstructure at the polymer–metal interfacial region, it is hard to get every segment or side-group along the coil of the first layer in contact with the metal, so the first layer of chain is supposed to contact the surface only at a few points along the chain with the remainder coiled about surface voids. When the cast solution is very dilute to produce low coverage, the adsorbed polymer is prone to form islands or clumps upon evaporating the solvent, resulting in an inhomogeneous surface under analysis. Thus, the film of polymer on metal must be a few hundreds of angstroms thick in order to cover the surface entirely while the interfacial region relates only to a few or a few tens of angstroms of polymer adjacent to the metal surface[1]. It is therefore difficult to measure the interfacial region without the interference of the polymer bulk.

Until recently, process technology had developed in a largely empirical fashion without specific knowledge of the nature of chemical bonding at interfaces. With the advent of more sophisticated surface analytical techniques, polymer–substrate interaction has begun to be studied at a more detailed molecular level. Among the various state-of-the-art tools in surface analysis, X-ray photoelectron spectroscopy (X.p.s.) is used to investigate core-level shifts of the polymer components, as well as those of the metal atoms themselves, in order to elucidate the nature of the bonding between metal and polymer. Since X.p.s. linewidths are comparable to the chemical shifts involved, peak overlap is a problem and unambiguous assignments have not been possible. Also, the uncertainties inherent in X.p.s. analysis of polymer–metal interactions stem mostly from differential charging of the sample surface during an X.p.s. measurement[2]. Differential charging leads to artefacts in the X.p.s. spectra, which may be mistaken for chemical bonding effects. Moreover, metals can be studied by the use of electron spectroscopy, but only if the polymer layer is absent or is less than 3–5 nm thick because of the limitation of the mean free paths of the photoemitted electron in the energy range of interest. However, it is difficult in practice to cast synthetic polymers as a uniform monolayer film onto metals. In the manufacture of coatings or adhesives on metals, a 'thin layer' may mean a thickness of hundreds of nanometres. Surface vibrational spectroscopy, with its high resolution, should provide insight into these problems. Indeed, a significant step has been taken by Pireaux *et al.* who have used high-resolution electron energy loss spectroscopy to study the interactions of photoresistive polyimide films with metal surfaces[3]; however, uncertainties in the interaction mechanisms coupling the electron beam to surface vibration prevent a straightforward interpretation of these experiments. Infra-red (i.r.) reflection-absorption spectroscopy could provide rich information about the surface film[4–7], but mostly from the bulk. Both i.r. and Raman spectroscopy could hardly observe the inside structure of a 10–30 Å layer of polymer near the surface without the interference of the bulk polymer, which is at least hundreds of angstroms thick. Because of the

---

* To whom correspondence should be addressed

0032-3861/94/12/2488–07

difficulty of experimental measurement of the microstructure at the interface, details of the physical chemistry, such as surface bonding, molecular orientation, catalysis under various conditions, diffusion of metal ions and the electrochemical properties in the interfacial region, are still not understood. It is therefore necessary to develop new techniques to investigate the interfacial structure with minimal interference from the bulk polymer.

The discovery of surface-enhanced Raman scattering (SERS) by Fleishman and others is probably one of the most important developments in the area of surface science in the past two decades[8-10]. Local electromagnetic effects on certain roughened materials (e.g. gold, silver and copper) enhance the Raman signal by factors of up to 10^6 and make detection of monolayer straightforward[8]. Enhanced Raman spectra that are 10^5–10^6 times as strong as normal Raman scattering were reported[11]. SERS is ideal for the study of polymer–metal interfaces since it enhances almost exclusively the first monolayer of molecules adjacent to the surface. That makes it possible to examine the interfacial region between metal and polymer as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interface[12].

Another advantage of SERS for polymer study is its fluorescence-quenching property. Normal Raman spectra cannot be obtained from many samples because of the curtain of fluorescence that hides them. Even if the fluorescence is assumed to arise from an impurity that is present at the parts-per-million level, with a fluorescent quantum yield of only 0.1, 10 fluorescent photons will be produced for every Raman photon. In the visible excitation region, most polymers are not amenable to Raman analysis because of fluorescence. Adsorption of molecules on the SERS active metal surface causes fluorescence quenching in highly fluorescent compounds[8].

Since the original SERS work involving pyridine adsorbed on silver electrodes and sols, most of the reported SERS spectra of polymers were recorded from electrochemical cells, aqueous environments or in vacuum[13-16]. It was reported that spin-casting of a polymer solution onto silver island films could be characterized by SERS[12,17,18]. However, we found that the SERS effect of vacuum-deposited silver island film is not stable at elevated temperature. This disadvantage limited the application of SERS as a general tool to analyse the polymer–metal interface. Recently, HNO_3-etched metal foils for Raman study of adsorbates were prepared in this and other laboratories[19,20]. This new sampling technique exhibits a strong SERS effect on surface adsorbates and better thermal stability[21]. In the present study, thin-layer coatings made by solution casting are investigated on the newly developed Raman-enhancing silver and copper substrates, in order to elucidate the adsorption and desorption of polymer chain and catalysis at the interface and to study the oxidation of metal under the polymer overlayer. For comparative purposes, i.r. reflection-absorption spectroscopic investigations were also performed to elucidate the character of the SERS method in polymer–metal systems. This work is part of a programme intended to explore the relationships between the physical chemistry at the interface of the composites and the macroscopic properties, such as mechanical strength, corrosion inhibition, durability of the materials under various environments, etc.

EXPERIMENTAL

Preparation of metal substrate

Commercial silver or copper foil of thickness 0.025 mm was immersed into a freshly prepared 2–5 M nitric acid solution at 30°C. Vigorous agitation was applied. After 2–3 min, a sponge-type surface with substantial roughness was created. The roughness of the etched metal surface was about 10–100 nm as measured by electron microscopy[19]. After etching, the metal foils were thoroughly rinsed with water and dried in air. The etched metal foils were then ready for polymer doping. As reported previously, the silver substrates prepared by the nitric acid etching method showed SERS sensitivity one order higher than those prepared by the vacuum deposit method[19-21].

Sample doping methods

Polybenzimidazole, benzotriazole, benzimidazole, an epoxy resin (Epon 828) and 3-mercaptopropyltrimethoxysilane were obtained from Aldrich and used without purification. The azole compounds were dissolved in dimethylformamide (DMF) to make solutions of concentration 0.03%. Two sample doping methods were used to apply the polymers onto metal foils. The first was 'spread-casting': the controlled amount of solution was spread uniformly onto a 2 cm^2 foil, and the solvent was evaporated slowly. In order to control the speed of solvent evaporation, the foil coated with the solution was put into a beaker surrounded with gaseous DMF. The majority of the solvent was evaporated in about 24 h. The second sampling method was 'dip-coating'. A foil was immersed into a polymer solution at 50°C for 5 min and, after withdrawal of the sample, the solvent was evaporated slowly. Film thickness was calculated based on concentration of the solution, density of the sample and area of the metal surface.

Raman spectra were recorded with a SPEX-1403 Raman spectrometer. The incident laser excitation was 647.1 nm from a Kr^+ laser source with an output of 40–100 mW. A back-scattering geometry in air was used for all samples.

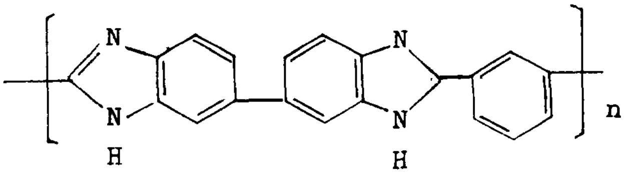
Fourier transform infra-red (FT*i.r.*) *reflection-absorption measurements*

Polymer was coated onto smooth silver foil, and the i.r. reflection-absorption spectra were recorded with a Nicolet 170SX FT-IR spectrometer at 4 cm^{-1} resolution. The reflection accessory was placed in the sample beam and the angle of incidence was 80°. The i.r. radiation was polarized parallel to the plane of incidence by the use of a gold wire grid polarizer.

RESULTS AND DISCUSSION

Measurement of chain segment adsorption and orientation of polybenzimidazole on silver

The chemical structure of the polymer used for this study is shown below. These structures seem to be SERS active on a properly roughened metal substrate.



Polybenzimidazole

The SERS spectra of polybenzimidazole (PBIMH), shown in *Figure 1a* and *b*, were recorded from samples coated on roughened silver foils by spread-casting and dip-coating methods respectively. For the purpose of comparison, the i.r. reflection-absorption spectra of PBIMH on smooth silver foils prepared by the same sampling methods are shown in *Figure 1c* and *d*. We were not able to observe the normal Raman scattering from PBIMH solid or film because of the strong fluorescence but excellent Raman spectra were recorded from the roughened silver foil by surface enhancement of the polymer–metal interface and quenching of the fluorescence, as shown in *Figure 1*. However, comparing the SERS spectra of *Figure 1a* and *b*, one finds observable differences between them. This is an important feature of the SERS phenomenon at the polymer–silver interface, since these two spectra were recorded from the same polymer solution but with different sample doping methods. Of even more interest, the sample that gave the SERS spectrum of *Figure 1a* could be converted to one that could provide a SERS spectrum similar to *Figure 1b*, after the sample prepared by the spread-casting method was heated at 130°C for 5 h. We propose that the spectral differences and their transition are due to the surface geometry change including desorption and adsorption of the polymer chains. A successful basis for analysis of SERS spectra with regard to orientation of adsorbate was worked out in the form of 'surface selection rules'[22–26]. These rules are based on the electromagnetic theory of SERS intensity, which indicates that, via resonance interaction with surface plasmons of the metal, incident light increases the electromagnetic field at the surface of small metallic particles, which in turn amplifies both the scattered intensity and the Raman excitation intensity. Since the local fields are highest normal to the surface, normal modes of the surface molecule involving changes in molecular polarizability with a component normal to the surface are subject to the greatest enhancement. This same type of analysis has been successfully applied by other authors[27,28]. The SERS spectrum of *Figure 1b* shows strong bands near 1620 and 1005 cm^{-1}, which are very weak in the SERS spectrum of *Figure 1a*, while *Figure 1a* shows a band at 510 cm^{-1}, which is almost absent in *Figure 1b*. In the Raman spectra of heterocyclic compounds, the bands near 1000 and 1620 cm^{-1} are due to in-plane ring bending and stretching respectively, and the band at 510 cm^{-1} is due to out-of-plane ring vibration[29,30]. The normal mode of out-of-plane vibration involves a changing dipole moment which is perpendicular to the plane of the molecule. In contrast, the change of dipole moment accompanying an in-plane vibration is parallel to the plane of the molecule. In the SERS spectrum of *Figure 1b*, the in-plane vibrations of the ring at 1005 and 1620 cm^{-1} are intensified, but the out-of-plane vibration at 510 cm^{-1} is absent. On the basis of surface selection rules, we propose that the rings of polybenzimidazole chain segments which interacted with the metal stand up on the surface when the polymer is applied onto silver by the dip-coating method. In the SERS spectrum of *Figure 1a*, the out-of-plane vibration of the ring at 510 cm^{-1} is enhanced, but the in-plane vibrations are very weak, indicating that the rings of the polymer chain segments which interacted with the metal are lying down

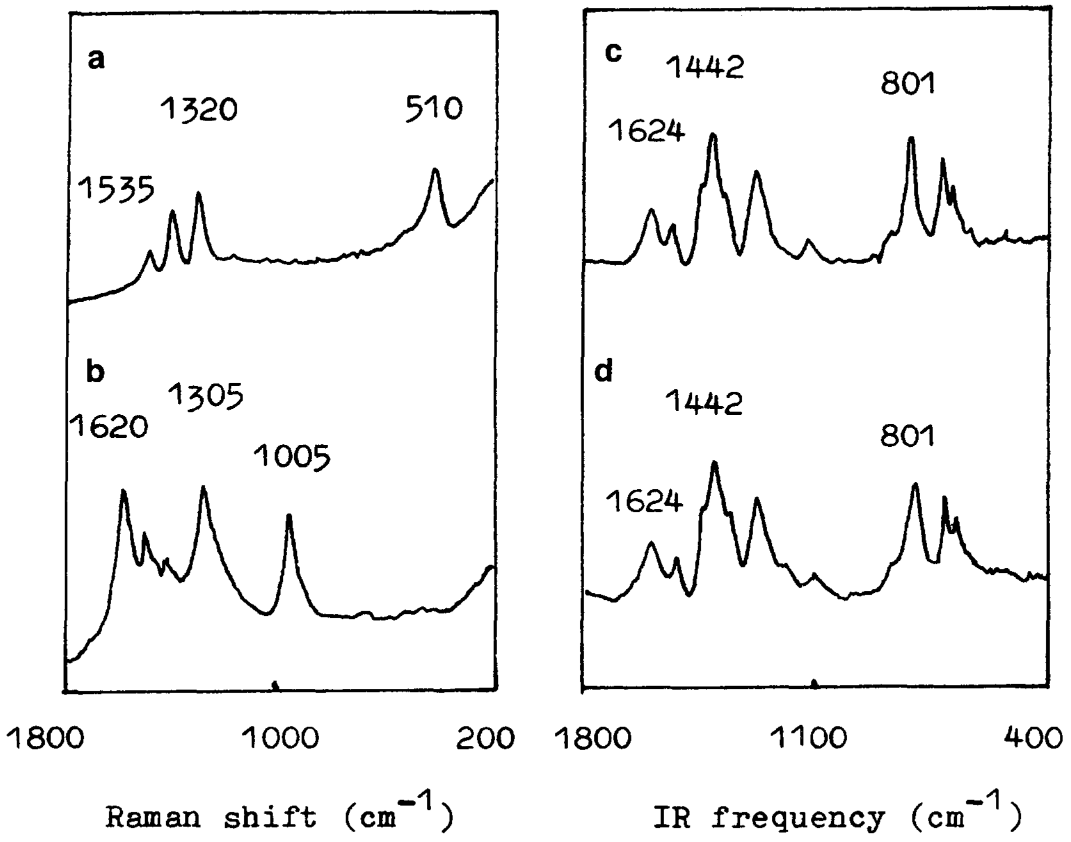


Figure 1 Spectra of polybenzimidazole on silver: (a), (b) SERS spectra of (a) spread-cast and (b) dip-coated samples; (c), (d) i.r. reflection-absorption spectra of (c) spread-cast and (d) dip-coated samples

flat on the surface. This means that, by slow evaporation of the polymer solution spread on silver foil, a flat orientation of the polymer chain segment is obtained. Upon heating, these segments stand up. The flat bonding geometry of the aromatic ring could translate to a bonding through the nitrogen lone pair (N-bonded through donation); as a result, the rings are standing up. However, the i.r. reflection-absorption spectra for the two samples prepared by spread-casting and dip-coating respectively did not show any differences related to the orientation of the bonds, as shown in *Figure 1c* and *d*. As a matter of fact, these spectra are quite similar to the transition i.r. spectrum of the polymer. Reflection-absorption i.r. can also exhibit a high degree of polarization since only the parallel component has surface absorption. Much evidence is presented in the literature showing such anisotropy. Since the thickness of the polymer film was about 600 ± 50 Å in this study, the i.r. spectra provide information mainly about the bulk film with little knowledge of the interfacial region. There is little difference between *Figure 1c* and *d* while remarkable changes can be observed between *Figure 1a* and *b*, indicating that there is no evidence of segmental or molecular orientation in the bulk material, except at the interfacial region. This clearly indicates that the SERS is an excellent technique to give insight into structural information about the adsorption state of the polymer chain adjacent to the metal.

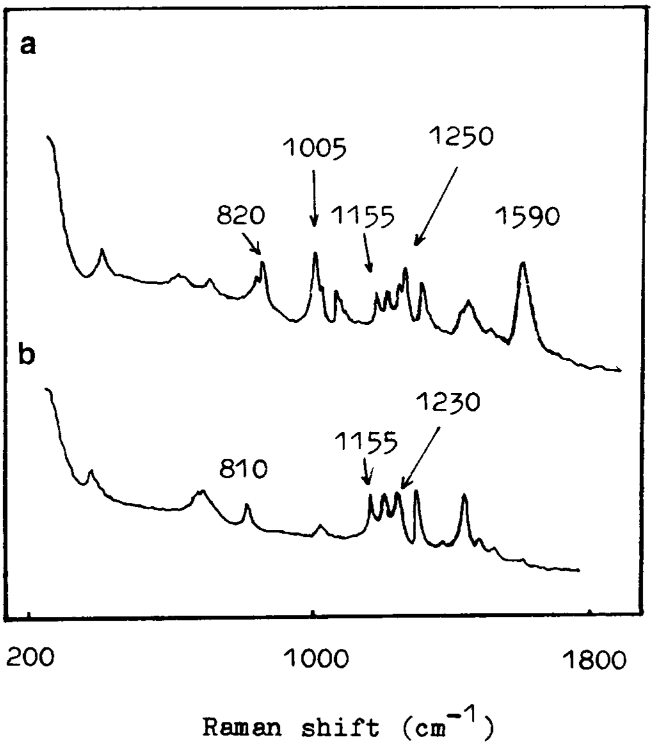


Figure 2 SERS study of silane coupling agent at the interface: (a) SERS spectrum of an epoxy resin cured on top of silane; (b) SERS spectrum of the silane adsorbed on the surface of silver

Observation of coupling agents at the interface of a polymer–metal composite

Silane coupling agents are well known adhesion promoters for epoxy resins with various substrates. I.r. reflection-absorption and diffuse reflection techniques have been widely used to identify the coupling agents on the surfaces of metals or glasses[31]. In this section, we demonstrate that SERS is a highly sensitive method to identify the coupling agent monolayer at the polymer–metal interface. The sampling procedure is as follows. The SERS substrate of silver foil was initially immersed into a hydrolysed coupling agent solution in DMF (concentration 0.001 M) for 3 min. As reported by Garoff *et al.*[32], this method resulted in rather uniform coverage of the adsorbates on metal foil controlled by the concentration of the adsorbates in solution. After withdrawal, the excess liquid was blown off with nitrogen and the solvent was evaporated slowly under the conditions described above. It was found that a saturated surface was attained with a doping solution concentration of 0.001 M. Accordingly, our doping solution was kept at this concentration. This method appeared to provide good SERS spectra for adsorbates that could be dissolved in volatile solvents. After a SERS spectrum was recorded from the metal adsorbed with monolayer 3-mercaptopropyltrimethoxy silane, the foil was immersed into an epoxy resin (Epon 828) at 100°C for 1 h. After withdrawal, the physisorbed materials were washed with acetone, and the surface was examined again by Raman spectroscopy. The thickness of the coating was about 1000–1200 Å. *Figure 2b* shows the SERS spectrum of the silane coupling agent adsorbed on silver foil. The Raman lines between 1155 and 1230 cm^{-1} were attributed to Si–O–Si stretching modes of the hydrolysed silane. The curing of an epoxy resin on top of the adsorbed silane is evident from *Figure 2a*. The new bands in the SERS spectrum at 1005 and 1590 cm^{-1} are due to the vibrational modes of the aromatic ring of the epoxy resin, while the band at 1250 cm^{-1} was attributed to the C–O–C stretching mode. Another characteristic Raman line of the cured epoxy resin is located at 820 cm^{-1}, which can be assigned to the out-of-plane deformation. Recently, chemisorbed benzotriazole on metal was found to be able to increase the adhesion of polymer to metal[33]. *Figure 3* shows its SERS spectra on silver and the cured epoxy resin. The ring stretching mode at 1390 cm^{-1} and the ring deformation mode at 790 cm^{-1} are the characteristic Raman lines of the chemisorbed benzotriazole[34], while the Raman lines at 1595, 1250, 1005 and 820 cm^{-1} are evidence for the cured epoxy resin.

For the purposes of comparison, i.r. reflection-absorption spectroscopy was applied to examine epoxy coatings on metal foils. Smooth silver foils were pretreated with the silane and benzotriazole, respectively, and cured with the epoxy resin. The thickness of the coating was controlled to be similar to the samples for SERS studies in *Figures 2* and *3*. I.r. spectra in *Figure 4a* and *b* were recorded from the cured epoxy resin initiated by silane and benzotriazole respectively, and the physisorbed material was washed away with acetone. The two i.r. spectra are essentially identical. The bands at 1605, 1250 and 815 cm^{-1} are the characteristic vibration modes of the epoxy resin. No significant i.r. bands could be observed in *Figure 4c*, which was recorded from a silver foil treated by a similar method as the samples for *Figure 4a* and *b* but without any pretreatment with coupling agents. We propose that little epoxy resin was chemisorbed on the neat silver foil. Although i.r. spectra indicate that the epoxy resin was cured on the surfaces of metal adsorbed with silane or benzotriazole, few characteristic bands of these coupling agents could be observed in *Figure 4a* and *b*. I.r. mainly provides information from the bulk of coating when it is much thicker than the

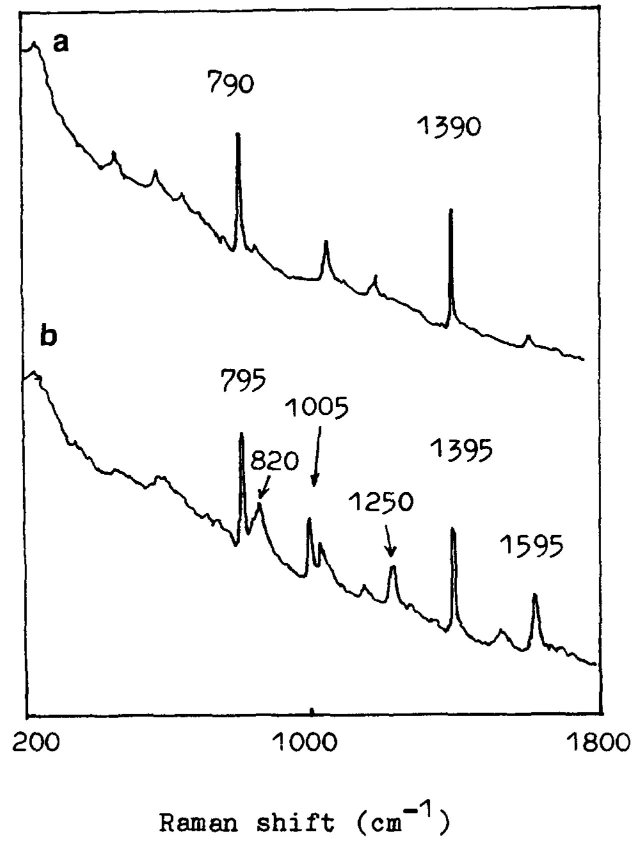


Figure 3 SERS study of benzotriazole at the interface of epoxy resin and metal. (a) SERS spectrum of benzotriazole adsorbed on silver; (b) SERS spectrum of an epoxy resin cured on top of the chemisorbed benzotriazole

interfacial region. However, *Figures 2a* and *3b* indicate clearly the Raman bands of silane and benzotriazole as well as the cured epoxy resin. Since SERS mainly enhanced the first monolayer or first few layers near the metal surface, it becomes highly informative in that the anthetic adsorption state and the microstructure of the interface can be revealed without interference from the bulk film.

Observation of oxidation of copper under the polymer film overlayer

The air oxidation of naked copper and of copper covered with polymeric films can be monitored with SERS. The spectra in *Figure 5a* are from copper foil which was washed with distilled water after etching. On exposure to air, broad bands centred around 590 and 520 cm^{-1} gradually appeared, which were due to the symmetric and asymmetric vibrations of copper(I) oxide. The limiting oxide thickness was reached in about 2 h. This is in agreement with the isotherms found by Rhodin[35] using a vacuum microbalance at 323 K. The oxide thickness after 2 h is approximately seven monolayers[36,37]. Benzimidazole is reported to react with the copper surface forming a polymeric film which is supposed to prevent the surface from further oxidation[38]. No observable signals in the region of 630–400 cm^{-1} can be detected in the spectra of benzimidazole-treated copper after 1–4 h exposure at room temperature, as shown in *Figure 5b*. There, the onset and intensity of the oxide band were monitored as a measure of the surface oxidation of copper substrates with films of either polybenzimidazole or benzimidazole cast onto the surface; emphasis will be placed only in this vibrational frequency

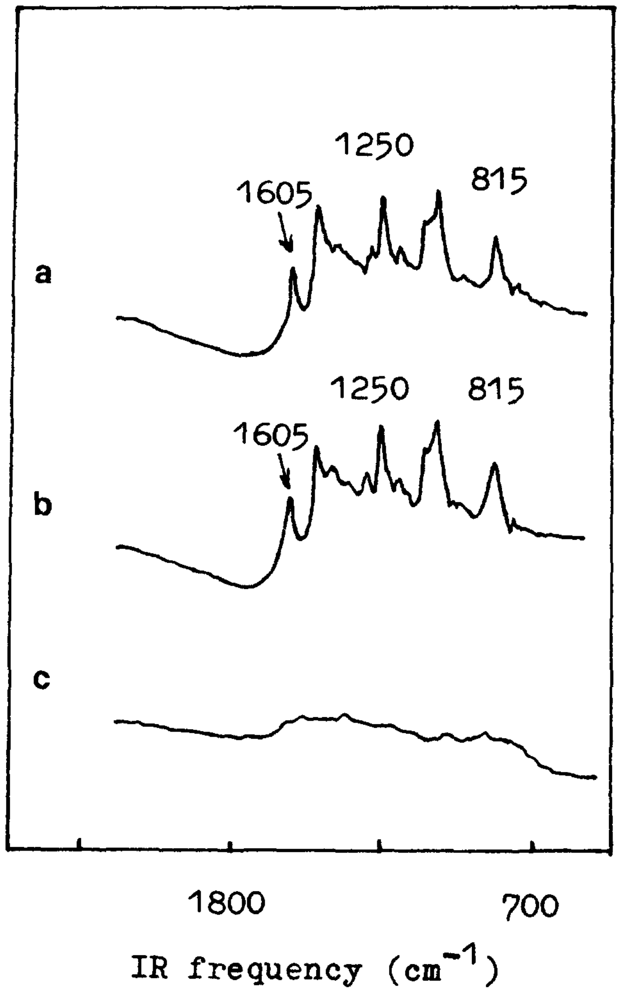


Figure 4 I.r. reflection-absorption study of epoxy resin cured on metal: (a) epoxy resin cured on top of silane adsorbed on silver; (b) epoxy resin cured on top of benzotriazole adsorbed on silver; (c) epoxy resin cured on neat surface of silver foil

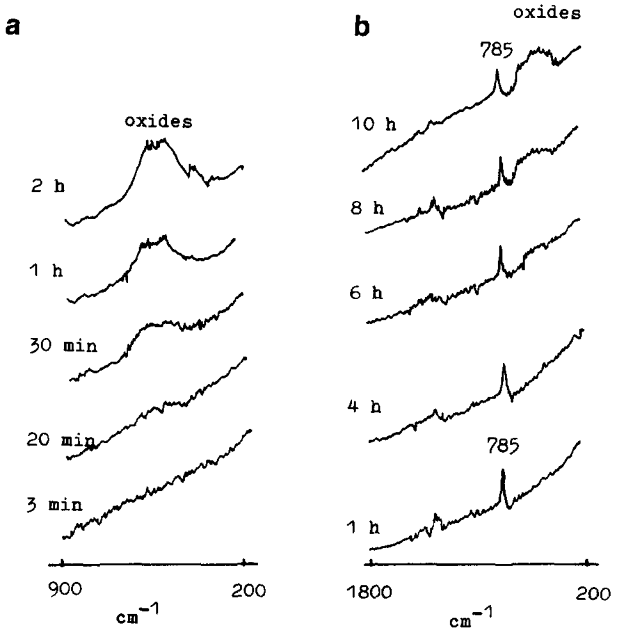


Figure 5 (a) SERS spectra of a chemically etched copper foil after exposure in air for various times; (b) SERS spectra of copper foil treated with benzimidazole for various exposure times (shown adjacent to each spectrum)

region in the following discussion. SERS studies show that benzimidazole can prevent surface oxidation of copper for only a few hours. At 200°C, the *in situ* SERS spectra in *Figure 6a* show that copper oxidizes quickly. This prompts us to use polymer to overcome this weakness so long as it does not degrade under the applied temperature. Polybenzimidazole is well known for its heat resistance. However, the appearance of oxide bands in SERS spectra recorded from the copper surface covered with polybenzimidazole implies that this polymer does not possess substantial resistance to oxygen permeation, as illustrated by the initial spectrum (0 h heating) in *Figure 6b*. It is commonly held that oxygen permeability decreases by decreasing the chain mobility, e.g. by crosslinking, by decreasing the hydrophilic character of the macromolecules, and by increasing the density of molecular packing up to crystalline structure. Rigid as the polybenzimidazole chain is, it cannot suppress oxidation even at room temperature. This may be due to the fact that there are pinholes on the metal surface that are not covered by the polymer. Upon heating to 200°C for 10 h, the oxide band intensity became more prominent as shown in *Figure 6b*, indicating the acceleration of surface oxidation. It is noticeable that the SERS effect remains so strong at this temperature that Raman signals originated from adsorbed polybenzimidazole are still of high quality. Preliminary work on nitric acid-etched silver foils showed that this kind of SERS-active substrate possesses satisfactory thermal stability at relatively high temperatures; SERS on nitric acid-etched metal foils seems to be a very promising technique for mechanistic studies of the reactions. *Figure 7* illustrates *in situ* SERS spectra of polybenzimidazole and benzimidazole co-adsorbed from a solution of their mixture. Oxide film formation did not occur even when the treated copper had been heated to 200°C for 10 h. This property is very important since copper surfaces treated with either polybenzimidazole or benzimidazole alone oxidized in a few minutes at 200°C, as illustrated in *Figure 6*. We therefore conclude that the surface loci left by polybenzimidazole have been filled with benzimidazole. This corrosion-inhibition effect on copper surface co-adsorbed with polybenzimidazole and benzimidazole is synergistic and may be explained by the physicochemical mechanism of corrosion protection by organic coatings[39]. The physicochemical mechanism consists in blocking diffusion of corrosive agents, such as water and oxygen, and of corrosion stimulants. This barrier action of organic coatings may be enhanced significantly by fillers, pigments or extenders which greatly increase the length of diffusional pathways through the cross-section of the coating films. We have now confirmed that benzimidazole is prone to react with metallic copper under mild conditions[40]; the surface reaction product copper(I) benzimidazolate fills up the pinholes left by polybenzimidazole, and by acting as a barrier greatly retards oxidation. This point was confirmed by a prolonged heating test in which oxide bands were ultimately observable after heating at 200°C for 125 h, as shown in *Figure 7*.

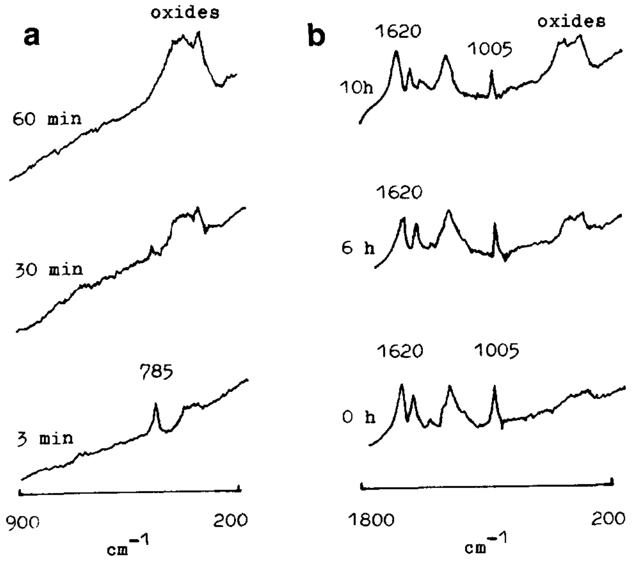


Figure 6 *In situ* SERS spectra of copper foil at 200°C in air. (a) The foil was pretreated with benzimidazole; (b) the foil was pretreated with polybenzimidazole. The heating time is shown beside each spectrum

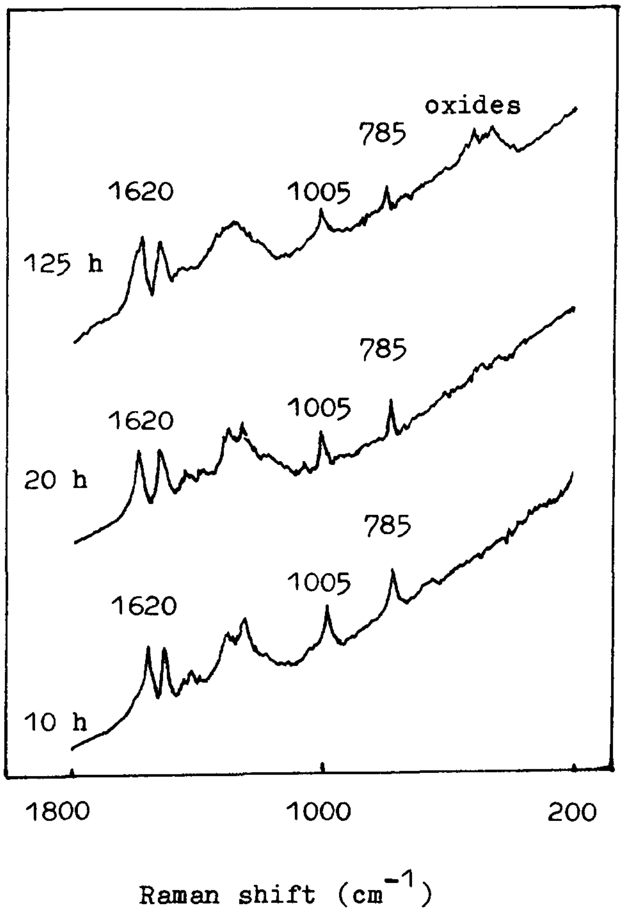


Figure 7 *In situ* SERS spectra of copper foil after heating at 200°C for various times. This foil had been pretreated with polybenzimidazole and benzimidazole. The heating time is shown beside each spectrum

CONCLUSION

We believe that the present results provide a novel and potentially important demonstration of the use of metal substrates as a means of generating observable and intense SERS spectra for polymer–metal interfacial studies. Polymer species adsorbed at the actual interface show critical orientation, adsorption and desorption, catalysis and oxidation which cannot be revealed by *FT*i.r. reflection-absorption spectroscopy or unenhanced Raman scattering under the same conditions. We therefore anticipate that the principles outlined here might be applied to the studies of physical chemistry at the interface of polymer–metal systems.

ACKNOWLEDGEMENTS

The authors are indebted to the Chinese University Funds for Doctoral Studies and the Analytical Center of Nanjing University and the National Science Foundation of China.

REFERENCES

1 Ishida, H. (ed.) 'Controlled Interphase in Composite Materials', Elsevier, New York, 1990
2 Pertsin, A. J. and Pashunin, Yu. M. *Appl. Surf. Sci.* 1990, **44**, 171
3 Palmberg, P. W. and Rhodin, T. N. *J. Appl. Phys.* 1968, **39**, 2425
4 Koenig, J. L. 'Spectroscopy of Polymers', American Chemical Society, Washington, DC, 1992
5 Jolley, J. G., Geesey, G. G., Hankins, M. R., Wright, R. B. and Wichlacz, P. L. *Appl. Spectrosc.* 1989, **43**, 1062
6 Dowrey, A. E. and Marcott, C. *Appl. Spectrosc.* 1982, **36**, 414
7 Xue, G., Liu, S., Jin, Y. and Jiang, S. *Appl. Spectrosc.* 1987, **41**, 1172
8 Fleischman, M., Hendra, P. J. and McQuillan, A. *J. Chem. Phys. Lett.* 1974, **26**, 163
9 Jeanmaire, D. J. and Van Duyne, R. P. *J. Electroanal. Chem.* 1977, **84**, 1
10 Albrecht, M. G. and Creighton, J. A. *J. Am. Chem. Soc.* 1977, **99**, 5215
11 Chang, R. and Furtak, F. (eds) 'Surface Enhanced Raman Scattering', Plenum Press, New York, 1982
12 Boerio, F. J. *Thin Solid Films* 1989, **181**, 423
13 Heart, S. M., Grieser, F. and Barraclough, C. G. *Chem. Phys. Lett.* 1983, **95**, 154
14 Lee, P. C. and Meisel, D. *Chem. Phys. Lett.* 1983, **99**, 262
15 Barnickel, P. and Wokaun, A. *Mol. Phys.* 1989, **67**, 1355
16 Tashiro, K., Matsushima, K. and Kobayashi, M. *J. Phys. Chem.* 1990, **94**, 3197
17 Boerio, F. J., Tsai, W. H. and Montaudo, G. *J. Polym. Sci. B: Polym. Phys.* 1989, **27**, 1017
18 Venkatachalam, R. S., Boerio, F. J., Roth, P. S. and Tsai, W. H. *J. Polym. Sci. B: Polym. Phys.* 1988, **26**, 2447
19 Xue, G., Ding, J. and Zhang, M. *Chin. Sci. Bull.* 1991, **36**, 194
20 Carron, K. T., Xue, G. and Lewis, M. L. *Langmuir* 1991, **7**, 2
21 Xue, G. and Dong, J. *Anal. Chem.* 1991, **63**(20), 2393
22 Moskovits, M. and Suh, J. S. *J. Am. Chem. Soc.* 1985, **107**, 6826
23 Moskovits, M., Dilella, D. P. and Maynard, K. J. *Langmuir* 1988, **4**, 67
24 Creighton, J. A. *Surf. Sci.* 1983, **124**, 209
25 Moskovits, M. and Suh, J. S. *J. Phys. Chem.* 1984, **88**, 22
26 Moskovits, M. and Suh, J. S. *J. Phys. Chem.* 1984, **88**, 1293
27 Muniz-Miranda, M., Neto, N. and Sbrana, G. *J. Phys. Chem.* 1988, **92**, 954
28 Ni, F. and Cotton, T. M. *J. Raman Spectrosc.* 1988, **19**, 429
29 Dollish, F. R., Fateley, W. G. and Bently, F. F. 'Characteristic Raman Frequencies of Organic Compounds', John Wiley, New York, 1973, Ch. 8
30 Green, J. H. S. and Barnard, P. W. B. *J. Chem. Soc.* 1963, 640
31 Pluddemann, E. P. 'Silane Coupling Agents', Plenum, New York, 1982
32 Garoff, S., Stephens, R. B., Hanson, C. D. and Sorenson, G. K. *Opt. Commun.* 1982, **41**, 257
33 Xue, G., Wu, P., Dai, Q. and Chen, R. *Angew. Makromol. Chem.* 1991, **188**, 51
34 Xue, G., Ding, J., Lu, P. and Dong, J. *J. Phys. Chem.* 1991, **95**, 7380
35 Rhodin, T. N. *J. Am. Chem. Soc.* 1950, **72**, 5102
36 Tompkins, H., Sharama, S. P. and Pasteur, G. *Surf. Interf. Anal.* 1983, **5**, 101
37 Tompkins, H. and Sharma, S. P. *Surf. Interf. Anal.* 1982, **4**, 261
38 Sundberg, R. J. and Martin, R. B. *Chem. Rev.* 1974, **74**, 471
39 Funke, W. 'Polymeric Materials for Corrosion Control' (Eds R. A. Dichie and F. L. Floyd), ACS Symposium Ser. 322, ACS, Washington, DC, 1986, p. 222
40 Xue, G., Zhang, J., Shi, G. and Wu, P. *J. Chem. Soc. Perkin Trans. II* 1989, 33