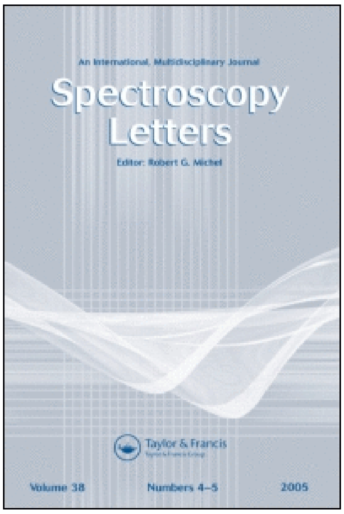

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The FT-Raman Study of Reaction of 4-Aminophenyl Disulfide and Epoxy on Silver Surface

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THE FT-RAMAN STUDY OF REACTION OF 4-AMINOPHENYL DISULFIDE AND EPOXY ON SILVER SURFACE

Key Words: Self-assembling films, Epoxy-silver interphase, 4-aminophenyl disulfide (APDS), Fourier transform Raman spectroscopy, Surface-Enhanced Raman Scattering spectroscopy

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ABSTRACT

4-Aminophenyl disulfide (APDS) can cleave and be chemisorbed on etched silver foil to form an assembled film. The film can serve as coupling agent to form

an interphase between silver and epoxy bulk. The coupling action and mechanism of APDS between silver and epoxy polymer were characterized by Fourier transform surface-enhanced Raman scattering spectroscopy.

INTRODUCTION

During the past years, most of our attentions were devoted to the studies of the fundamental mechanisms of adhesion in order to establish quantitative relationships between the intrinsic properties of the solids in contact, the properties of the interface and the final performance of multiple component materials such as adhesive joints, coatings and paints. As the orientation and restructuring of polymers involves chemical, physicochemical and physical mechanism, it was difficult to understand them thoroughly. The formation of well-defined organic surface phases by the immersion of a clean gold substrate in a solution of a long chain w-substituted dialkyldisulfide was first reported in 1983[1]. Recently the spontaneous self-assembly of organic sulfide at Au, Ag and Cu surfaces have been studied and some study results suggest that self-assembled monolayer films are densely packed in a crystalline arrangement[2-4]. The self-assembled films formed through spontaneous interfacial adsorption from solution endow the metal surface with special properties.

J.Shultz found that the adhesive strength of a polyethylene (PE)/aluminum (Al) is very low. When PE was replaced with a 1% by weight acrylic acid grafted PE, the adhesive strength increases. However, unexpectedly the surface properties of both polymers are identical. They thought that polymers exhibited different surface energy when in contact with different medium. It was only when in contact with the polar aluminum that the carboxylic groups of the grafted polymer would orient themselves towards the metal to form strong bonds.[5] In other words, when polymer contacts with different substances, it will adjust its segments to them and does the best to resemble their properties to that of substances. This is also identical with the soft-hard acid-base theory. If we prepare well-ordered monolayer film formed by the adsorption of disulfide with an active terminal functional group such as OH and NH_2 from the solution onto the surface of above metals, and then the end group of the disulfide can react with some polymer. They can present a coupling action between metal and polymer and form an interphase resulting from the orientation and restructuring of polymers at the interfaces whose properties are different from the bulk polymer. The interface makes it possible to promote the adhesion strength.

SERS is a new developed nondestructive instrument to probe the interphase between various adsorbates and metallic surface. Boerio pointed out that SERS is good for the study of polymer-silver island interfaces since it enhances almost exclusively the first monolayer of molecules adjacent to the metal. 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[6]. They used SERS to characterize the interface between an silver island film and pyromellitic diimide

(PMDI). PMDI is adsorbed or chemisorbed end-on in a vertical conformation with one imide group adjacent to the surface. There are two kinds adsorption. One is chemisorption on the metal surface, the other is random adsorption away from the surface. Yong, J.T. et al determined the molecular structure of interphase formed by curing an epoxy/4,4'-diaminodiphenysulfone (DADPS) adhesive against rough silver substrates using SERS and X-ray photoelectron spectroscopy (XPS). Their studies showed that DADPS was adsorbed through one of the NH_2 groups with an end-on conformation and there is a thin DADPS-rich interphase between the bulk adhesive and the silver substrate, and that the locus of failure was partially within this layer[7].

HNO_3 etched silver and copper foils for Raman measurement were reported by our and other laboratories[8-10]. The new sampling technique exhibits a strong SERS sensitivity for surface adsorbates and better thermal stability. In the present study, the curing reactions of an epoxy compound is investigated on the top of chemisorbed APDS on freshed foils.

EXPERIMENTAL

Preparation of metal substrates

Silver foils of 0.025 mm thickness purchased from Aldrich Co. were immersed into 5-6M HNO_3 solution at room temperature. After several seconds, a number of tiny bubbles were formed near the surface of silver. A milky and sponge-type surface with substantial roughness was created a few minutes latter. The roughness of etched metal surface was about 10-100nm as measured by electron microscopy[11].

The etched silver foils were thoroughly rinsed with water and dried in air and were ready for APDS and polymer sampling.

Sampling methods of APDS and polymer

APDS was dissolved in ethanol to made a 0.001M solution. The etched silver substrates were dipped into the solution at room temperature for several minutes. After withdrawing, the exceed liquid was blown off with nitrogen and the samples were dried in air. The pretreated samples were ready for polymer sampling or SERS measurement.

Epoxy resin (bisphenenol A) was dissolved in acetone at the weight concentration of 0.5%. The etched samples and pretreated samples were dipped in it for five minutes and then dried in air. Above samples were cured at 110°C for one hour or at room temperature for 24 hours.

Surface-Enhanced Raman Scattering spectroscopy

The SERS spectra were measured on a Bruker model RFS 100 Fourier Raman spectrometer. A Ge-detector operated at liquid nitrogen temperature was used. The incident laser excitation was 1064nm from an air-cooled diode pumped Nd-YAG laser source with an output of 50 mw. The spectral resolution was 4.0 cm^{-1}.

RESULTS AND DISCUSSION

The APDS molecules are short stiff chains with active group. It can be chemisorbed on fresh etched silver. Fig.1 represents A: the Raman spectrum of neat

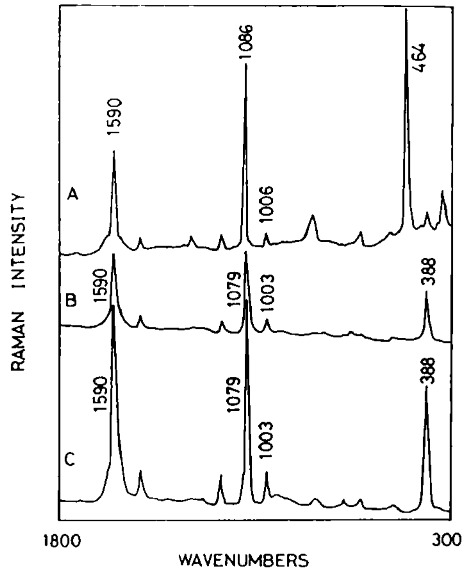

Fig. 1 The spectrum of A: the Raman spectrum of neat APDS and B: the SERS spectrum APDS on etched silver foil

solid APDS, and B: the SERS spectrum of APDS adsorbed on silver, C: the spectrum of the same sample as B after heating at 110°C for 1h. The bands at 1590 cm^{-1} in A, B and C were all assigned to benzene ring vibration. The phenylene-S stretching vibration bands and the ring vibration appeared at 1086, 1079, 1079 cm^{-1} and 1006,1003 1003 cm^{-1} in A,B and C respectively. In spectrum A, the strongest peaks at 464 cm^{-1} was attributed to the S-S stretching vibration. In spectrum B and C, this band disappeared, and there were new strong peaks at 388 cm^{-1}. This was the most informative. They meant the disappearance of S-S bond and indicated that the S-S bond cleaved and binded to the surface to form Ag-S bonds[12]. According to the "surface selection rules" by Moskovits et al and others[13-16], only the bands of bond perpendicular to the surface were enhanced, we can confirm the cleavage of S-S bond and the formation of silver amonibenzenethiolate. The H_2N-C_6H_4-S- was chemisobed perpendicularly to the surface on end with well-organized structure as shown in Fig.2.The resemblance of Fig.1C and Fig.1B indicated that the monolayer was stable at 110°C in air. Although defects in these structures would be expected because of the complex surface morphology of the silver surface including crystallographic faceting and surface roughness and so on, the surface was saturated and covered with -NH_2 groups. This presented a great deal of active points which could react with epoxy groups resulting in a continuous interphase of Ag-S-C_6H_4-epoxy. Fig.3 showed the SERS spectra of differently treated silver surface. Fig.3.A is the spectrum of neat epoxy. There is not any peak in A, this shows that no chemisorption occurs between epoxy and silver, or it's likely that epoxy was physisorbed on the silver surface. As SERS enhances almost exclusively the first monolayer of molecules adjacent to the surface, in other words, SERS disclosed the short-range condition near the metal surface, not the polymer bulk condition. Some of peaks in pure epoxy resin spectrum shown in Fig.4 didn't appear in its SERS spectrum. Spectrum B, which is almost the same as spectrum Fig.1 B, is that of epoxy adsorbed on APDS film on etched silver after curing at room temperature for 24 hours. In this case we thought that the adsorption of epoxy on the pretreated silver is random from the solution and the epoxy heaped on the surface without any orientation. As the aromatic amine is chemically nonactive to epoxy group at room

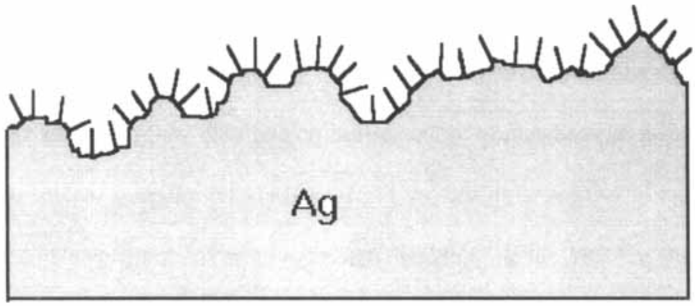

Fig. 2 The sketch diagram of self-assembled film of APDS on etched silver foil

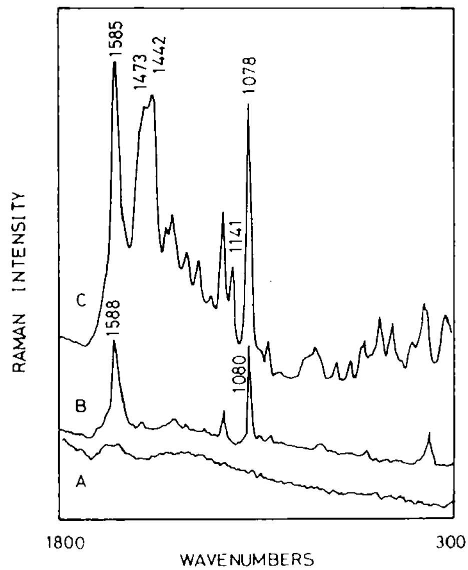

Fig.3 The Surface Enhanced Raman Spectra on etched silver foils of: A: epoxy; B: epoxy on APDS self-assembled film after curing at room temperature for 24 hours; C: epoxy on APDS self-assembled film after curing at 110°C for an hour

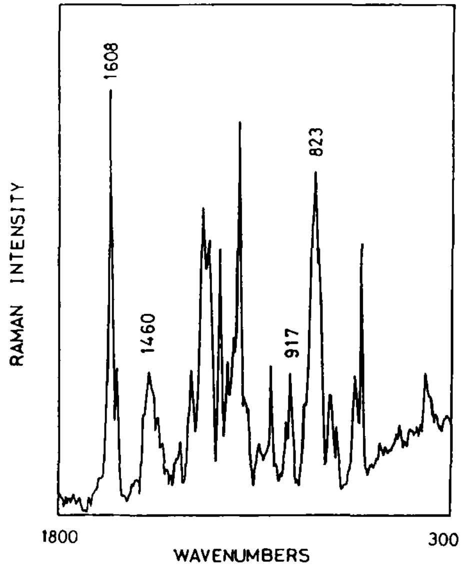

Fig. 4 The Raman spectrum of neat epoxy

temperature, epoxy compound only covered physically the $-NH_2$ groups on the surface as shown in Fig.5. Spectrum C is the that of epoxy on silver surface pretreated with APDS after curing at 110°C for 1h. By comparing B and C, we found there are several new peaks in C. The 1473 cm^{-1} peak corresponds to $O-CH_2$ deformation. The band at 1442 cm^{-1} was assigned to CH_3 deformation vibration. The peak at 1141 cm^{-1} was caused by the C-C stretching vibration. No effort was made to assign the remaining weak bands. Above typical peaks confirmed the reaction of epoxy group with $-NH_2$ at high temperature and APDS' coupling action (see the sketch diagram of coupling action in Fig.6). Epoxy resin, whose epoxide number was 0.51, was a prepolymer of large size with sporadic epoxy groups.

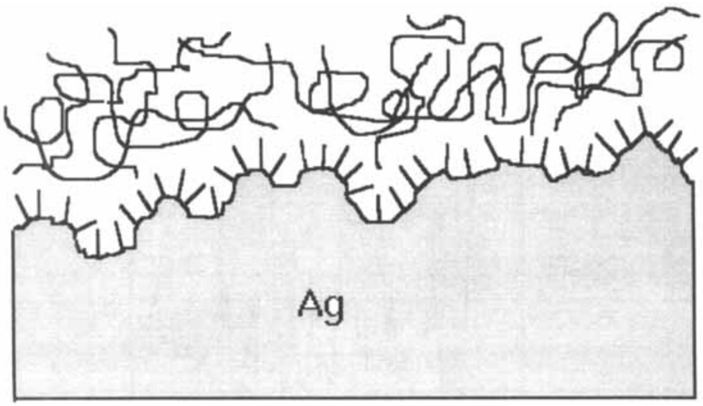

Fig. 5 The sketch diagram of epoxy compound on the APDS self-assembled film on etched silver foil

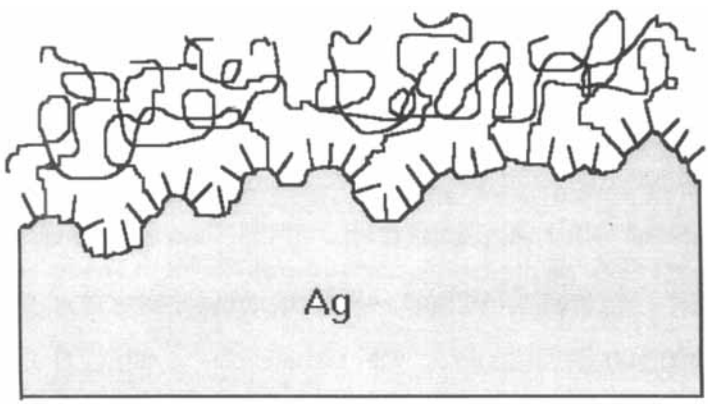

Fig. 6 The sketch diagram of reaction of epoxy with APDS attached to etched silver foil

Because of the epoxy group quantity and the movement difficulty in bulk, only a little amount of -NH_2 groups reacted with them. This might indicate that there was insufficient epoxy groups available to occupy all the SERS-active surface sites of NH_2 groups so that there was strong APDS peaks in spectrum B. The spectrum of epoxy cured with ethylene diamine at room temperature, it resembles Fig.3 A(not shown). The aliphatic amnie, such as ethylenediamine, is more active to epoxy than aromatic amine. It is ready to react with epoxy at room temperature and forms a net structure. When the silver coils were dipped in the solution of ethylenediamine and epoxy, a simple physical adsorption occurred. The samples of epoxy-APDS-Ag cured with ethylenediamine were the same as spectrum Fig.3 B. (not shown). Therefore there is not any new signals in its spectrum except that of APDS. Structurally, the reaction between epoxy and aromatic amine established a continuous interphase between silver and epoxy bulk. The sample of spectrum Fig.3 A was also heated at 110°C for an hour, there was not any change. This also confirmed above reaction.

CONCLUSION

SERS spectra obtained from APDS showed that S-S bond can cleave and form 4-aminopheylthiolate when it reacted with fresh etched silver foils. This led to the formation of active self-assembled film of above salt. The SERS spectra of epoxy/APDS/silver indicated that the 4-aminopheylthiolate served as a coupling agent and the surface NH_2 groups reacted with epoxy, resulting in a continues interphase between silver and epoxy bulk.

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