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Surface-Enhanced Raman Scattering From Model Acrylic Adhesive Systems

by

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From Model Acrylic Adhesive Systems

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ABSTRACT

Surface-enhanced Raman scattering (SERS) has been observed from a model acrylic adhesive deposited onto silver island films. SERS spectra of the adhesive system were very similar to SERS spectra of o-benzoic sulphimide (saccharin), a component of the curing system of the adhesive, and to normal Raman spectra of the sodium salt of saccharin. When saccharin was replaced in the curing system by benzoic acid, SERS spectra of the adhesive were similar to SERS spectra of benzoic acid and to normal Raman spectra of of benzoic acid salts. The intensity of the SERS spectra was independent of the thickness of the adhesive films, indicating that the observed Raman signal was characteristic of the interface and not of the bulk of the films. These results demonstrate that saccharin and benzoic acid were preferentially adsorbed at the silver surface to form metal salts and that surface-enhanced Raman scattering can be used for non-destructive characterization of interphases between polymer films and SERS-active metal substrates as long as the films are not so thick that normal Raman scattering from the bulk is comparable in intensity to the SERS from the interphase.

I. Introduction

Surface-enhanced Raman scattering (SERS) is a phenomenon in which the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of certain metals is enhanced by as much as 10^6 compared to the cross section for normal Raman scattering. Although many theories of SERS have been reported, it now appears that two mechanisms are responsible for most of the enhancement. One is associated with the large electric fields that can exist at the surfaces of metal particles with small radii of curvature and is only obtained for metals for which the complex part of the dielectric constant is small (1). The other mechanism is related to distortions of the polarizability of the adsorbed molecules by formation of charge-transfer complexes with the metal surface (1). Enhancement due to the charge-transfer mechanism is restricted to the molecules immediately adjacent to the substrate but enhancement due to electromagnetic mechanisms may extend a few tens of angstroms from the metal surface.

Since the enhancement in SERS is very large but restricted to the first few molecular layers adjacent to the substrate, we considered that SERS would be an extremely effective technique for non-destructive determination of the molecular structure of interphases between polymer systems and metals. We investigated SERS from thin films of poly (α-methylstyrene) spin coated onto silver island films from dilute solutions and found that the intensity of the spectra remained approximately constant when the thickness of the films was varied by an order of magnitude, from approximately 100 A to 1000 A (2).

These results demonstrated that SERS from the polymer films was an interfacial rather than bulk effect (2). The normal Raman scattering by the bulk of the polymer film was so weak it was not observed as long as the film was thinner than approximately a thousand angstroms. What was observed was the strongly enhanced scattering by the molecules adjacent to the silver surface.

We also investigated SERS from polymer bilayers deposited on silver island films (3). Samples were prepared by spin-coating thin films (approximately 100 A) of polymers such as polystyrene, poly (α-methylstyrene), poly (4-vinylpyridine), and diglycidyl ether of bisphenol-A onto silver substrates and then overcoating them with much thicker films of a second polymer such as poly (4-styrene sulfonate). The results obtained confirmed that SERS could be used for non-destructive characterization of interphases. Raman scattering was observed from both polymers as long as the thickness of the film adjacent to the silver was less than about 100 A in thickness. However, Raman scattering was observed from the polymer adjacent to the silver but not from poly (4-styrene sulfonate) when the thickness of the film adjacent to the substrate was more than about 100 A in thickness.

We are particularly interested in using SERS for non-destructive characterization of interphases formed by anaerobic acrylic adhesives. These adhesives, which are used as thread locking and gasketing compounds, consist of an acrylic monomer and a cure system containing several components. Polymerization of the monomer proceeds by a redox mechanism at ambient temperatures but little is known regarding the mechanisms by which some metals and some components of the cure system accelerate the reaction. Similarly, it is not known how the extent of polymerization varies as a function of distance away from the substrate surface and into the adhesive.

A few investigations of the polymerization of anaerobic acrylic adhesives in solution have been reported. Okamoto (4) investigated the solution polymerization of a model anaerobic adhesive consisting of methyl methacrylate (MMA) monomer with the cure system N,N dimethyl-p-toluidene (DMPT), o-benzoic sulfimide (BS), and cumene hydroperoxide (CHP). He found that the rate of polymerization was given by

$$R_p = [MMA]^{3.3}\ [BS]^{0.36}\ [DMPT]^{0.34}\ [[CHP]^{0}$$

Since only trace amounts of the peroxide CHP were needed to catalyze the reaction, Okamoto speculated that the oxidizing agent in this system was most likely a trace of molecular oxygen and/or hydrogen peroxide. The reducing agent appeared to be a charge transfer complex between BS and DMPT.

Kothandaraman and Arumugasamy (5) reported that a charge-transfer complex formed between N,N-dimethylaniline and p-toluene sulphonyl chloride was a redox initiator for polymerization of methyl methacrylate in acetonitrile at 50°C. It was suggested that polymerization was initiated by N-methylanilinomethyl radicals formed by decomposition of the complex. Neither N,N-dimethylaniline nor p-toluene sulphonyl chloride acted as an initiator when used separately.

Parravano (6) investigated the effect of palladium black on polymerization of several monomers by hydrazine sulfate. Rapid polymerization was observed for methyl methacrylate but not for acrylonitrile or methacrylonitrile. It was suggested that polymerization of methyl methacrylate monomer was induced by the catalytic decomposition of hydrazine sulfate at the surface of palladium black. Acrylonitrile and methacrylonitrile acted as poisons to the catalytic decomposition of hydrazine and were not polymerized under similar conditions. Even though polymerization was initiated by decomposition of hydrazine at the surface of palladium black, the reaction would continue if the palladium was isolated from the liquid, indicating that reactions could be initiated at catalyst surfaces and projected into the surrounding medium for propagation.

Very little information is available regarding the molecular structure of interphases formed between anaerobic acrylic adhesives and metal substrates. However, Clark (7) used reflection-absorption infrared spectroscopy (RAIR) and x-ray photoelectron spectroscopy (XPS) to characterize the failure surfaces of lap joints prepared using acrylic adhesives and steel and galvanized steel adherends and showed that acidic components of the adhesives segregate to the interface and form salts.

The primary purpose of this paper is to describe results that we have obtained using SERS as a non-destructive technique to determine the structure of the interphase between a model anaerobic acrylic adhesive and silver substrates. SERS spectra of o-benzoic sulfimide (saccharin), a component of the adhesive system, are reported for the first time and band assignments are discussed. Band assignments in SERS spectra of benzoic acid, which was used in place of saccharin in some formulations of the adhesive, are also reviewed.

II. Experimental

The acrylic adhesive was a model consisting of the monomer triethyleneglycol dimethacrylate (TRIEGMA), cumene hydroperoxide, o-benzoic sulfimide (saccharin), and acetylphenylhydrazine. However, several experiments were carried out with saccharin replaced by benzoic acid. The composition of the adhesive is summarized in Table I. Acetylphenylhydrazine, saccharin, cumene hydroperoxide, and TRIEGMA were supplied by Loctite Corporation and used as-received. TRIEGMA was purified by washing with aqueous NaOH and dried in a rotary evaporator at room temperature in vacuo before shipment. Saccharin and acetylphenylhydrazine were recrystallized from ethanol. Benzoic acid and the sodium salts of saccharin and benzoic acid were obtained from Aldrich and used as-received.

Substrates for SERS were prepared by slow thermal evaporation of silver island films onto glass slides. The slides were cleaned by immersion in 0.1N NaOH solutions for one hour, rinsed in 0.1N hydrochloric acid solutions for one hour, rinsed in distilled water in an ultrasonic cleaner, and blown dry in a stream of nitrogen. The slides were immediately placed in a vacuum chamber equipped with sorption, sublimation, and ion pumps and a quartz crystal oscillator thickness monitor and pumping was initiated. When the pressure reached 10^{-6} Torr, silver was evaporated onto the slides at a rate of about 1 A per second to a final thickness of about 45 A. Thin films of the adhesive, saccharin, and benzoic acid were deposited on silver island films by spin-coating from dilute solutions. In a few cases, films were deposited by spinning the undiluted adhesive onto silver island films. The thickness of the adhesive films spin-coated onto silver island films was estimated by spinning films from the same solutions onto silver films that were several thousand angstroms in thickness and examining the adhesive films with an ellipsometer. Samples were prepared for normal Raman spectroscopy by placing a small amount of the liquid or powdered sample into a capillary tube.

All Raman spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, ITT FW-130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. In SERS experiments, the slits of the monochromator were set for a spectral resolution of 10 cm^{-1}. The laser beam was incident on the samples at an angle of 65^o relative to the normal to the sample surface and was polarized parallel to the sample surface. Scattered light was collected by an f/0.95 lens and focussed onto the entrance slit of the monochromator. SERS spectra were obtained using the 5145 A line of the laser, a scan rate of 50 cm^{-1}/min, and time constant of 10 sec. Similar techniques were used for obtaining normal Raman spectra but the slit width was 5 cm^{-1} and the time constant was 2 sec. Ellipsometry was carried out using a Rudolph Research Model 436 Ellipsometer.

An experiment was carried out to determine if silver accelerated polymerization of the adhesive system. A film of silver several hundred angstroms in thickness was evaporated onto a clean glass slide. The slide was placed on the bottom of an aluminum mold lined with fluorocarbon tape and de-aerated adhesive was poured into the mold. The mold was placed into a container and purged with nitrogen overnight, allowing the adhesive to polymerize. A control experiment was carried out in which adhesive was allowed to cure against a clean glass slide in a similar mold. The cured specimens were examined qualitatively to determine their rigidity. Scrapings taken from the samples were mixed with KBr, pressed into pellets, and examined by infrared spectroscopy to determine the extent of polymerization. The spectra were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared spectrophotometer.

III. Results and Discussion

A. *Effect of Silver on the Rate of Polymerization*

It was qualitatively determined that silver accelerated polymerization of the adhesive. When the adhesive was cured against the silver-coated glass slide overnight, a rigid solid was obtained. However, adhesive cured against a clean glass slide for the same length of time was softer and more flexible. These conclusions were substantiated by analysis of the bands near 1638 and 1720 cm^{-1} in infrared spectra of the adhesive which were assigned to the C=C and C=O stretching modes, respectively. The intensity of the band near 1638 cm^{-1} relative to that near 1720 cm^{-1} was less for the adhesive cured against glass coated with silver than for the adhesive cured against clean glass, indicating that the extent of polymerization was greater for the sample cured against silver-coated glass.

B. SERS spectra of acrylic adhesive

SERS spectra shown in Figures 1A and 1B were obtained from films of the adhesive spin-coated onto silver island films from acetone solutions having concentrations of 1% and 5%, respectively. The spectrum shown in Figure 1C was obtained from a film spin-coated from the undiluted adhesive. The spectra were dominated by strong bands near 1600, 1360, 1306, 1175, 1155, 1025, 720, and 609 cm^{-1}. Weaker bands were also observed near 1470, 1266, 658, and 552 cm^{-1}.

It was expected that films spun from the most concentrated solutions would be the thickest and exhibit the most intense Raman scattering. However, reference to Figure 1 shows that the SERS intensities of films spun from 1% and 5% solutions of the adhesive and from the undiluted adhesive were virtually identical even though the thicknesses of the films ranged from approximately 100 A for the film spun from the 1% solution to 500 A for that spun from the adhesive itself.

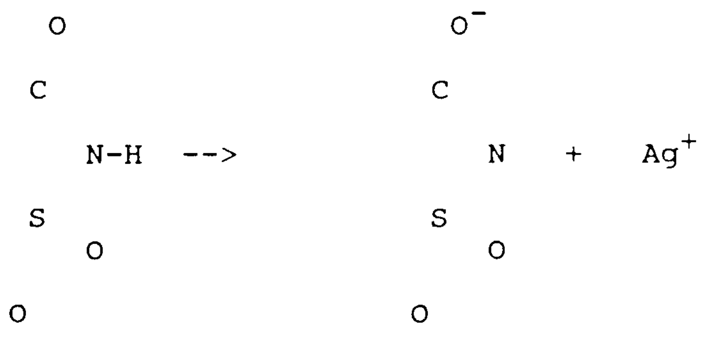
SERS spectra of the adhesive deposited on silver island films were completely different from normal Raman spectra of the monomer. As shown in Figure 2, Raman spectra of TRIEGMA were characterized by strong bands near 1730 and 1650 cm^{-1} that were assigned to $\nu(C=O)$ and $\nu(C=C)$, the stretching modes of the CO and CC double bonds, respectively. The band near 1650 cm^{-1} was not expected to appear in SERS spectra of the adhesive due to polymerization of the monomer. The band due to the carbonyl group was expected but was not observed.

SERS spectra of the adhesive were, however, similar to SERS spectra of saccharin (see Figure 3A) and to normal Raman spectra of the sodium salt of saccharin (see Figure 3B). As a result, most of the bands observed in the SERS spectra of the adhesive were assigned to vibrational modes of the sulphonyl group and the substituted benzene ring. Three bands characteristic of the sulphonyl group were expected, corresponding to $\nu_s(SO_2)$, $\nu_a(SO_2)$, and $\delta(SO_2)$, the symmetric and asymmetric stretching and deformation modes, respectively. There have been no previous investigations of the Raman spectra of saccharin but Baxter (8) has investigated the infrared spectra of a number of sulphonamides, including saccharin. Based on Baxter's results, we have assigned the strong bands near 1360 and 1175 cm^{-1} to $\nu_a(SO_2)$ and $\nu_s(SO_2)$, the asymmetric and symmetric stretching modes of the sulphonyl group, respectively. The band near 552 cm^{-1} was assigned to $\delta(SO_2)$, the deformation mode.

Most of the remaining bands observed in the SERS spectra of the adhesive were attributed to vibrations of the benzene ring and can be discussed in terms of the numbering system proposed by Wilson (9). Thus, the band near 1600 cm^{-1} was assigned to $\nu(8a)$, a tangential ring stretching mode. Bands near 1155 and 1025 cm^{-1} were assigned to the CH in-plane bending modes $\nu(15)$ and $\nu(18b)$, respectively. $\nu(1)$, a radial ring stretching mode, was assigned to the strong band near 720 cm^{-1}. The weak band near 1470 cm^{-1} was attributed to $\nu(19b)$, a tangential ring stretching mode, and the band near 609 cm^{-1} was attributed to $\nu(6a)$, a radial ring stretching and bending mode. The strong band near 1308 cm^{-1} and the moderately strong band near 1270 cm^{-1} were attributed to n(14), a tangential ring stretching mode, and n(3), a CH in-plane bend, respectively.

A strong band characteristic of the C=O stretching mode was observed near 1707 cm^{-1} in normal Raman spectra of saccharin (see Figure 3C). That band was not observed in SERS spectra of the adhesive or saccharin or in normal Raman spectra of the sodium salt of saccharin. However, weak bands were observed near 1658 and 1644 cm^{-1} in spectra of the salt and assigned to a C=N stretching mode.

The SERS spectra of the adhesive were similar to SERS spectra of saccharin and were independent of the film thickness deposited on the silver island films. Thus, it was concluded that the SERS spectra of the adhesive were characteristic of the interface rather than the bulk adhesive and that saccharin, a relatively minor component of the adhesive, segregated to the interface and adsorbed onto the silver surface by dissociation to form a salt as shown below:



It is interesting to note that the intensities of several bands were much greater in the SERS spectra than in the normal Raman spectra. The band near 1600 cm^{-1} assigned to $\nu(8a)$ was weak in normal Raman spectra of the salt but was the strongest band in the SERS spectrum. Similarly, the band near 609 cm^{-1}, which was attributed to $\nu(6a)$, was weak in normal Raman spectra of the salt but strong in SERS spectra.

There are several reasons for bands to have different intensities in SERS and normal Raman spectra. Bands which are "normally allowed" for the free molecule may have considerably different intensities in SERS. According to the theory developed by Moskovits for Raman scattering by molecules near metal surfaces, the strongest bands are related to modes transforming as α_{ZZ}, where Z is perpendicular to the surface, and having motions mostly perpendicular to the metal surface (10). The next most intense bands are those transforming as α_{XZ} and α_{YZ} while the weakest bands are those transforming as α_{XY}. Bands which are "normally forbidden" under the symmetry of the free molecule may appear in SERS spectra because of a decrease in symmetry brought about by the formation of surface complexes or because of the contribution of higher order terms to the polarizability (11, 12).

o-Disubstituted benzene rings as in saccharin have at most C_{2V}^* symmetry and all of the vibrational modes of the rings are allowed in normal Raman spectra of the free molecule. No normally forbidden modes were expected in the SERS spectra and none were observed. Under C_{2V}^* symmetry, modes 1, 2, 6a, 7a, 8a, 9a, 15, 18b, 19b, and 20b transform as α_{zz} (13) and should correspond to the strongest bands in the SERS spectra. However, modes 2 and 20b are CH stretching modes and occur at frequencies above those studied here. Modes 9a and 7a are related to CX in-plane bending and CX stretching, respectively, and occur at frequencies below those studied. Thus, the bands corresponding to modes 1, 6a, 8a, 15, 18b, and 19b were expected to be strongest in SERS and, as noted in Table 1 and Figure 3A, all of these modes appeared with significant intensity in the SERS spectra. These results imply that saccharin is adsorbed with the C_2 axes of the o-disubstituted rings approximately perpendicular to the surface and that the increased intensity of the bands near 1600 and 609 cm^{-1} in SERS spectra of the adhesive and of saccharin is related to an orientation effect.

It is interesting to consider the intensity of the band near 786 cm^{-1}. This band, which was assigned to $\nu(12)$, was clearly observed in normal Raman spectra of the salt but not in SERS spectra of saccharin. Under C_{2v}^* symmetry, $\nu(12)$ belongs to the B_2 species and transforms as α_{xy} (13). Considering the selection rules described above, the band near 786 cm^{-1} was expected to be weak in SERS spectra.

No evidence for adsorption of acetylphenylhydrazine (APH) or cumene hydroperoxide (CHP) at the surface of the silver island films was observed in the SERS spectra of the adhesive. Normal Raman spectra of monosubstituted benzene derivatives such as APH and CHP are usually characterized by a very strong band between 990 and 1010 cm^{-1} that is associated with the vibration $\nu(12)$

(14). However, as indicated above, the only band observed near this frequency in SERS spectra of the adhesive was near 1026 cm^{-1} and was attributed to ν(18b) in adsorbed saccharin.

Other results that we have obtained using x-ray photoelectron spectroscopy (XPS) to characterize interphases formed between the same adhesive and metal substrates such as iron, copper, aluminum, and zinc indicate that APH does segregate to the adhesive/metal interphase (15). The difference between the SERS and XPS results may indicate that APH preferentially adsorbs from the adhesive onto iron, copper, aluminum, and zinc but not onto silver. However, it seems more likely that the difference between the SERS and XPS results is related to differences in the techniques. APH and saccharin may both segregate to the interphase but APH may not compete with saccharin for sites on the surface of silver. Since XPS is somewhat less surface sensitive than SERS, APH may be detected in the interphase using XPS but not SERS.

C. SERS spectra of adhesive containing benzoic acid

When benzoic acid was substituted for saccharin and the adhesive was spun onto silver films, the SERS spectra shown in Figure 4 were obtained. These spectra are virtually identical to the SERS spectra of benzoic acid (see Figure 5A) and to the normal Raman spectra of the sodium salt of benzoic acid (see Figure 5B), indicating once again that the strong acids in these adhesives were adsorbed dissociatively onto the metal substrates and that the observed Raman signal was characteristic of the adhesive/substrate interface and not the bulk of the adhesive.

No evidence for the adsorption of acetylphenylhydrazine (APH) or cumene hydroperoxide (CHP) onto the silver surface was obtained when the adhesive with benzoic acid was cured against silver. The strongest line in the Raman and SERS spectra of these compounds is usually $\nu(1)$, near 1000 cm^{-1}. However, scattering by adsorbed benzoate species dominated the SERS spectra, especially near 1000 cm^{-1}.

SERS spectra of the adhesive containing benzoic acid were characterized by strong bands near 1612, 1015, and 852 cm^{-1} and by weaker bands near 1518, 1466, 1400, 1151, 1035, 694, 620, and 452 cm^{-1}. Several of the observed bands were assigned to vibrational modes of carboxylate groups. Thus, the band near 1400 cm^{-1} was attributed to $\nu_s(COO^-)$, the symmetric stretching mode of the carboxylate group. The band near 694 cm^{-1} was assigned to $\delta(COO^-)$, the carboxylate deformation mode and the band near 452 cm^{-1} was assigned to $\delta(COO^-)$ coupled with $\nu(6a)$, a radial ring stretching mode. The asymmetric carboxylate stretching mode $\nu_a(COO^-)$ was expected near 1600 cm^{-1} but was obscured by a strong band assigned to a ring stretching mode (see below).

Most of the remaining bands observed in the SERS spectra of the adhesive were assigned to modes of the substituted benzene ring. Thus, the bands near 1612 and 1466 cm^{-1} were assigned to the tangential ring stretching modes $\nu(8a)$ and $\nu(19a)$, respectively. The band near 1151 cm^{-1} was assigned to the CH in-plane bending mode $\nu(15)$ and the strong bands near 1015, 852, and

620 cm^{-1} were assigned to radial ring stretching modes $\nu(12)$, $\nu(1)$, and $\nu(6b)$, respectively.

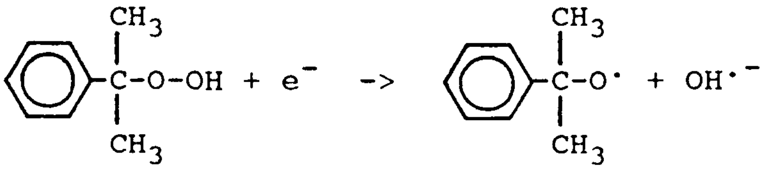
Somewhat different assignments have been proposed by others. For example, Chaozhi et al (16) attributed the band near 852 cm^{-1} to $\nu(6a)$. However, $\nu(6a)$ is located at much lower frequencies for mono-substituted benzene (17) rings and cannot be assigned to the band near 852 cm^{-1}. Lewandowski and Baranska assigned the band near 852 cm^{-1} in Raman spectra of sodium benzoate to the symmetrical deformation of the carboxylate group (18). Boerio and Roth (19) carried out the normal coordinate analysis of terephthalate and terephthalate-d_4 ions and assigned the band near 852 cm^{-1} to a ring stretching mode. Ernstbrunner (20) carried out normal coordinate analysis of p-nitrobenzoate and made a similar assignment. Based on the normal coordinate analyses, we have assigned the band near 852 cm^{-1} to $\nu(1)$.

Chaozhi (16) attributed the band near 452 cm^{-1} to either a carboxylate in-plane rock or to the $\nu(16a)$ ring mode. $\nu(16a)$ is usually observed as a weak band in the Raman spectra of mono- and para-substituted benzenes (21) and the carboxylate rocking mode is also expected to be weak. However, $\nu(16a)$ is very strong in the SERS spectra of compounds such as s-triazine having D_{3h} symmetry (22). In such cases, $\nu(16a)$ belongs to the symmetry species E'', as do α_{YZ} and α_{XZ} and, considering the selection rules described above, is expected to have considerable intensity in the SERS spectra. However, in benzoates the monosubstituted benzene rings have C_{2v} symmetry (13). $\nu(16a)$ belongs to the symmetry species A_2, as does α_{XY}, and, considering the selection rules once again, is not expected to have significant intensity in the SERS spectra. Results obtained from the normal coordinate analysis of the terephthalate (19) and p-nitrobenzoate (20) ions indicate that the band near 452 cm^{-1} in the SERS spectra of benzoic acid should be assigned to carboxylate in-plane bending coupled with the radial ring stretching mode $\nu(6a)$.

Several significant differences were noted when SERS spectra of benzoic acid and normal Raman spectra of sodium benzoate were compared to normal Raman spectra of benzoic acid (see Figure 5C). Several bands in the normal Raman spectra of benzoic acid were assigned to the carboxylic acid group. Thus, the medium intensity band near 1640 cm^{-1} was assigned to the C=O stretching mode. The weak band near 1450 cm^{-1} was related to CO stretching and OH in-plane bending and the band near 426 cm^{-1} was assigned to the deformation mode $\delta(COOH)$.

The salts formed at the interface by dissociation of the strong acids may play an important role in the polymerization of the adhesive. As indicated earlier, the adhesive considered here is a model anaerobic system that polymerizes rapidly at room temperature by a redox mechanism in the presence of certain metals. The metal ions in the salts are undoubtedly oxidized while the hydroperoxide is reduced to form radicals which

$$M^{+n} \rightarrow M^{+(n+1)} + e^{-} \qquad (1)$$



(2)

initiate polymerization of the monomer.

Interaction of metal ions with APH may also be an important factor in accelerating the polymerization. APH may break down at the metal surface to form radicals which also initiate polymerization. APH may also be oxidized while metal ions are reduced to their original valence state, thus enabling reaction

$$M^{+(n+1)} + e^{-} \rightarrow M^{+n} \qquad (3)$$

2 to be repeated. However, more work will be required in order to elucidate this and other aspects of the polymerization of the acrylic adhesive.

The results described above also indicate that SERS can be used for non-destructive characterization of interphases between metal substrates and polymer films as long as the polymer film is not so thick that normal Raman scattering from the bulk of the film is comparable in intensity to the SERS signal from the interphase. The thickness of polymer film at which bulk scattering becomes significant obviously depends on the Raman cross section of the polymer. Current indications are that interphases between metals and polymer films approximately a thousand angstroms thick can be investigated. However, careful measurements are in progress and will be reported elsewhere.

IV. Conclusions

SERS spectra obtained from a model acrylic adhesive consisting of the monomer triethylene glycol dimethacrylate and a curing system containing saccharin, acetylphenylhydrazine, and cumene hydroperoxide were similar to SERS spectra of saccharin and to normal Raman spectra of the sodium salt of saccharin. When saccharin was replaced by benzoic acid, SERS spectra of the adhesive deposited on silver were similar to SERS spectra of benzoic acid and to normal Raman spectra of metal salts of benzoic acid. Moreover, the intensity of the SERS spectra was independent of the thickness of the films, indicating that the observed Raman scattering was characteristic of the interface, not of the bulk adhesive. These results demonstrate that saccharin and benzoic acid segregated to the interface and adsorbed onto the silver substrate dissociatively to form metal salts.

These salts are thought to be important factors in the curing reaction of the adhesive. Metal ions undoubtedly catalyze decomposition of the hydroperoxide to form radicals that initiate polymerization of the monomer. Metal ions may also catalyze formation of radicals from APH but more information will be required before the role of APH in the polymerization of the monomer can be determined.

It is evident that SERS can be used as a non-destructive technique technique for characterizing the interface between metals and polymers as long as the thickness of the polymer film is not so great that normal Raman scattering by the bulk of the film becomes comparable in intensity to the SERS from the interface. The thickness of polymer film at which that happens obviously depends on the Raman cross section of the polymer and we have not carried out careful determinations. However, present results indicate that films as thick as about 1,000 A can be examined.

IV. Acknowledgements

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Table I. Composition of the model acrylic adhesive system.

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triethylene glycol dimethacrylate - 10.790 grams
o-benzoic sulfimide - 0.090 grams
acetylphenylhydrazine - 0.075 grams
cumene hydroperoxide - 0.300 grams

Table II. Bands observed in the SERS spectra of the acrylic adhesive and of saccharin and in the normal Raman spectra of saccharin and its sodium salt (cm^{-1}).

Adhesive (SERS)	Saccharin	Sodium salt	Saccharin (SERS)	Assignment
	437			$\nu(18a)$
552	535	555	556	$\delta(SO_2)$
	602			
609	628	620	612	$\nu(6a)$
658		658	649	
720	712	722	725	$\nu(1)$
	785	786		$\nu(12)$
		806		
		1020		
1025	1025	1030	1026	$\nu(18b)$
	1125			
	1138			
		1153		
1155	1170	1161	1160	$\nu(15)$
1175	1185	1176	1178	$\nu_s(SO_2)$
1266	1265	1264	1270	$\nu(3)$
1306	1308	1308	1308	$\nu(14)$
	1344			
1360	1362	1350	1362	$\nu_a(SO_2)$
1470	1472	1470	1472	$\nu(19b)$
1600	1604	1606	1605	$\nu(8a)$
		1644		$\nu(C=N)$
		1658		
	1707			$\nu(C=O)$

Table III. Bands observed in the SERS spectra of benzoic acid and the adhesive with benzoic acid and in the normal Raman spectra of benzoic acid and its sodium salt (cm^{-1}).

Adhesive (SERS)	Benzoic Acid	Sodium Salt	Benzoic Acid (SERS)	Assignment
452		408	450	$\delta(COO^-) + \nu(6a)$
	426			$\delta(COOH) + \nu(6a)$
620	620	620	628	$\nu(6b)$
694		683	688	$\delta(COO^-)$
	815	827	831	
852		850	848	$\nu(1)$
1015	1005	1010	1010	$\nu(12)$
	1031	1034	1035	$\nu(18a)$
1151	1140	1148	1148	$\nu(15)$
1172	1165	1163	1163	$\nu(9a)$
	1188	1188		
1320				
1400			1394	$\nu_s(COO^-)$
1466	1450	1440	1450	$\nu(19b)$
1518			1498	$\nu(19a)$
		1594		
1612	1610	1610	1608	$\nu(8a)$
	1640			$\nu(COOH)$

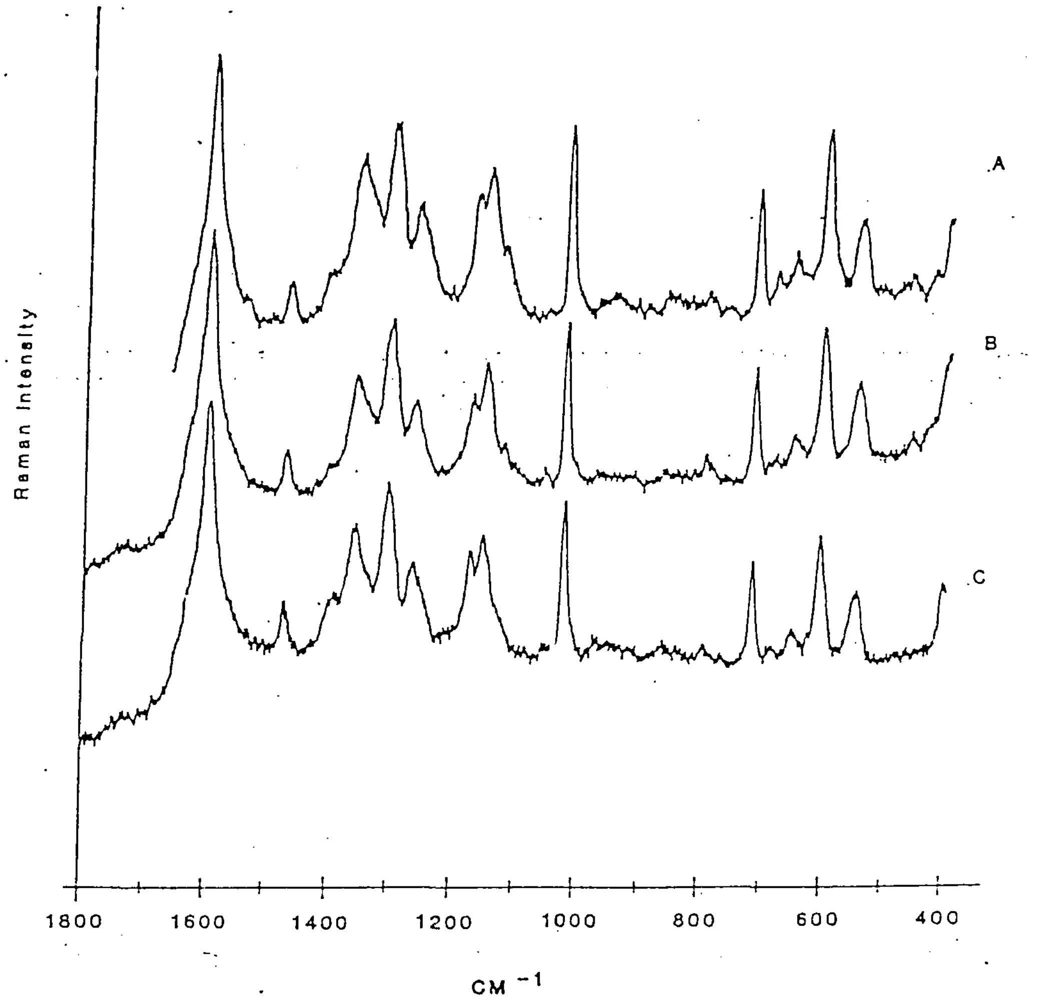

Figure 1. SERS spectra obtained when the acrylic adhesive was spin-coated onto silver island films from (A) - 1% and (B) - 5% solutions in acetone and (C) - from the bulk. The scale factor was 5x10^3 counts/sec and the laser power was 100 mW in all cases.

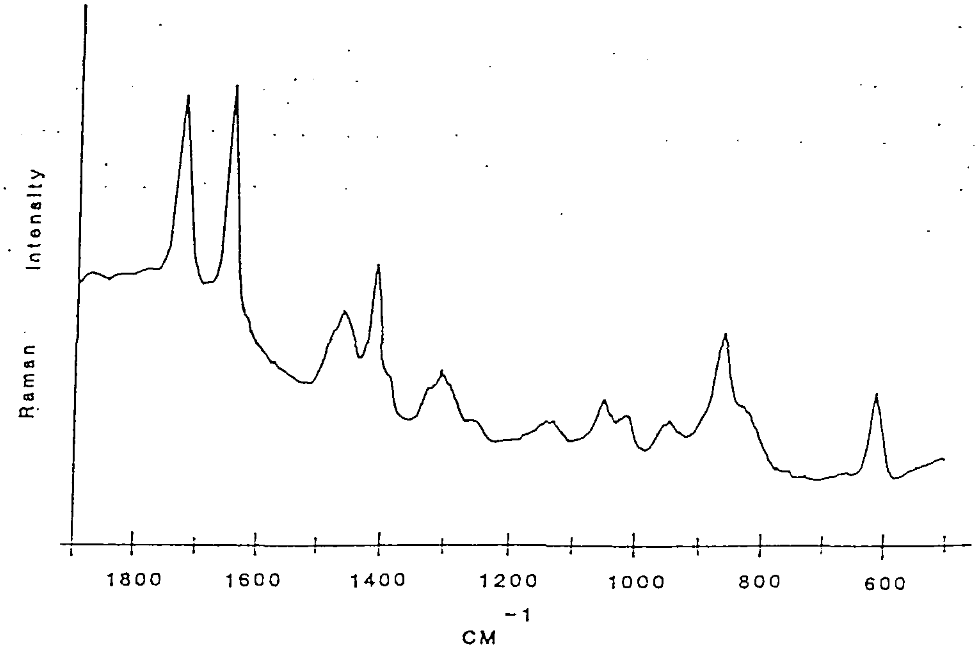

Figure 2. Normal Raman spectrum of triethylene glycol dimethacrylate (TRIEGMA).

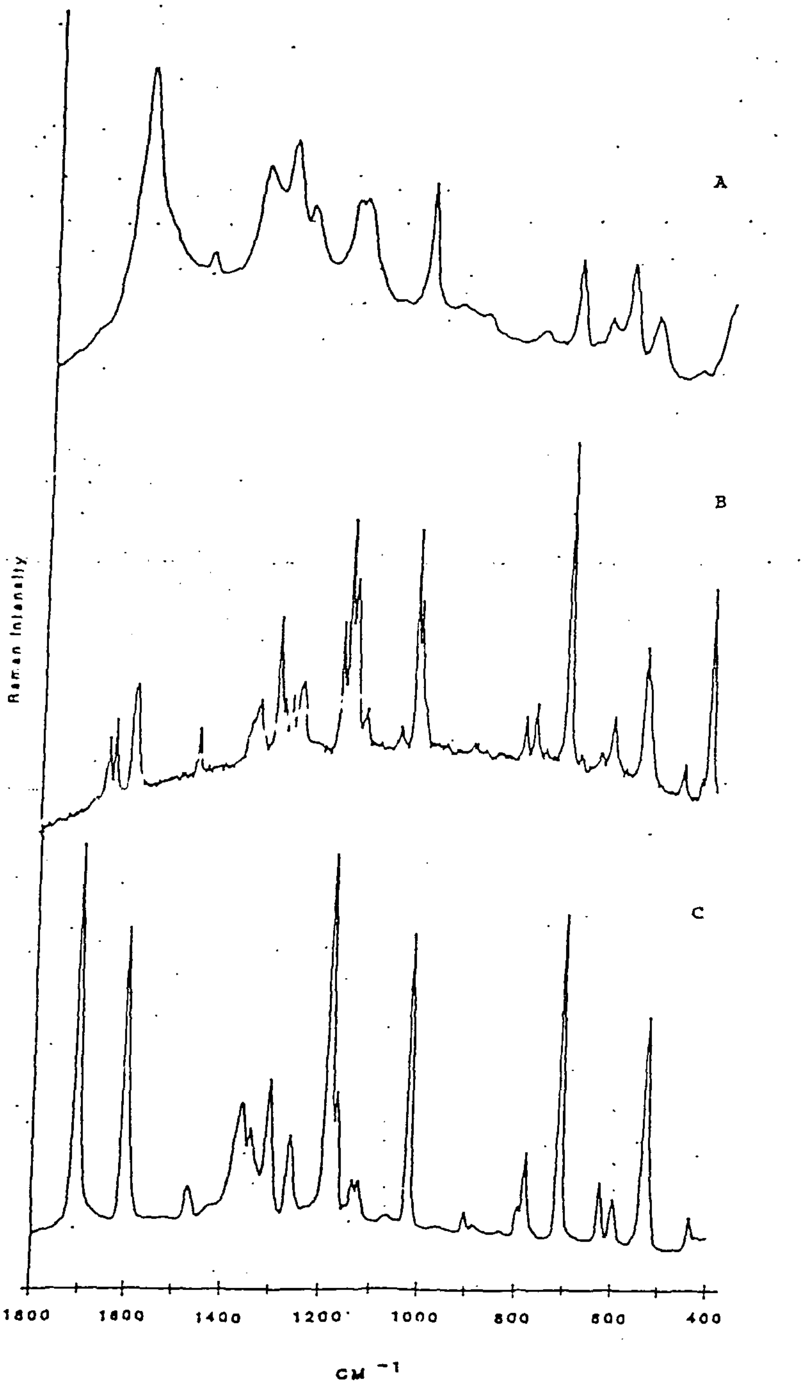

Figure 3. (A) - SERS spectrum from saccharin spin-coated onto a silver island film from a 0.1% acetone solution, (B) - normal Raman spectrum of the sodium salt of saccharin, and (C) - normal Raman spectrum of saccharin.

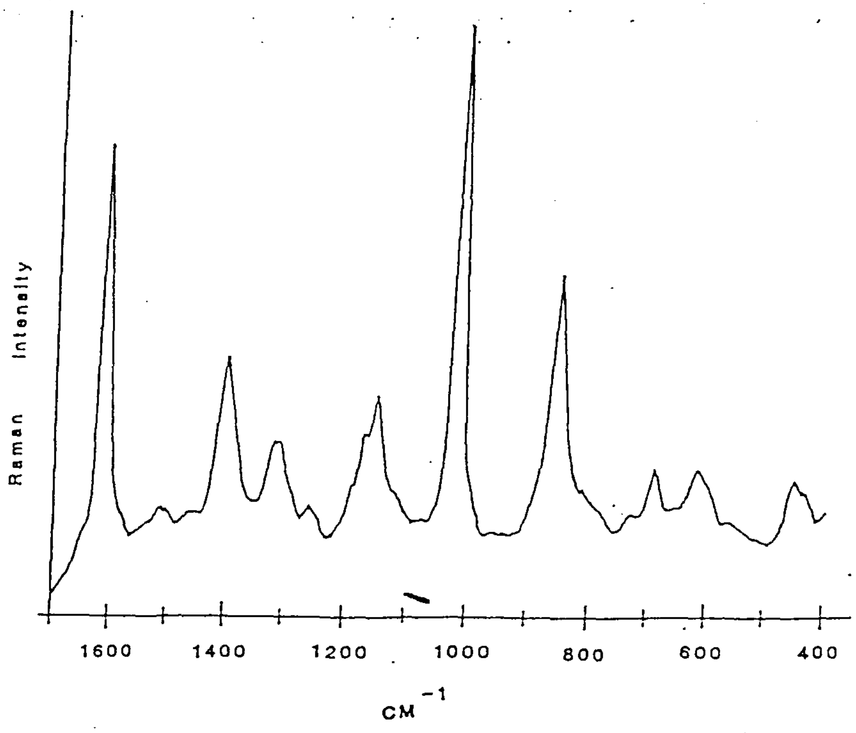

Figure 4. SERS spectrum obtained when the acrylic adhesive with benzoic acid substituted for saccharin was applied to a silver island film and allowed to cure. The laser power was 100 mW.

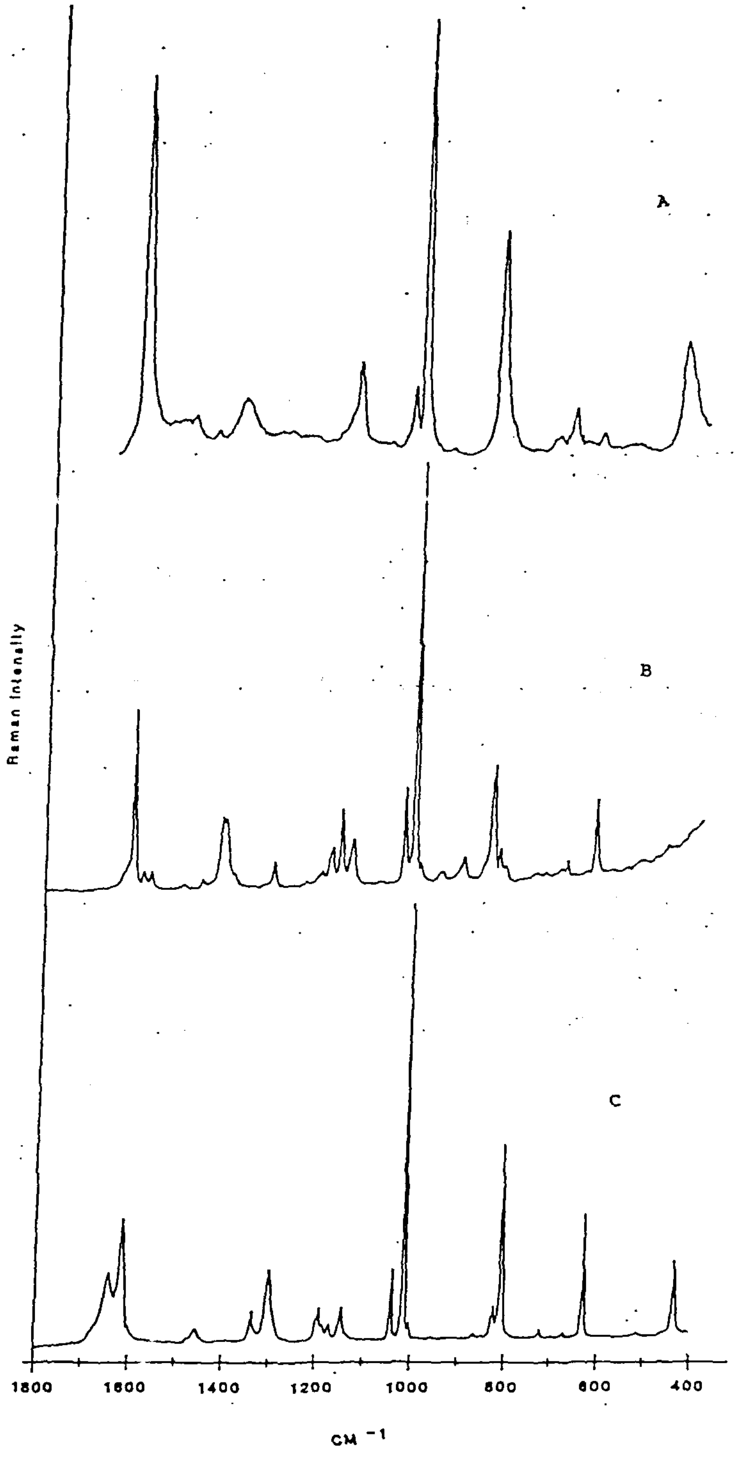

Figure 5. (A) - SERS spectrum of benzoic acid spin-coated onto a silver island film from a 1% solution in acetone, (B) - normal Raman spectrum of sodium benzoate, and (C) - normal Raman spectrum of benzoic acid.

Figure 1. SERS spectra obtained when the acrylic adhesive was spin-coated onto silver island films from (A) - 1% and (B) - 5% solutions in acetone and (C) - from the bulk. The scale factor was 5×10^3 counts/sec and the laser power was 100 mW in all cases.

Figure 2. Normal Raman spectrum of triethylene glycol dimethacrylate (TRIEGMA).

Figure 3. (A) - SERS spectrum from saccharin spin-coated onto a silver island film from a 0.1% acetone solution, (B) - normal Raman spectrum of the sodium salt of saccharin, and (C) - normal Raman spectrum of saccharin.

Figure 4. SERS spectrum obtained when the acrylic adhesive with benzoic acid substituted for saccharin was applied to a silver island film and allowed to cure. The laser power was 100 mW.

Figure 5. (A) - SERS spectrum of benzoic acid spin-coated onto a silver island film from a 1% solution in acetone, (B) - normal Raman spectrum of sodium benzoate, and (C) - normal Raman spectrum of benzoic acid.

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