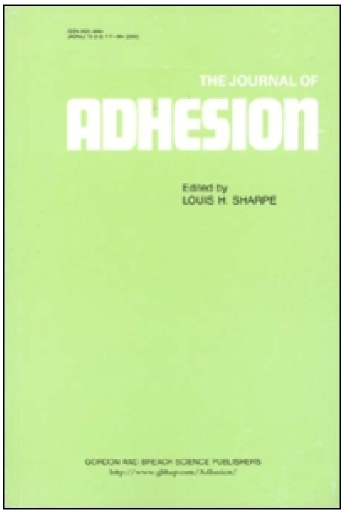

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Raman Spectroscopy of Laminated Polymer Films by Integrated Optical Techniques

J. D. Swalen[a]; N. E. Schlotter[a]; R. Santo[a]; J. F. Rabolt[a]
[a] IBM Research Laboratory, San Jose, California, U.S.A.

To cite this Article Swalen, J. D. , Schlotter, N. E. , Santo, R. and Rabolt, J. F.(1981) 'Raman Spectroscopy of Laminated Polymer Films by Integrated Optical Techniques', The Journal of Adhesion, 13: 2, 189 — 194
To link to this Article: DOI: 10.1080/00218468108073185
URL: http://dx.doi.org/10.1080/00218468108073185

J. Adhesion, 1981, Vol. 13, pp. 189–194
0021-8464/81/1302-0189 $06.50/0

Raman Spectroscopy of Laminated Polymer Films by Integrated Optical Techniques

J. D. SWALEN, N. E. SCHLOTTER, R. SANTO, and J. F. RABOLT

IBM Research Laboratory, San Jose, California 95193, U.S.A.

(*Received February 24 1981; in final form May 11 1981*)

Raman spectra have been observed from two adjacent thin polymer films and the interfacial region. This has been made possible by the application of integrated optical techniques to Raman spectroscopy. The observed Raman spectra have their strongest intensity contributions from regions near the optical field intensity maxima, which can occur in either film or at the interface. Both the optical intensity and the scattering volume are increased significantly and Raman spectra with good signal-to-noise ratios can be obtained. The method will be briefly illustrated and spectra for a thin film of poly(styrene) on a film of poly(vinyl alcohol) will be shown for various (modes) optical profiles.

A polymer film deposited upon another exhibits adhesive interactions at the interface. The strength of this interaction however has been difficult to measure but is crucial in many applications of laminate bonding. We have recently applied a technique based on integrated optics[1–3] to measure the Raman spectra of molecules in thin films.[4–9] In this way signal-to-noise ratios were increased significantly and changes in vibrational frequencies and intensities were observed when a single dye monolayer was deposited on a glass surface.[7]

Integrated optics is a method for propagating light with increased intensity through a thin film the thickness of which is on the order of a micron. Current engineering interest in these structures arises from the ability to perform optical signal processing on a coherent wavefront in a specific mode. Its application to Raman spectroscopy is attractive because of the larger

---

Presented at the Annual Meeting of The Adhesion Society, Savannah, GA, U.S.A., February 22–25, 1981.

scattering volume, the higher optical field intensity, and the better imaging of the scattering onto the slit of a double monochromator. Modes are characterized by their nodes in optical field across the film and propagation vectors depend on the refractive indices of the film and surrounding media and the film thickness. Coupling light into a film is conveniently accomplished by pressing a high index half prism on top of the film. This is shown schematically in Figure 1. Changing the angle ϕ changes the propagation vector's direction in the film and leads to the conducting modes (different m values).

Intuitively, a propagating mode exists when the sum of the phase shifts which occur upon reflection at each interface plus the phase shift in the light travelling back and forth across the film is a multiple of 2π. The Raman method has now been extended to double layers and in particular to Raman scattering from the interfacial region.

Schematically the film structure is illustrated in the bottom of Figure 1. In this instance film 1 is poly(styrene) and film 2 is poly(vinyl alcohol). The films were prepared[10] by spinning with a Headway Research, Inc. spinner at 3000 rpm. The poly(vinyl alcohol) film was spun onto the substrate from a 10%

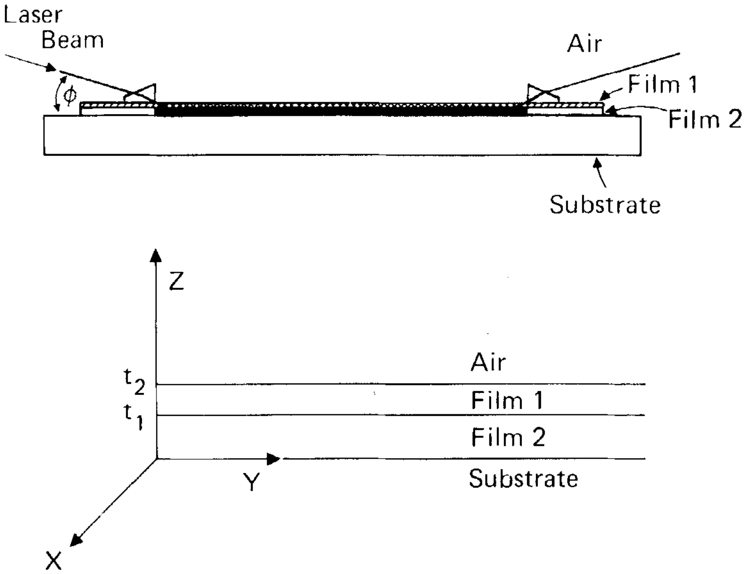

FIGURE 1 Schematic of thin laminate films on a substrate and the laser coupling of the light through the film structure. The angle ϕ is varied to couple to different modes. The outcoupled beam is shown at the upper right from the right half prism. Film 1 is poly(styrene); $t_1 = 0.435\,\mu\text{m}$ with a refractive index at $\lambda = 488.0$ nm of 1.6008 for TE. Film 2 is poly(vinyl alcohol); $t_2 = 1.740\,\mu\text{m}$ and $n = 1.5306$.

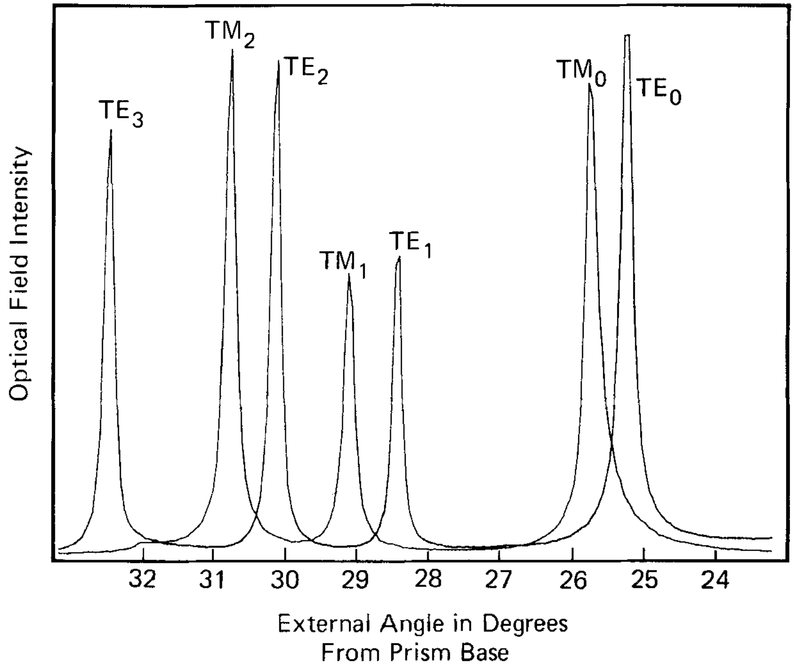

FIGURE 2 Optical conduction intensity through the layered structure as a function of angle for both TE and TM polarization. The TE angles are 24.94, 28.56, 30.00, and 32.08 degrees and the TM angles are 28.58, 30.10, and 32.18 degrees, both with a 45 degree prism of LaSF5 Schott glass $n = 1.8954$ at 488.0 nm.

water solution which had been filtered through an 8 micron Millipore filter. The poly(styrene) film was then spun on top from a 6% chlorobenzene solution.

The outcoupled beam intensity (the beam at the upper right corner of Figure 1) is a maximum at each mode. This is shown in Figure 2 where TE designates those modes which propagate with their optical electric vector in the plane of the film whereas TM modes propagate with the optical magnetic vector in the plane of the film. The $m = 0$ mode was predominantly in the poly(styrene) layer, the $m = 1$ mode was predominately in the poly(vinyl alcohol) layer, and the higher modes have propagation in both regions. This is shown in Figure 3 where the optical fields (proportional to $|E|^2$), calculated from the angles measured in Figure 2 and the eigenvalue equation, are plotted as a function of distance across the film layers.

The corresponding Raman spectra are shown in Figure 4 for the modes $m = 0$ to $m = 3$. The $m = 0$ spectrum is predominately that of poly(styrene) while the $m = 1$ spectrum is primarily of poly(vinyl alcohol) with a small

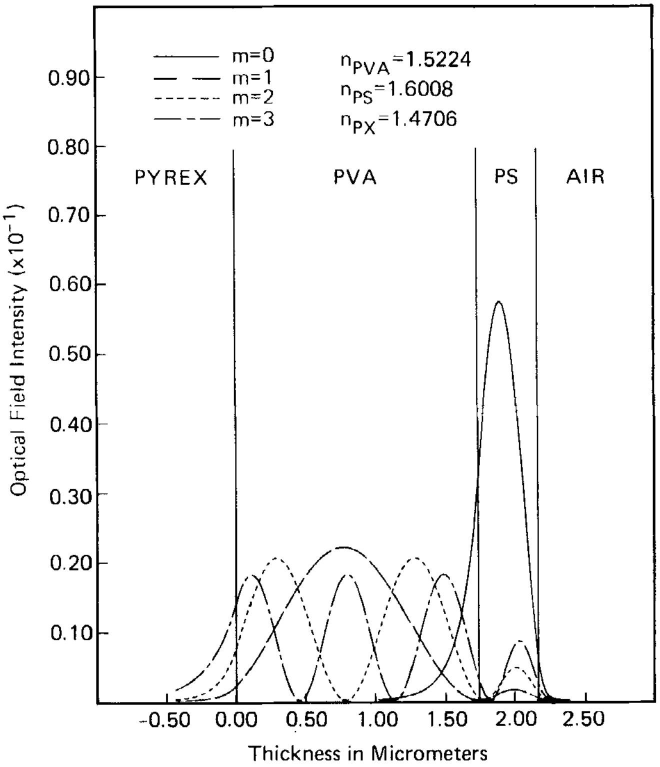

FIGURE 3 Optical field intensity across the film structure for the four TE modes.

contribution from poly(styrene) in the 1000 cm^{-1} region. The other two spectra exhibit the spectral features of both polymers. Notice in Figure 3 how the optical field increases in the poly(styrene) layer from *m* = 1 to 3 and there is a corresponding increase in the characteristic Raman bands in Figure 4.

It should be noted that the Raman scattering cross section of poly(styrene) is much larger than that of poly(vinyl alcohol) because of the presence of phenyl side groups in the former. Hence even in waveguide modes where there is a lower optical field intensity within the poly(styrene) layer it contributes considerably to the Raman spectrum, since the scattering intensity is proportional to both optical field intensity and scattering cross section. An interesting observation can also be made by considering the increased penetration of the evanescent tail of the guided wave into the pyrex substrate at large *m* values. Pyrex in general is a poor Raman scatterer. However, at high *m* values, scattering from the ~450 cm^{-1} vibration of pyrex is visible in Figure 4.

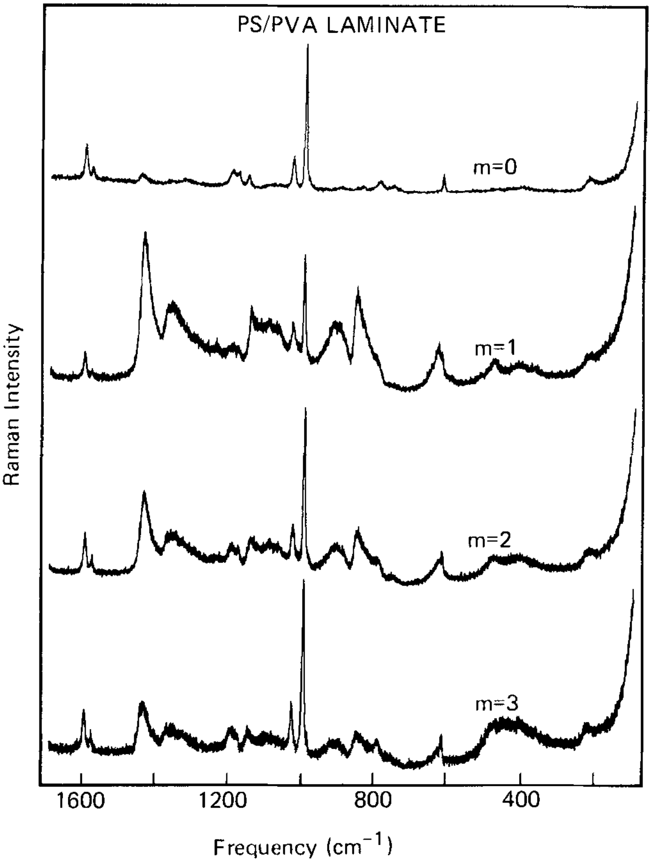

FIGURE 4 Raman spectra (100–1700 cm^{-1}, bandpass = 4 cm^{-1}, 488.0 nm, no smoothing) for the four modes $m = 0$ to $m = 3$, top to bottom.

As seen in Figure 4 both the $m = 0$ and $m = 1$ spectra overlap portions of the interfacial region while the $m = 2$ and $m = 3$ spectra are mainly superpositions of the pure film spectra. By a detailed analysis currently in progress,[9] it should be possible, in principle, to use digital substraction techniques to determine the nature of the adhesive interaction at the film/film interface.

References

1. P. K. Tien, *Applied Optics* **10**, 2395 (1971).
2. D. Marcuse, *Theory of Dielectric Optical Waveguides* (Academic Press, NY, 1974).
3. J. D. Swalen, *J. Phys. Chem.* **83**, 1438 (1979).

4. Y. Levy *et al.*, *Opt. Commun.* **11,** 66 (1974).
5. Y. Levy and R. Dupeyrat, *J. Phys. Coll.* **C5 38** (supp 11), 253 (1977).
6. J. F. Rabolt, R. Santo, and J. D. Swalen, *J. Appl. Spectroscopy* **33,** 549 (1980).
7. J. F. Rabolt, R. Santo, and J. D. Swalen, *ibid.* **34,** 517 (1980).
8. J. F. Rabolt *et al.*, *IBM J. Res. Div.* (in press).
9. J. F. Rabolt *et al.*, *J. Polymer Sci.* (to be published).
10. J. D. Swalen *et al.*, *IBM J. Res. Dev.* **21,** 168 (1977).