

NOTE:

**Evidence from Infrared Ellipsometry for Covalent Bonding  
at a Polymer/Polymer Interface with Relevance to  
"Lock-Up" in Pressure-Sensitive Adhesive Laminates**

**T.R.E. Simpson and J.L. Keddie\***

Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, UK

**Abstract**

*In a novel application, infrared spectroscopic ellipsometry is used to provide clear evidence for the formation of a covalent bond at a polymer/polymer interface. Specifically, there is evidence for the formation of a Si-O-C bond resulting from a reaction between the silyl (SiH) group of a poly(hydrogen methyl siloxane) crosslinker used in poly(dimethyl siloxane) and the carboxylic acid group of poly(acrylic acid). This covalent bond formation could explain the source of the "lock-up" that is sometimes found between acrylic pressure-sensitive adhesives and a silicone-coated release liner.*

**Keywords:** Lock-up; Bonding; Ellipsometry; Silicone; Pressure-Sensitive Adhesive; Acrylic; Interface

**Running Title:** IR Ellipsometry of Bonding at Adhesive Interfaces

---

\* Corresponding author. Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, UK. E-mail: j.keddie@surrey.ac.uk

## INTRODUCTION

A pressure-sensitive adhesive is commonly placed in contact with a release liner coating, prior to its use in its final position in securing a tape or label to a surface [1,2]. Several studies have determined the important influence of the viscoelasticity [1,3] and chemical composition [4] of the release liner coating on the debonding process. The coating on the release liner, which is often composed of a crosslinked silicone, is designed to be chemically inert, so that physical and polar attraction - but not *covalent* bonding - occurs with the adhesive. Hence the adhesive can be debonded from the release layer under a relatively low applied force [1,5].

A problem, usually referred to as "lock-up" in the adhesives industry [4,6,7,8,9], is sometimes encountered when the adhesive does not debond from the coating on the release liner. In a photocrosslinking silicone system, lock-up has been attributed to covalent bonding between the silicone coating and the adhesive [6]. It is speculated that the problematic bond formation results from incomplete chemical curing of the silicone [10] and - in UV-curing systems - to unwanted chemical reactions [9]. There are no reports in the literature, however, that determine conclusively the reasons for lock-up.

To tackle the problem of lock-up, numerous analytical techniques, such as X-ray photoelectron spectroscopy (XPS), methods of IR spectroscopy, and ESCA, could in principle be employed to identify any chemical bond at the polymer/polymer interface. XPS has a limited penetration depth and thus is only applicable to the near-surface region. Buried interfaces are probed by removing the top layers. As an example, one recent study [11] used XPS and time-of-flight secondary ion mass

spectrometry to show that covalent bonds do indeed form at an interface between an adhesive and a substrate. Clear evidence was provided for the existence of a bond between an epoxy group in the adhesion promoter on a metallic substrate and a curing agent in the adhesive.

There have recently been developments in the application of sum-frequency IR spectroscopy in the determination of structure at polymer/polymer interfaces [12]. Specifically, the spatial orientation of the methyl group in poly(butyl methacrylate) at an interface with poly(styrene) has been determined.

The technique of attenuated total reflection (ATR) FTIR spectroscopy has been used elsewhere [13] to detect bonding between poly(dimethyl siloxane) and a glass substrate. Particularly relevant here, it has also been used to verify transfer of silicones to the surface of a pressure-sensitive adhesive [14]. A drawback of ATR-FTIR spectroscopy is that it cannot be applied easily to buried interfaces that cannot be coupled with an IR-transparent ATR crystal. The technique is sensitive to depths from the surface on the order of the wavelength of the radiation. ESCA has provided even greater sensitivity to the transfer of silicones to adhesive surfaces [14, 15].

Infrared spectroscopic ellipsometry (IRSE) has been applied more often lately to polymer thin films and coatings, having previously been applied mainly to semiconductors and inorganic materials [16,17]. IRSE is attractive because it is non-invasive, able to be used over a range of temperatures and ambient atmospheres, and is sensitive to "buried" films and interfaces [18]. There are numerous reports of the technique being used to identify chemical groups in polymers created by plasma

processing [19,20,21] or by chemical crosslinking [22]. The technique is highly sensitive: it is able to detect molecular monolayers [23]. To date, however, there are no reports of IRSE being used to probe covalent bond formation at polymer/polymer interfaces.

Here we show that IRSE can be used to identify chemical bond formation at the interface between two polymer films. A film of poly(acrylic acid) (PAA) is used as a model for an adhesive, whereas poly(dimethyl siloxane) (PDMS) is used because it is a typical material for coatings on release liners. A reaction is widely suspected between the PAA's carboxylic acid group (COOH) and the silyl group (SiH) of a poly(hydrogen methyl siloxane) crosslinker in the PDMS [4], but there has been hitherto no proof of the reaction reported in the literature, to the best of our knowledge.

## **MATERIALS AND PROCEDURES**

PAA films were used as a model for a typical acrylic adhesive. Poly(styrene) films were used as a non-reactive surface for comparison. The substrates for all experiments were IR-reflective, p-doped silicon wafers with an orientation of <100> and used as received. Thin films of PAA and PS were deposited on the substrates by spin-casting dilute solutions using a photoresist spin-coater (Cammex Precima Ltd., Colchester, UK). A 5 wt.% solution of PAA in pentane and a 2 wt.% solution of poly(styrene) in toluene were used to deposit films ranging in thickness between 75 and 100 nm. The PS (Polymer Laboratories, UK) had a weight-average molecular weight  $M_w$  of  $3.20 \times 10^5 \text{ g mol}^{-1}$  and a polydispersity ( $M_w/M_n$ ) of 1.04. The PAA

(Aldrich Chemical Co., UK) had  $M_w = 1.08 \times 10^6 \text{ g mol}^{-1}$  with  $M_w/M_n = 8$ . The films were allowed to dry at room temperature for several days prior to further use.

The silicones used in these experiments were vinyl-terminated PDMS and a trimethylsilyl-terminated poly(hydrogen methyl siloxane) crosslinker with a chemical formula of  $(\text{CH}_3)_3\text{Si-O}\{-\text{SiH}(\text{CH}_3)\text{-O}\}_{25}\text{-Si}(\text{CH}_3)_3$  (Dow Corning Ltd, UK). The vinyl-terminated polymer, with a nominal chemical formula of  $[\text{CH}_2=\text{CH-Si}(\text{CH}_3)_2\text{-O}\{-\text{Si}(\text{CH}_3)_2\text{-O}\}_{150}\text{-Si}(\text{CH}_3)_2\text{-CH}=\text{CH}_2]$ , has an average degree of polymerisation of 150. The crosslinking reactions in these same materials have been analysed previously by IRSE [22].

Silicone films were deposited (onto the surfaces of Si, PS or PAA) by spin-coating from a dilute solution in analar-grade pentane. Films of SiH crosslinker were deposited from either a 1 wt.% or a 2 wt.% solution. A second type of silicone film was deposited from a 1 wt.% solution of a blend of PDMS and SiH crosslinker (weight ratio of PDMS:SiH crosslinker of 4:1).

Ellipsometry spectra were obtained using a Fourier transform infrared ellipsometer (Model GESP5-FTIR, SOPRA Sa., Bois-Colombes, France). In a typical measurement, eight scans were performed for each spectrum and 32 spectra were averaged. A total measurement took approximately 75 min. to acquire. A spectral resolution of  $16 \text{ cm}^{-1}$  was used over a spectral range of 650 to  $4000 \text{ cm}^{-1}$ . Higher resolution measurements, at  $4 \text{ cm}^{-1}$  resolution, were also performed, over the spectral range of 650 to  $2000 \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

### Optical Density

An overview of IRSE is required to understand the results presented herein. Ellipsometry measures the change in the state of polarisation in light after it is reflected from a planar surface. The change in the polarisation is mathematically expressed by the ellipticity,  $\rho$ , a complex number defined as

$$\rho = \tan \psi e^{i\Delta}, \quad (1)$$

where  $\psi$  is related to the relative change in the amplitude of the light, and  $\Delta$  is related to the relative change in the phase of the light [16,18]. It has been thoroughly demonstrated [16-24] that IR ellipsometry is sensitive to chemical changes at a surface, and the data are often best presented in terms of the optical density,  $D$  [18,20,24]. Measurements of the optical density of a surface are obtained from the initial ellipticity  $\rho_o$  of an original surface prior to a chemical change and the final ellipticity  $\rho_f$  of the same surface after the change. As  $D$  is defined as

$$D = \ln \left( \frac{\rho_o}{\rho_f} \right), \quad (2)$$

it follows from Equation 1 that the real component of  $D$ ,  $\text{Re } D$ , is a function of  $\psi$  only, and the imaginary component,  $\text{Im } D$ , is a function of  $\Delta$  only. Specifically,

$$\text{Re } D = \ln \left( \frac{\tan \psi_o}{\tan \psi_f} \right) \quad (3)$$

and

$$\text{Im } D = i(\Delta_o - \Delta_f), \quad (4)$$

where the superscripts  $o$  and  $f$  refer to the original and final measurements, as before. If an IR-active chemical bond is created on the original surface, a peak appears in the

Re  $D$  spectrum and a step with a negative slope appears in the Im  $D$  spectrum. On the other hand, if a bond disappears, then the *opposite* is found: a *valley* appears in the Re  $D$  spectrum, and a step with a *positive* slope appears in the Im  $D$  spectrum [16,20,24]. In summary,  $D$  spectra highlight the changes that occur at an interface but are not outright IR spectra of the materials at an interface.

### **Transfer of Crosslinker to PAA Substrate**

Initial experiments, using a SiH poly(siloxane) crosslinker, examined whether the silicone material is transferred to a PAA surface under light pressure. A film of the SiH crosslinker was spin-cast from a 2% wt. solution onto PS-coated silicon substrates to deposit a *ca.* 30 nm film (as measured with visible ellipsometry). A PAA film on silicon was placed in direct contact with the SiH crosslinker film, and the laminate was placed under light pressure. A PS film on silicon was likewise laminated against a SiH crosslinker film for comparison.

After four days of contact, the substrates were de-laminated. IRSE spectra were then recorded to determine whether any silicone transfer had occurred to either the PAA or the PS surfaces. The results are presented in Figure 1, which shows the Re  $D$  spectra for the PAA and PS films obtained by consideration of the data before and after exposure to the SiH crosslinker film.

There are no gain or loss peaks in the Re  $D$  spectrum obtained from the PS surface, indicating that the surface is unchanged by the contact with the SiH crosslinker, within the resolution of the technique. No transfer of crosslinker to the PS surface has occurred. In comparison, loss peaks are identified in the Re  $D$

spectrum for the PAA surface. Specifically, the data indicate loss peaks at  $1180\text{ cm}^{-1}$  assigned to the C-O stretch of C-OH and at  $1743\text{ cm}^{-1}$  assigned to the C=O stretch. Both of these are strong absorptions within the IR spectrum of the COOH group of PAA [25]. If there is a layer adsorbed on the PAA surface, however, then the COOH groups will be absent or at a lower concentration. Hence, there is a "loss" of COOH groups and a valley is found in the *Re D* spectrum.

One might have expected to observe *gain* peaks associated with the various groups in the SiH crosslinker, but these are not found. Their concentration at the interface is assumed to be below the sensitivity of the technique. Nevertheless, the adsorbed layer on the PAA surface is presumed to be the SiH crosslinker. From this experiment alone, however, it is not possible to conclude whether the SiH crosslinker is attached to the PAA through physisorption or through chemisorption (*i.e.* chemical bonding).

### **Covalent Bond Formation between Crosslinker and PAA**

A second series of experiments aimed to determine whether there is any *chemical* interaction between silicone coating formulations and a PAA surface. The contact time between the silicone and acrylic was increased to raise the concentration of any newly-formed bonds from any reaction. Samples were prepared by depositing a blend of PDMS and SiH crosslinker (4:1 weight ratio) as a thin film (*ca.* 25 nm) on PS-coated Si substrates. The silicone surface was then laminated onto PAA films cast on Si substrates. The resulting laminate (silicone/PAA/silicone blend/PS/silicon) was placed under light pressure at room temperature for 31 days. The samples were then de-laminated and allowed to stand for a further 20 days in air. IRSE analysis



confirmed the transfer of the silicones onto the PAA surface, whereas the PS surface showed no presence of silicones. The PAA surface was next rinsed five times with pentane using a spin-coater (10 sec. spin at 4000 rpm) and re-analysed with IRSE.

Figure 2 shows the Re and Im  $D$  spectra for a PAA surface rinsed with pentane after contact with the silicones. These are compared to the spectra from a SiH crosslinker film (22 nm thick according to ellipsometry) deposited onto a silicon substrate, thus serving as a reference for identification of the silicone absorption bands. Assignments for the observed gain peaks are listed in Table 1. Peaks associated with the crosslinker *i.e.* the Si-O-Si stretch (*c.*  $1125\text{ cm}^{-1}$ ) and the symmetric  $\text{H}_3\text{C-Si}$  deformation ( $1257\text{ cm}^{-1}$ ) [26], occur as gain peaks in the spectra from *both* types of sample. These results mean that the crosslinker is retained on the PAA surface even after a pentane rinse.

More significantly, evidence for the formation of a bond between the crosslinker and the PAA surface is found in the spectra presented in Figure 3. The relative weakness of gain peaks corresponding to the Si-H bend ( $903\text{ cm}^{-1}$ ) and stretch ( $2160\text{ cm}^{-1}$  [26] not shown in the figure) in the spectrum from the PAA surface might be explained by the chemical reaction of most of the SiH groups in the crosslinker. This result raises the possibility of bond formation between the silicone and the PAA.

This possibility is confirmed through the gain peaks/steps associated with Si-O-C and Si-O-CO bonds ( $820, 945$  and  $1019\text{ cm}^{-1}$ ) [26] that are observed in spectra from the PAA surface (Figure 3b and d) but *not* in the spectra from the neat crosslinker. (Figure 3a and c). These bonds are not present in the crosslinker nor in

the PDMS. (Additional ellipticity measurements on the PAA substrates confirmed that there is no interference from PAA in this region.) The gain peaks for the Si-O-C bond are relatively strong in comparison to the others in the spectra, indicating their relative abundance.

The probable reaction mechanism for the Si-O-C bond formation is shown in Figure 4. Upon closer examination of Figures 2b and 2d, it is apparent that an additional gain peak and step are centered around *ca.* 1150 cm<sup>-1</sup> (number 3 in Table 1). This absorption is attributed to the stretch of the acrylic ester (-C-(C=O)-O-) that is created by the reaction between the carboxylic acid groups of PAA and the silyl (SiH) groups in the crosslinker. Such a reaction has been suspected by workers in the field, but this is the first convincing evidence that the reaction indeed takes place.

Note that the reaction in Figure 4 is apparently occurring at room temperature and in the absence of a catalyst [22,27,28]. In most applications, the formulation would contain a catalyst, which speeds up the rate of SiH hydrolysis and SiH reactions. It is also possible that SiOH groups (formed via hydrolysis of SiH) could react with the carboxylic acid groups. It is relevant to note that a pressure-sensitive adhesive laminate would usually be stored at room temperature, and the reaction is clearly possible under these conditions. The same transfer experiment, when repeated with only PDMS and no crosslinker, showed no retention of any transferred silicone *after rinsing* with pentane. This result is consistent with the conclusion that SiH is reacting with PAA.

## CONCLUSIONS

Using infrared spectroscopic ellipsometry, we have provided evidence for the formation of a covalent bond at a polymer/polymer interface. Specifically, there is evidence for the formation of a Si-O-C bond resulting from a reaction between a silyl (SiH) group of a crosslinker used in vinyl-terminated poly(dimethyl siloxane) and the carboxylic acid group of poly(acrylic acid). An incomplete crosslinking reaction would lead to the continued presence of reactive SiH groups in a silicone coating. These groups might be the cause of the lock-up problem in silicone/acrylic adhesive laminates.

## ACKNOWLEDGEMENTS

Funding for the infrared ellipsometer and for TRES was provided by the UK's Engineering and Physical Sciences Research Council. We thank Dow Corning Ltd. for donating the vinyl-terminated PDMS and the crosslinker. We benefited from useful discussions with Dr. Bhukan Parbhoo (Dow Corning Ltd., UK), Dr. Chantal van Dinteren (Acrosil Europe BV, The Netherlands) and Dr. George Orlych (International Paper, USA). We also thank Drs. Parbhoo and Orlych for their close reading of the manuscript and several helpful suggestions.

## REFERENCES

- 
- [1] Gordon, G.V. and Schmidt, R.G., *J. Adhesion* **72**, 133-156 (2000).
- [2] A.J. Kinloch, *Adhesion and Adhesives - Science and Technology* (Chapman and Hall Ltd., New York, 1987).

- [3] Gordon, G.V., Perz, S.V., Tabler, R.L., Stasser, J.L., Owen, M.J., Tonge, J.S., *Adhesives Age* **41**, 35-42 (1998).
- [4] Gordon, G.V., Leaym, T.M., Owen, M.J., Owens, M.S., Perz, S.J., Stasser, J.L., Tonge, J.S., Chaudhury, M.K., Vorvolakos, K.A., and Hongquan, S., *Adhesives Age* **43**, 41-44 (2000).
- [5] Owen, M.J., *JOCCA - Surf. Coatings Intern.* **79**, 400-407 (1996).
- [6] Frances, J.-M., Kerr, S., and Pinto, O., *Adhesives Age* **45**, 30-34 (2002).
- [7] Oonk, M., Afera Technical Seminar Proceedings (2002).
- [8] Ducey, M., *Adhesives & Sealants Industry* **10**, 26-29 (2003).
- [9] Kerr, S.R., Radl, M., Fitzgerald, T., Pinto, O., Frances, J.-M., *Adhesives & Sealants Industry* **7**(6), 28-33 (2000).
- [10] Elliott, D., *Craig Label Industry News*, **28**(2), 1-2 (2001).
- [11] Rattana, A., Hermes, J.D., Abel, M.-L., and Watts, J.F., *Int. J. of Adh. Adh.* **22**, 205-218 (2002).
- [12] Chen, C.Y., Even, M.A., Wang, J., and Chen, Z., *Macromolecules* **35**, 9130-9135 (2002).
- [13] Botter, W., Ferreira Soares, R., and Galembeck, F., *J. Adhesion Sci. Technol.* **6**, 791-805 (1992).
- [14] Nakao, K. and Nishimura, Y., *J. Adhesion* **46**, 117-130 (1994).
- [15] Duel, L.A. and Owen, M.J., *J. Adhesion* **16**, 49-59 (1983).
- [16] Drévillon, B., *Thin Sol. Films* **313-314**, 625-630 (1998).
- [17] Tsankov, D., Hinrichs, K., Röseler, A. and Korte, E.H., *Phys. Stat. Sol. A* **188**, 1319-1329 (2001).
- [18] Keddie, J.L., *Curr. Opin. Coll. Interf. Sci.* **6**, 102-110 (2001).

- [19] Yan, L., Gao, X., Bungay C., Woollam, J.A., *J. Vac. Sci. Technol. A* **19**, 447-454 (2001).
- [20] Vallon, S., Drévilion, B., and Poncin-Epaillard, F., *Appl. Surf. Sci.* **108**, 177-185 (1997).
- [21] Bungay, C.L., Tiwald, T.E., Thompson, D.W., DeVries, Woollam, J.A. and Elman, J.F., *Thin Sol. Films* **313-314**, 713-717 (1998).
- [22] Simpson, T.R.E., Parbhoo, B., and Keddie, J.L., *Polymer* **44**, 4829-4838 (2003).
- [23] Korte, E.H., Hinrichs, K., Röseler, A., *Spectrochimica Acta Part B* **57**, 1625-1634 (2002).
- [24] Garcia-Caurel, E., Drévilion, B., De Martino, A., and Schwartz, L., *Appl. Opt.* **41**, 7339-7345 (2002).
- [25] D.H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th Ed. (McGraw Hill, New York, 1989) Ch. 2, pp. 29-62.
- [26] D.R. Anderson, *Analysis of Silicones*, A.L. Smith (ed.) (J. Wiley & Sons Inc., London, 1974). Chap. 10, pp. 247-286.
- [27] Lewis, L.N. and Lewis, N., *J. Am. Chem. Soc.* **108**, 7228-7231 (1986).
- [28] D.R. Thomas, *Siloxane Polymers*, S.J. Carson and J.A. Semlyen (ed.), (PTR Prentice Hall: Englewood Cliffs, NJ, 1993) Ch. 12.

**Table 1.** Positions and Assignments of IR Absorption Peaks Shown in Figures 2 and

3

Peak Number	Assignment <sup>†</sup> [26]	Peak Position (cm <sup>-1</sup> )	
		SiH Crosslinker film on Si	Residual layer on PAA
1	$\nu(\text{Si-O-Si})$	1126	1119
2	Symmetric $\delta(\text{H}_3\text{C-Si})$	1257	1257
3	$-\text{C}-(\text{C}=\text{O})-\text{O}-$	n.a.	<i>ca.</i> 1150
4	$\gamma(\text{H}_3\text{C-Si})/\gamma(\text{H}_3\text{C})_3\text{-Si}$  $/\nu(\text{Si-C})$	775	768
5	$\gamma(\text{H}_3\text{C})_3\text{-Si}/\nu(\text{Si-C})$	835	840
6	$\delta(\text{Si-H})$	903	900
7	Si-O-C	n.a.	820
8	Si-O-CO	n.a.	945
9	Si-O-CO	n.a.	1019
*	Not assigned	860, 927	860

<sup>†</sup> Notation:  $\nu$  = stretching vibration;  $\delta$  = bending vibration;  $\gamma$  = deformation vibration; n.a. = not applicable because this chemical group is not present in the substance or observed in the spectra.

## Figure captions

**Figure 1.** Re  $D$  spectrum obtained from a PAA film surface (bold line) and a PS film surface (light line) after de-lamination from a SiH crosslinker film. Loss peaks are observed at  $1180\text{ cm}^{-1}$  (**A**) and at  $1740\text{ cm}^{-1}$  (**B**) and attributed to C-OH and C=O stretching vibrations, respectively, in the carboxylic acid group (COOH) of PAA.

**Figure 2.** (a) Re  $D$  spectra for a SiH crosslinker film on a silicon substrate and (b) a PAA film after de-lamination from a silicone film and a pentane rinse, showing the spectral region from  $1050$  to  $1300\text{ cm}^{-1}$ . The corresponding Im  $D$  spectra for the same two samples are shown in c and d. The assignments of the numbered gain peaks are listed in Table 1.

**Figure 3.** Re  $D$  (a and b) and Im  $D$  (c and d) spectra for the same two samples shown in Figure 2, over the spectral region from  $650$  to  $1050\text{ cm}^{-1}$ . The assignments of the numbered gain peaks are listed in Table 1.

**Figure 4.** Proposed reaction mechanism for the creation of the observed Si-O-C bond. The dashed lines encircle the reactive groups leading to the bond formation.

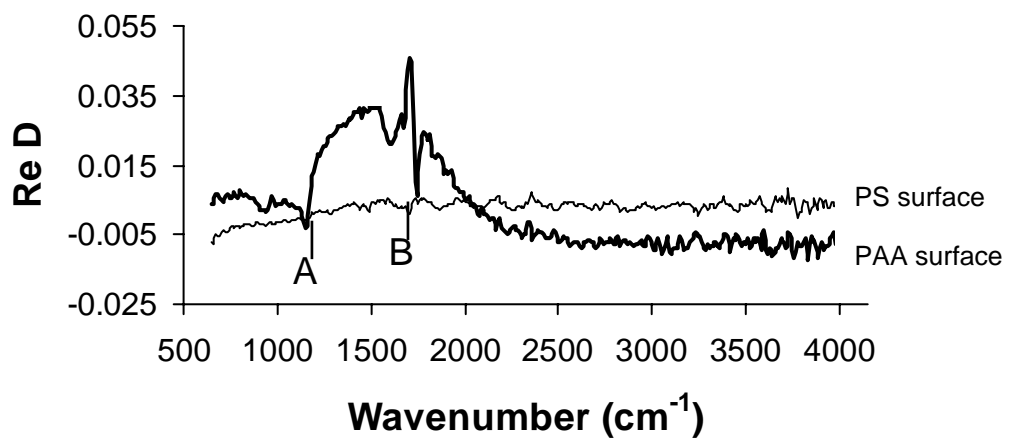


Figure 1



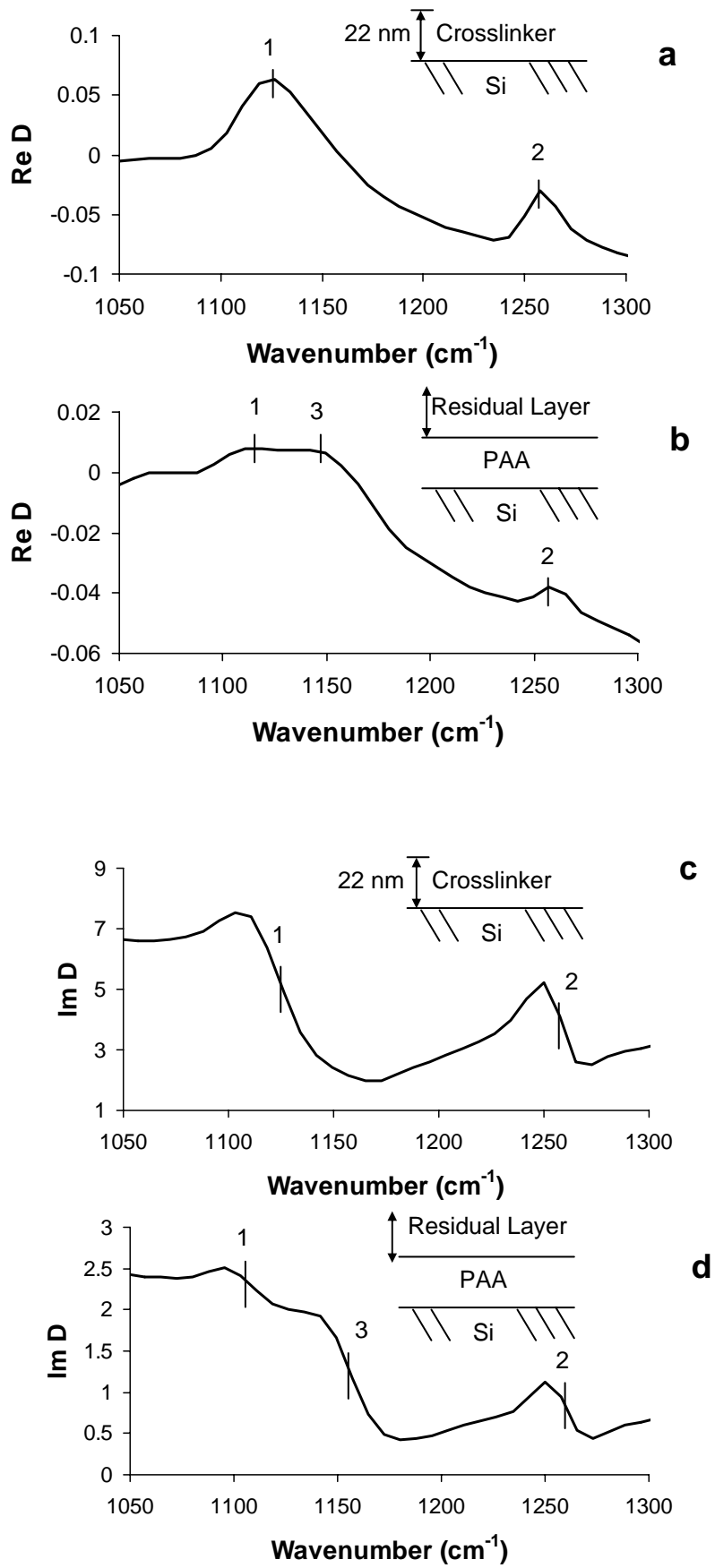


Figure 2

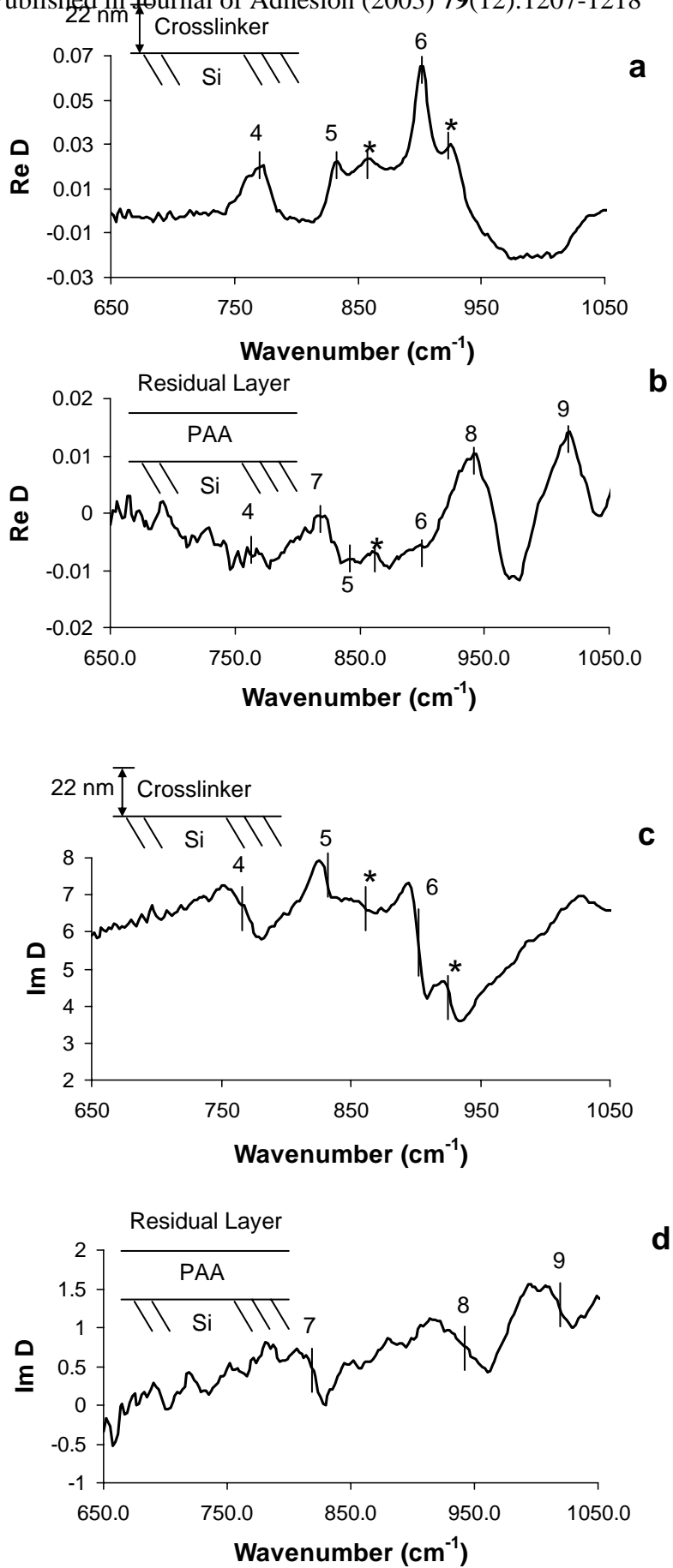


Figure 3

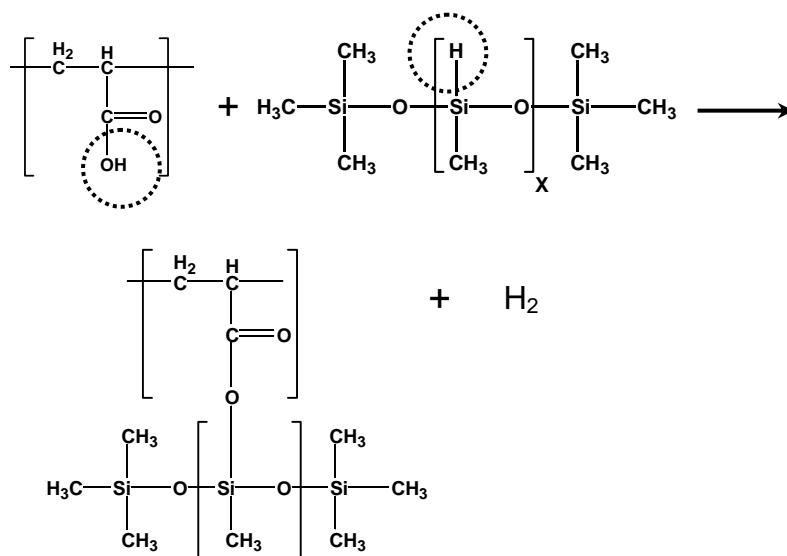


Figure 4