Characterization of glass–epoxy adhesion using JKR methods and atomic force microscopy

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Abstract

The adhesion between an industrial-grade epoxy elastomer and a silanated glass surface was studied using the JKR (Johnson, Kendall and Roberts) technique. Both short-term and longer-term interactions were monitored between the two components. Different silane coupling agents and coating procedures are applied to the glass surfaces, and their effects on the adhesion measurements are investigated. The topography of the silanated surfaces was studied using atomic force microscopy, and correlations were made with the JKR adhesion data. An extensive error analysis was also conducted in an attempt to extract the deterministic content of the data from experimental scatter. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Identification of the basic phenomena responsible for glass/epoxy adhesion has proven necessary in both the composite and adhesive industries. In general, an important goal of adhesion research has been to evaluate and differentiate between the various chemical and physical factors that promote adhesion. Technical barriers that have previously impeded the achievement of this goal are two-fold: the slow development of physical test methods that accurately measure adhesive forces, and the limitation of analytical techniques designed to explain the nature of chemical and physical forces at an interface [1]. Progress has recently been made in both of these areas, which has contributed to the current understanding of interfaces.

The present study serves to establish the experimental protocol for a longer term program to identify and understand fundamental physicochemical mechanisms that lead to glass/epoxy adhesion. Two popular techniques are employed to examine the interactions between an epoxy elastomer and a silanated glass, namely the JKR (Johnson, Kendall and Roberts) adhesion test and atomic force microscopy. An overview of this adhesive–substrate system, the characterization methods used in this work, and the recent progress made in this area is presented below.

Epoxy resins have been widely used in composite and adhesive applications, since they shrink only about 3% upon curing [2]. Furthermore, no small molecules that can interfere with bonding are created during curing, since the solidification reactions occur by addition polymerization. Cured epoxy resins, however, are notorious for their brittleness. For this reason, the technology of epoxies as adhesives advanced considerably when it was first shown that toughening of epoxy resins could be achieved by the addition of elastomers without a substantial reduction in their mechanical properties [3]. More recently, Pocius et al. [4] developed a resin system based upon an in-situ formation of pre-phase-separated elastomer particles.

1.1. Silane coupling agents

Coupling agents with dual functionality are widely used to join two materials by the formation of chemical bonds between the adherends. This method of chemical bonding has had success in producing durable adhesive joints, even under severe humidity and thermal conditions [5]. Shear strength between graphite fibers and epoxy matrices has been sought by the addition of polar groups to increase the attraction between the fiber surface and the polar epoxy matrix [6]. The increased interest in composites for mass production applications has led to the use of glass fiber instead of carbon fiber to drive down costs [7]. As a result, researchers have focused their efforts on elucidating glass/epoxy adhesion mechanisms.
Improvement in the interfacial shear strength between glass and epoxy has been attributed to the use of a coupling agent [7,8], although a greater advantage of the silane was the increase in the adhesive bond’s resistance to moisture attack. It has been seen that epoxy will readily bond to clean glass, but the interface is highly susceptible to hydrolysis. Apart from improving the durability of adhesion between polymers and inorganic reinforcements, organosilanes have been shown to prevent cure inhibition by mineral fillers. In both polyesters and epoxies, it was observed that silane treatments of fillers overcome cure inhibition as measured by cure exotherms [9,10].

According to Dwight et al. [11], several studies of the mechanical properties of composites have suggested that silanes form primary chemical bonds with both glass substrates and polymeric resins [12]. Although there is a large amount of indirect evidence supporting the theory of surface bond formation, direct evidence is somewhat limited [1]. Miller and Ishida have cited a few references that, at the time, reflected the majority of the direct spectroscopic evidence for the presence of adsorbate-surface covalent bonds. For instance, Miller and Ishida themselves observed the formation of a covalent bond between organofunctional trialkoxysilane adsorbate molecules and a lead-oxide surface using diffuse reflectance infrared spectroscopy [1,13]. The resulting surface bond was the plumbosiloxane linkage (Pb–O–Si). Culler [1,14] monitored the adsorption of γ-aminopropyltriethoxysilane (γ-APS) from aqueous solution on silicon oxide using Fourier transform infrared (FTIR) spectroscopy. It was observed that the bands in the region 1200–1000 cm\(^{-1}\) because the Si–O–Si bonds had shifted in frequency as a function of concentration in solution. Azzopardi and Arribart [15] conducted an in-situ FTIR experiment to investigate the evolution of an organosilane layer at the interface between a solution and a flat silica surface. According to the authors, previous experimental approaches have been mainly based on ex-situ analysis of the surface after treatment.

Spectroscopic studies by Chiang and Koenig [10,16] focused on the interaction between the silane coupling agent and the polymeric resin system. They observed that aminofunctional silanes were unsuitable for reinforcements in anhydride-cured epoxy composites, since the anhydride had reacted with primary amine groups of the silane to form cyclic imides. Although complete reaction of the epoxy and anhydride was obtained, some of the potential crosslinking in the interphase region was lost [10,16].

Dwight et al. [11] have challenged the common assumption that silanes readily form perfect mono- or multi-layers of uniform thickness when grafted onto a glass surface. In their work, SEM photomicrographs of aminosilane-treated E-glass fibers instead revealed that the silane coupling agent had adsorbed in patches [11]. While success in grafting homogeneous close-packed monolayers of octadecyltrichlorosilane (OTS) on silicon wafers has been reported in the literature [17–19], it is evidently not a trivial accomplishment. Each experimental procedure required careful optimization of a variety of processing parameters, including humidity, solvent proportions, temperature and reaction time.

### 1.2. Adhesion testing

Examples of adhesion tests include peeling, blister and fiber fragmentation tests. When performing a peel test, one of the simplest and most widely used methods of measuring adhesion [20], it is assumed that no energy is expended in bending the strip away. Contrarily, it has been observed that the irreversible work of deforming the sharply bent portion at the peel front may lead to an overestimation of the true fracture energy [2,21], depending on how the test is conducted. However, recent improvements in the analysis of peel test data have led to better estimates of the true fracture energy [22].

Like peel tests, blister tests are also less sensitive to the thermodynamic work of adhesion, since the measurements are often dominated by bulk viscoelastic energy losses incurred from deformation of the sample at room temperature [2,23]. However, the blister technique is attractive for measuring the adhesion of thin films to a rigid substrate since the test geometry leads to realistic failure processes [2].

The fiber fragmentation test has been a popular adhesion test in the composites community for determining the interfacial shear strength between a reinforcement fiber and the surrounding resin matrix [8,24,25]. Not only does this test involve using a glass fiber (or glass fibers) rather than a glass plate, but it also allows the study of interfacial properties on exposure to hygrothermal conditions [8]. There are, however, a number of limitations associated with this technique, most of which involve the assumptions and approximations that are required to extract the interfacial shear strength and work of adhesion from experimental data [2,25].

Another adhesion test, based upon the theory of Johnson et al. [26], has been applied in a number of systems to determine the intrinsic work of adhesion required to separate two surfaces. An important advantage of the JKR technique is that it enables one to assess the interfacial contribution to the adhesive strength, as the test is typically performed at low crack velocities [21,27,28]. A brief description of the JKR theory and analysis are presented below.

#### 1.3. JKR technique

The JKR experiment involves bringing a convex elastomer in contact with another solid substrate and, consequently, adhesive forces will deform the solids and increase their interfacial contact area [23,26–30]. The JKR theory is an extension of the classical Hertz result [31] on the deformation of two elastic bodies in contact with one another to include the effect of interfacial energy.
work of adhesion. In the absence of interfacial forces, the load applied to the two spheres, \( P \), and the amount by which the spheres are deformed in the center of their contact area, \( \delta \), are given by the Hertz relations:

\[
P = \frac{K\alpha^3}{R} \quad \text{(1a)}
\]

\[
\delta = \frac{a^2}{R} \quad \text{(1b)}
\]

where \( a \) is the radius of the circular contact area and \( R \) and \( K \) are effective radii of curvature and elastic constants. In the case in which an elastomeric hemisphere or lens is in contact with a rigid flat surface, \( R \) depicts the radius of curvature of the sphere and \( K \approx 16E/9 \), where \( E \) is the Young’s modulus of the lens [23] (Fig. 1).

In the presence of interfacial forces, \( P \) and \( \delta \) are given by the JKR relations:

\[
P = \frac{K\alpha^3}{R} - \sqrt{6\pi K\alpha^5 G} \quad \text{(2a)}
\]

\[
\delta = \frac{a^2}{R} - \sqrt{\frac{8\pi aG}{3K}} \quad \text{(2b)}
\]

where \( G \) is the energy release rate. Inverting Eq. (2a) yields the following expression for the contact radius, \( a \):

\[
a^3 = \frac{R}{K} \left\{ P + 3\pi GR + \left[ 6\pi GR + (3\pi GR)^2 \right]^{0.5} \right\} \quad \text{(3)}
\]

At equilibrium (\( \Delta a = 0 \)), the Griffith criterion states that \( G = W \), where \( W \) is the thermodynamic adhesion energy, reflecting only the instantaneous interactions between the two solids [29,32]. As Eqs. (2a) and (2b) illustrate, the main principle behind the JKR theory is that the load required to create a contact area of radius \( a \) is smaller than that predicted by Hertz [26,27,29].

Combining Eqs. (2a) and (2b) also leads to the following expression for \( \delta \), a form of the equation that is used and discussed in the data analysis:

\[
\delta = \frac{a^2}{3R} + \frac{2P}{3aK} \quad \text{(4)}
\]

A typical adhesion experiment is performed in three parts.

The first stage is known as the loading process, which involves compressing the elastomeric lens against a flat surface under controlled loads. At each load increment, \( a \), \( P \) and \( \delta \) are measured. If \( R \) is known, a simultaneous nonlinear curve fit of Eqs. (2b) and (3) allow \( W \) and \( K \) to be determined. In the second stage, the elastomer remains in contact with the substrate for a fixed period of time. During this time interval, the evolution of physical and chemical interactions may lead to an enhancement in the adhesion energy. The final stage, or the unloading process, entails rapidly decompressing the elastomeric lens and monitoring \( a \), \( P \) and \( \delta \) as functions of time. One can then determine the fracture velocity, \( -da/dt \), as a function of the strain energy release rate, \( G \):

\[
G = \frac{\left( P - \frac{K\alpha^3}{R} \right)^2}{6\pi K\alpha^3} \quad \text{(5)}
\]

An underlying assumption is made in the JKR analysis, namely that an equilibrium state can be attained at each step during loading. However, this assumption must be thoroughly tested, since the time required to reach equilibrium can vary substantially between systems [23].

### 1.4. Atomic force microscopy

Apart from adhesion strength testing and spectroscopic methods, atomic force microscopy (AFM) has received recognition for its potential to provide new insight into the study of adhesion failure [33,34]. Among the near-field microscopies, AFM is the only imaging technique that can be applied to insulators while also being capable of revealing information at the atomic scale.

AFM has recently been employed to characterize adhesion failure achieved by peeling an elastomeric polyurethane film from a glass substrate [33,34]. According to Creuzet et al., a description of the mode of failure propagation can be obtained with AFM, since it permits both the observation and local characterization of surfaces on a scale ranging from 5 Å to 100 μm. In their work, AFM observations of the glass surface after failure led them to conclude that the failure was never purely interfacial. Among their glass samples was one composed of microscopic islands of polymer residue possessing an organized structure, and based on this topography, they proposed a fibrillation failure mechanism [33,34].

AFM has also been used to observe stages in the formation of self-assembled OTS monolayers on silicon wafers at different temperatures [17]. An AFM image of an incomplete silane monolayer formed at 12°C after a reaction time of one minute depicted a disordered phase. However, after 90 min. an AFM scan revealed that the layer had evolved into a thicker and more ordered phase.
1.5. Overview of present work

The JKR adhesion test has traditionally been used to examine the adhesion between well-characterized elastomers and reproducible substrates [23,26–30]. However, in the present study the JKR technique is applied to a system notorious for possessing a number of uncontrollable parameters. Nevertheless, by tracking these variables during the course of this study, it is shown how the significance of the JKR data can be evaluated.

2. Experimental section

2.1. Preparation of epoxy elastomers

The elastomers were prepared by mixing stoichiometric quantities of the epoxy resin, diglycidyl ether of bisphenol A (DGEBA), with a diamine curing agent, Jeffamine ED-900 (Fig. 2). The mixture was stirred for several minutes under a nitrogen atmosphere at room temperature and was subsequently degassed. Small drops of the reactive mixture were then deposited onto fluorinated glass surfaces (microscope slides coated with perfluorotetradecyl trichlorosilane). As previously described [27,29], a drop of elastomer with a thickness smaller than its capillary length will readily adopt the shape of a spherical cap on these nonwetting surfaces. The final step entailed placing the samples in a petri dish and allowing them to cure in an oven for several hours.

Three separate batches of epoxy elastomers (labeled A–C) were formulated during the course of this work, all possessing different cure histories. The extent of reaction or ‘degree of cure’ of each batch was determined using differential scanning calorimetry (DSC). A more extensive description of the processing conditions of each batch can be found in Appendices A and B. In general, it is important to note that the lenses were stored at 0°C between experiments.

2.2. Silane treatments of glass surfaces

The glass surfaces used in this work were silicon–silicon dioxide (Si/SiO2) substrates that had been chemically treated using two different coupling agents: octadecyltriethoxysilane (OTE) and γ-aminopropyltriethoxysilane

\[
\text{CH}_3\text{CH(NH}_2\text{)-CH[OCH(CH}_3\text{)CH}_2\text{|-(OCH}_2\text{CH}_2\text{|m-[OCH}_2\text{CH(CH}_3\text{)]n-NH}_2\text{}}
\]

Fig. 2. Chemical structures of the epoxy/amine system. (a) Diglycidyl ether of bisphenol A (DGEBA). (b) Jeffamine ED-900.

\[
\text{NH}_2\text{-(CH}_2\text{)}_3\text{-Si-(OCH}_2\text{CH}_3\text{)}_3
\]

\[
\text{CH}_3\text{-(CH}_2\text{)}_17\text{-Si-(OCH}_2\text{CH}_3\text{)}_3
\]

Fig. 4. Chemical structures of the organosilanes used in this study. (a) γ-aminopropyltriethoxysilane (APS); (b) octadecyltriethoxysilane (OTE).
Silicon wafers were cleaned in H$_2$SO$_4$/$H_2$O$_2$ solution, rinsed with H$_2$O, and dried under nitrogen. The precise silanation procedure of each of the silicon wafers can be found in Appendices A and B. It should be noted that in some cases OTS was used in place of OTE, but these molecules yield identical films upon reaction with the glass substrate.

2.3. The JKR experiment

The JKR apparatus is illustrated schematically in Fig. 3. The elastomeric lens was attached to a glass plate support which was fixed on a translating stage. The stage could be displaced vertically using a double precision micrometer (Newport Corp.). The procedure involved bringing the lens into contact with a silanated silicon wafer that was mounted on a plate connected to a force transducer (Hottin-ger Baldwin Messtechnik Load Cell). During the course of an experiment, vertical displacement of the stage was automated using a Powermax II 1.8 Step Motor. A resistive displacement transducer was used to measure the total displacement ($\Delta$) of the stage, while the force transducer measured the applied load, $P$. $\delta$ could then be computed as follows:

$$\delta = \Delta - \frac{P}{k},$$

where $k$ is the spring constant of the transducer.

A Nikon Measurescope MM-11 optical microscope equipped with a 10× objective lens was used in reflective mode to monitor the contact area through the transparent elastomeric lens. The microscope was connected to a COHU solid state camera that allowed frames to be downloaded into a computer image analysis system. (This describes JKR apparatus ‘C’ in Table 1. JKR setups ‘A’ and ‘B’ are described elsewhere [29]). The combination of the microscope and the two transducers permitted simultaneous measurements of $a$, $P$ and $\delta$.

Quasi-equilibrium loading experiments were performed by increasing the load by a fixed amount, $\Delta$, and then allowing the system to stabilize before recording $a$ and $P$. (This process was then repeated a number of times.) In this work, the lens was compressed by steps of 0.3 mm at a rate of 1 mm s$^{-1}$, and the time interval between data points was 90 s. Before unloading, the maximum load of the loading process was maintained for a set time of contact. The unloading experiment was modeled after an established experimental protocol [29]. ‘Step by step’ unloading was conducted, that is, $\Delta$ was decreased by 2 mm at a rate of 1 mm s$^{-1}$. However, instead of only recording the last set of points before the next step (as was the case in the loading experiment), all pairs of the contact radius and load [$a(t)$, $P(t)$] were acquired during the relaxation process when they had exceeded preset threshold values. This enabled the crack propagation rate, $\dot{a}/\dot{t}$, to be determined as a function of $G$, as illustrated in the Section 3.

It should be noted that any subsequent experiments involving the same treated silicon wafer were conducted on an unused area of the wafer, since the elastomer may have deposited residue. Also, all substrates were rinsed with a solvent and dried under nitrogen before use.

### Table 1
Summary of JKR loading experiments

<table>
<thead>
<tr>
<th>Wafer</th>
<th>JKR setup</th>
<th>Batch of lenses</th>
<th>Radius of lens [μm]</th>
<th>Age of lens at time of expt [days]</th>
<th>$W$ [mJ m$^{-2}$]</th>
<th>$K$ [MPa]</th>
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</table>
2.4. AFM imaging of glass substrates

AFM measurements were performed in the contact mode using an Autoprobe cp microscope (Park Scientific Instruments). A complete description of this technique can be found elsewhere [35]. The nominal spring constant of the cantilever was 0.2 N m$^{-1}$ (Microlever Type B) and the nominal force between the tip and the surface was set at 0.1 nN. Images consisted of 256 $\times$ 256 pixels, and the scanning frequency was 0.3 Hz per row of pixels. Images were generated with both a 100 $\mu$m and a 10 $\mu$m scanner. The vertical resolution was 1–2 Å. Finally, image processing was performed using the PSI Data Analysis Program. For all samples, several images were recorded on different locations of the substrate to verify the reproducibility of the observed features.

3. Results and discussion

3.1. JKR loading curves

Typical results obtained during a compression experiment are presented in Fig. 5. $a^3$ was plotted as a function of $P$ [Fig. 5(a)] and was fitted to Eq. (3) to extract $W$ and $K$, as described above. The symbols represent the data points and the solid line traces the fit to the data. $\delta$ was also monitored independently as a function of $a$ and $P$ [Fig. 5(b,c)], and these data were fitted to the JKR model [Eq. (4)]. As the curves illustrate, the suitability of the model was excellent, which suggested that the experiment had been performed within the constraints of the JKR theory. Other researchers have observed deviations from JKR predictions above a certain applied load for the relationships involving $\delta$, which they attributed to finite size effects [23,29,30]. It has been explained that finite size effects may be significant when a small hemispherical lens is compressed against a hard surface, due to the large discrepancy between the elastic moduli of the elastomeric lens and its rigid support [29]. If this discontinuity is located in a region where the deformation field is still large (as calculated for a semi-infinite elastomer), then the presence of the rigid support may act to impede deformation of the elastomeric lens [29].

In principle, the model fit [Eq. (2b)] to the data presented in Fig. 5(b) should yield similar values for $W$ and $K$ to those obtained by Eq. (3) [Fig. 5(a)]. However, numerical
experiments showed that the solution to Eq. (2b) was very sensitive to the initial input given to the algorithm. Therefore, \( W \) and \( K \) were determined solely by the use of Eq. (3), the more stable equation in this sense.

A summary of the loading experiments and the corresponding extracted values for \( W \) and \( K \) are presented in Table 1. Two parameters were varied, including the batch of epoxy lenses and the particular silanated silicon wafer that were used in each experiment. Additionally, the age of the epoxy lens on the day of the experiment, its radius, and the JKR apparatus that was used to perform the adhesion test were recorded.

3.2. Determination of uncertainty

An error analysis was carried out to explain the scatter in the extracted values of \( W \) and \( K \) for the two epoxy lens/substrate systems. Although the data for each system were not obtained under identical experimental conditions (see Table 1), an assumption was that the data sets were statistically equivalent. One of the purposes of the error analysis was to assess which variables had contributed most to the variations in \( W \) and \( K \), and the highlights of the analysis are presented in the next paragraph. The observed parameters included the silane treatment of the wafer, the lens batch, the age of the lens at the time of the experiment, the radius of the elastomeric lens, and the JKR apparatus used for a particular experiment.

As depicted in Fig. 6(a), defined structure is observed in the relationship between \( W \) and the wafer treatment. The circles depict the OTE-treated surfaces, while the squares represent the APS-treated surfaces. As noted in Appendix A and B, batch ‘A’ had reached 96% cure, while batches ‘B’ and ‘C’ had attained 97% and 99.9% conversion, respectively. (c) Relationship between \( K \) and the age of lens at the time of the experiment. No defined structure was observed.
imply that the APS coatings were less reproducible, or simply more heterogeneous than the OTE coatings.

The bulk modulus, $K$, was particularly sensitive to the batch of elastomeric lenses used [Fig. 6(b)]. As stated in Appendices A and B, each batch was subjected to a unique cure cycle. The increase in $K$ as a function of batch is consistent with what one would expect, since batch ‘A’ had only achieved 96% conversion, while the ‘degree of cure’ of batch ‘C’ had exceeded 99%. However, the age of the lenses at the time of each experiment did not appear to have an impact on the measurements of $W$ and $K$ [Fig. 6(c)]. Any residual curing of the elastomeric lenses that may have occurred was evidently too insignificant to raise $K$ above the experimental noise. Finally, one should note that no apparent structure was depicted in the plot of $K$ versus $R$, in contrast with previous observations [30].

### 3.3. JKR unloading curves

Hysteresis is often exhibited in the contact area profiles upon releasing the load applied to an elastomer/substrate system [Fig. 7(a)]. The line in Fig. 7(a) corresponds to the JKR model fit to the data taken during the compression or loading experiment and the symbols represent the unloading data. More specifically, this figure illustrates the unloading behavior of an epoxy elastomer that had been in contact with an APS treated silicon wafer for 35 min.

In this particular case, the $a^3$ vs $p$ unloading profile does not superimpose with the loading data. As previously suggested [23,29], the hysteresis between the loading and unloading curves can be an indication of specific interactions inside the contact area, which are due to the enhancement of adhesion between the two materials over time. However, it can also be a physical manifestation of the incomplete mechanical relaxation of the elastomer if the unloading or crack propagation rate is faster than the relaxation time. A finite time period is required for the stored mechanical energy associated with the imposed load to be balanced against the potential elastic energy arising from induced deformation of the elastomer by the surface forces and the surface energy due to the work of adhesion [30]. Unlike that observed in Fig. 7(a), the unloading behavior of an epoxy lens in contact with an OTE treated wafer for the same time length exhibited only minimal hysteresis [Fig. 7(b)]. This result not only implied that sufficient time was allowed for the system to undergo relaxation between each unloading step, but also suggested that no interdigitation or chemical reaction had occurred between the elastomer and the substrate during the 35 min period.

As described in Section 2, the unloading experiments were performed in accordance with the procedure outlined by Deruelle et al. [29]. The authors argue that their data analysis technique is superior to the more common ‘$a^3 = f(p)$’ characterization, since the observed hysteresis can depend strongly on the precise unloading conditions of the experiment [29]. The current approach permits direct measurement of the relationship between the velocity of crack propagation, $da/dt$, and the strain energy release rate, $G$, which can be enlightening when comparing different elastomer/substrate systems. Fig. 8 depicts a plot of $da/dt$ vs $G$ for both the epoxy/OTE and epoxy/APS systems. At a given crack speed, the fracture energy of the epoxy/APS system was found to be almost an order of magnitude higher than that of the epoxy/OTE system.

Although this result is intuitively obvious if one considers the gross chemical differences between the two substrates (the APS coated surface being polar and the OTE nonpolar), it only further exemplifies the sensitivity of the JKR technique for probing the molecular phenomena of adhesion. In studies reported by Agrawal and Drzal [36], the chemical
interactions at a polyurethane/glass interphase were investigated by pre-treating the glass surfaces with methyltrimethoxysilane and trimethylchlorosilane prior to adhesion testing by the block-shear method. However, the adhesion data showed no significant difference between the uncoated and the silane-treated glass substrates [36]. One may argue that a drawback of the JKR technique over other adhesion test methods is that it can be applied only to elastomers, although recently it has been demonstrated that the JKR method can be applied to glassy polymer samples by thinly coating a poly(dimethylosiloxane) (PDMS) lens with the polymer of interest [30,37].

3.4. Contact time dependence

The epoxy/APS system was further examined to better understand the time frame required for irreversible interactions to develop inside the contact area. The results shown in Fig. 9 come from six experiments with six different lenses.\(^1\) For the first lens, the contact time between the lens and the substrate was 7 min. For the second, third, and fourth lenses, the contact time was 35 min. The purpose of the third experiment was to demonstrate the reproducibility of the second. However, these results were not reproduced by the fourth experiment, which was performed using a

\(^1\) Note that an obvious dependence of $G$ on $\frac{da}{dt}$ is not depicted in Fig. 9, since the curves are displayed on a log-log plot. Additionally, it should be noted that the range of $G$ values is not much larger than the uncertainty in the measurement of $G$ itself. Therefore, these results are not meant to imply that viscoelastic losses did not occur in the epoxy elastomer, only that the experiment lacked the sensitivity required to measure such losses. The relationship between $G$ and $\frac{da}{dt}$ can be further studied through the use of a peel test, where $G$ can be measured over a wider range of crack speeds.
different APS substrate (wafer ‘A2’) from the one used in the second and third experiments (wafer ‘A4’, see Appendices A and B for details). For the fifth and sixth lenses, the contact times were 68 h and 7 days, respectively. The differences among these curves illustrate that there was significant evolution of the interfacial region on a time scale of days. Moreover, it is possible that interactions would have continued to build up over a period of weeks or months. The dependence of $G$ on the contact time at a fixed crack speed is displayed in Fig. 10, which demonstrates a method for

Fig. 10. Data derived from Fig. 9 displayed as adhesion energy as a function of contact time for a crack propagation rate of 0.1 mm s$^{-1}$.

Fig. 11. Discretized standard deviations ($\sigma_i$) of $G$ as a function of crack speed ($da/dt$). The cell width, $i$, is one-half an order of magnitude of $da/dt$. The circles depict a data pool from curves ‘3’ and ‘4,’ the squares from curves ‘2’ and ‘4’ and the triangles from curves ‘2’ and ‘3.’ Curves ‘2’, ‘3’, and ‘4’ from Fig. 9 are illustrated in the inset.
determining the rate of adhesion enhancement. As the graph illustrates, a progressive increase in energy is needed over time to propagate the fracture at this particular crack speed. It is probable that a saturation point exists, which could be achieved more readily if the experiment was performed at an elevated temperature.

Amine-terminated silane chains were grafted onto the glass substrate to serve as ‘molecular connectors.’ Unreacted oxirane groups in the elastomer adjacent to the silane layer were likely to have reacted with the layer’s pendant amine groups, leading to the formation of covalent bonds. It is also a known fact that hydrogen bonding readily occurs between molecules possessing bonds such as O–H and N–H. While individual hydrogen bond strengths are roughly an order of magnitude less than covalent bond energies, these interactions as a whole can produce large effects. Furthermore, since the elastomer had nearly reached full cure when it was placed in contact with the APS-treated surface, it is possible that hydrogen bonding played a more significant role than covalent bonding in establishing a strong interface between the epoxy elastomer and silanated substrate.

In any event, when the lens and substrate were pulled apart during the unloading experiment, the connector molecules themselves were exposed to air. In a theoretical model by de Gennes [38], it is estimated that the energy cost in doing so is proportional to the density of connectors and their length. It was impossible to predict these parameters for this particular system, since it was not feasible to produce perfect APS monolayers. Not only did the layers contain patches, but there was also evidence of polysiloxane deposits on the glass surfaces, as illustrated in the following section. Nonetheless, it can be assumed that the reaction of APS molecules (possibly covalently) with chains in the epoxy enabled these reacted epoxy chains to serve as ‘active connector molecules,’ much like those described by de Gennes [38].

Returning to an earlier discussion about the different APS substrates, two silanation procedures were used to prepare the APS treated wafers. Silicon wafers ‘A1,’ ‘A2,’ and ‘A3’ were silanated according to procedure ’a,’ and wafer ‘A4’ was coated according to procedure ‘b,’ which are described in Appendices A and B. As depicted in Fig. 9, the fourth curve is not statistically equivalent to the second and third
curves, which would imply that there were physical differences between the APS coatings. This is also depicted quantitatively in Fig. 11. Discretized standard deviations of $G_i$ (where $i$ denotes discretization) were computed for three sets of data: curves ‘2’ and ‘3’, curves ‘2’ and ‘4’, and curves ‘3’ and ‘4’. For example, the data points from curves ‘2’ and ‘3’ were combined to form a single data set, which was then divided into five groups according to the magnitude of corresponding $da/dt$ values. (Recall that curve ‘4’ was derived from adhesion data obtained with wafer ‘A2’, procedure ‘a’, while curves ‘2’ and ‘3’ were obtained with wafer ‘A4’, procedure ‘b’.) The group cell width was one-half an order of magnitude of $da/dt$, and the values of $da/dt$ depicted in Fig. 11 represent the group medians. Note that $\sigma_i$ values of curves ‘2’ and ‘3’, data from a single coating procedure, are substantially lower than values derived from the other combination of curves, data from two different coating procedures. These physical variations were explored further by acquiring AFM images of the silanated wafers.

### 3.5. AFM images of glass surfaces

Prior to examining the APS surface treatments, AFM scans of an OTE silanated wafer (‘O5’) were made for the purpose of establishing a reference. A $20 \times 20 \mu m$ image of the OTE substrate revealed small deposits of material on the surface, which were approximately $2 \mu m$ in diameter and $80 \AA$ in height. Measurements of the root-mean-square (rms) roughness of the wafer over $10 \mu m$ distances between the ‘islands’ ranged from 3 to 15 Å. The thickness of the layer determined by X-ray reflectivity was found to be 26.3 Å, while the average roughness over the sampling area was 4.9 Å. The measured value for the thickness closely matches the expected monolayer height of 26.2 Å [19]. A summary of X-ray reflectivity and contact angle measurements for several of the silanated substrates can be found in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Advancing contact angle</th>
<th>X-ray reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dodecane</td>
<td>Distilled H$_2$O</td>
</tr>
<tr>
<td>O1</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>O2</td>
<td>8.5°</td>
<td>NA</td>
</tr>
<tr>
<td>O3</td>
<td>28°</td>
<td>103°</td>
</tr>
<tr>
<td>O4</td>
<td>36°</td>
<td>113°</td>
</tr>
<tr>
<td>O5</td>
<td>35°</td>
<td>NA</td>
</tr>
<tr>
<td>A4</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Fig. 12(a) depicts a $20 \times 20 \mu m$ scan of an APS substrate that was coated using procedure ‘a’. Significantly larger deposits were observed on this substrate than the OTE surface, for these were approximately $5 \mu m$ in width and $800 \AA$. However, the APS wafer treated according to procedure ‘b’ yielded very different results [Fig. 12(b)]. A $40 \times 40 \mu m$ image exhibited a very smooth surface, as the rms roughness was found to be 2–3 Å over distances of $10 \mu m$. When a $0.8 \times 0.8 \mu m$ scan of the same surface was made (using the $10 \mu m$ scanner), small deposits of material could again be seen [Fig. 12(c)]. Nonetheless, these were significantly smaller than what had previously been observed, as the three-dimensional image illustrates [Fig. 12(c)]. In general, the AFM images indicated that the APS coatings were clearly something other than a simple monolayer. Although wafer treatment ‘b’ was cleaner and more reproducible than treatment ‘a’, it remains unclear whether these factors are important for enhancing adhesion. It is, however, evident at this point that the coating properties have some impact on the level of adhesion.

### 3.6. Evidence of cohesive failure?

After conducting the JKR unloading experiment, in which the epoxy lens had been in contact with the APS substrate for 7 days (corresponding to the sixth curve in Fig. 9), the substrate (wafer ‘A4’) was examined for epoxy residue using AFM. The portion of the wafer that had been in contact with the lens was delineated prior to the JKR experiment by etching a small circle on the surface. A large transparent object was observed with the optical microscope, which could not be swept away by the sharp tip of the micro-cantilever (unlike dust). The region of the substrate surrounding the debris was scanned by AFM and was found to be as smooth as it was prior to the experiment. The object itself was too large to be scanned by AFM; therefore, it was examined using a confocal tandem scanning reflected light microscope (TSM) (Tracor Northern). Fig. 13 displays an image of the object acquired by TSM, which had a measured length of $72 \mu m$, a width of $16 \mu m$, and a height of $2 \mu m$.

Infrared microscopy was used to test if the debris was indeed a piece of fractured elastomer. A background spectrum was taken outside the contact area on an untouched region of the APS-treated glass and subtracted from the spectrum of the fragment. Hence, Fig. 14 represents a background-subtracted spectrum of the microscopic residue inside the contact area. While the peaks displayed in the spectrum are rather broad (Fig. 14), they are representative of C–H, N–H, and O–H stretching regions between 2700 and $3700 cm^{-1}$ [39].

If the object depicted in Fig. 13 were epoxy, this would indicate that covalent bonds had been broken. The adhesive strength between the loading and unloading experiments was enhanced by a factor of approximately 30, if one takes the ratio of the average value for $G$ ($2.3 \ J m^{-2}$) to that for $W$ ($68 \ m J m^{-2}$). As Ahagon and Gent [5] discussed in their work, the ratio of dissociation energies for covalent bonds to that for van der Waals’ interactions is of the same order. The authors also indicated that they expected the absolute magnitudes of the adhesive strength to be higher.
since energy had been expended in stressing the molecular chains at the interface.

Additional evidence that supports the possibility of cohesive rupture is contained in the $a^3$ vs $p$ unloading curves that correspond to the fifth and sixth experiments in Fig. 9. Unlike the lenses that had only been in contact with the APS wafer for 35 min or less, the unloading of samples after a few days exhibited different behavior. The data presented in Fig. 7(a) displays a systematic decrease in the contact area with decreasing load. However, in Fig. 15 (contact time: 68 h), the contact area decreased quite suddenly after a certain point, causing the lens to become fully disengaged from the wafer after a single step in the displacement.

4. Summary

The JKR technique was used to gain an understanding of the mechanisms responsible for the apparent adhesion between an epoxy rubber and a silanated glass. Two silane coupling agents that were examined in this work included APS and OTE. In the first part of this work, the work of adhesion between the two materials ($W$) and the bulk moduli of the epoxy samples ($K$) were plotted as functions of a number of parameters to assess which of these parameters had contributed most to the variation in $W$ and $K$. For example, $W$ was found to be insensitive to the lens age, while $K$ exhibited sensitivity to % conversion in the epoxy.

The next part of this study involved measuring the energy needed to separate the epoxy elastomer from an APS-treated glass substrate. It was found to be nearly an order of magnitude higher than that required to separate the elastomer from an OTE-treated substrate, a possible indication of hydrogen
and covalent bond formation in the former case. The interactions between the epoxy and the APS-treated glass substrate were also studied by monitoring the contact time dependence on the measured adhesion. Significant evolution of the contact area between the two materials was observed over a period of days. Two distinct silanation procedures were used to prepare the APS substrates, which yielded considerably different coatings on each of the surfaces. These differences were reflected by the JKR adhesion measurements and were further substantiated by Atomic Force Microscopy. One of the glass substrates that had been used in a JKR experiment was examined for epoxy residue. A transparent fragment was observed with a confocal tandem scanning reflected light microscope. To assess whether this object could be fractured epoxy, chemical analysis was performed using infrared microscopy, and characteristic O–H, N–H, and C–H peaks were detected, providing evidence for cohesive failure.

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Appendix A. Preparation of epoxy lens batches (A, B, C)

A: lenses were cured at 77°C for 17 h. Approximate degree of conversion (based on DSC data): 96%.
B: lenses were cured at 79°C for 18 h. Approximate degree of conversion: 97%.
C: lenses were cured at 106°C for 25 h. Approximate degree of conversion: 99.9%.

Appendix B. Preparation of silanated silicon wafers (O1–O5 and A1–A4)

O1: silicon wafer was silanated with OTS in a low humidity environment. Wafer was immersed in the silane solution (18) for approximately 5 min before it was rinsed with toluene and dried under nitrogen.
O2: silicon wafer was silanated with OTS in a low-humidity environment, but was in contact with the silane solution for only 2 min before it was rinsed with toluene and dried under nitrogen. OTS had been distilled prior to use.
O3: silanation procedure was identical to that used for ‘O2,’ except that the exposure time of the wafer to the solution was increased to 30 min and the reaction was conducted in an ultrasonic bath at 18°C (temperature of bath).
O4: silicon wafer was silanated with OTE to yield an identical monolayer as above. It was prepared according to a procedure outlined by Peanasky et al. [40] at Corning Europe. However, the wafer was left in the silane solution for 4 days rather than the suggested time of 2 h [40].
O5: silanation procedure was identical to that used for ‘O4,’ except that it was prepared on site.
A1: silicon wafer was silanated with APS to yield an amine-terminated surface. (This wafer was also prepared at Corning Europe.) The following solution was first prepared: 75 g ethanol, 10 g H2O, and 2 g APS. Wafer was immersed in the solution for 15 min before it was removed and placed in a 60°C oven for approximately 20 min. Prior to use, it was dried with nitrogen; however, no solvents were applied to the surface (Procedure ‘a’).
A2: an unused portion of wafer ‘A1’ was immersed in ethanol for several days before being dried under nitrogen.
A3: silanation procedure, which was carried out on site, was identical to the one described above. Prior to use, it was washed with ethanol and dried under nitrogen.
A4: the same silane solution was prepared; however, before use it had first been stored in a refrigerator for

Fig. 15. Loading and unloading cycle of a JKR adhesion experiment, where the contact time between the lens and substrate was 68 h. The circles represent the data obtained during the loading experiment, the dashed line depicts estimated values for the first stage of the unloading process, and the squares represent the data from an unloading experiment as the lens became disengaged from the APS-treated substrate.
2 h (temperature of solution: 12°C). In this procedure the wafer was immersed in the solution for 5–6 min before being dried in a 60°C oven for 20 min. (Procedure ‘b’).

References